STUDY OF REACTIONS BETWEEN HIGHLY FUNCTIONALIZED LOW MOLECULAR WEIGHT POLYETHYLENE AND POLYAMINES TO PRODUCE THERMOSET MATERIALS

STUDY OF REACTIONS BETWEEN HIGHLY FUNCTIONALIZED LOW MOLECULAR WEIGHT POLYETHYLENE AND POLYAMINES TO PRODUCE THERMOSET MATERIALS

By

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A thesis Submitted to the School of Graduate Studies in Partial Fulfillment of the
Requirements for the Degree Doctor of Philosophy

McMaster University

McMaster University DOCTOR OF PHILOSOPHY (2012) Hamilton, Ontario (Chemical Engineering)

TITLE: Study of reactions between highly functionalized low molecular weight polyethylene and polyamines to produce thermoset materials

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PAGES: xvi, 145

ABSTRACT

Low molecular weight functionalized polyolefins are mainly used as additives in adhesive formulations, compatibilizing agents and aqueous dispersions. However, the low viscosity and functionality they offer has never been explored to generate high molecular weight products that offer improved processing routes for polyolefins as well as wider applications.

The aim of this thesis work was to investigate the preparation and characterization of thermoset material by reactions between a highly functionalized, low viscosity maleic anhydride grafted polyethylene and diamines. Reactions were performed both in solution and in the melt state to generate the target thermoset materials. Products from these reactions were extensively explored using different techniques to understand the reaction kinetics and mechanism. Thermosets generated were also characterized for the degree of crosslinking, thermal, mechanical and thermomechnical properties.

Reactions in solution showed that the degree of reaction could be easily controlled by manipulating the concentration of reactants in the reaction mixture. Mixing torque data from the melt blender generated during reactions in the melt phase suggested that reaction between anhydride and amine moieties in these systems happen at much slower rate than widely reported for conventional high molecular weight polymeric systems. Unlike a single or two closely merged peaks in mixing torque associated with melting of polymer and chain extension and crosslinking due to reaction between anhydride and amine functionality widely reported, two separate peaks were observed in this study. A combination of FTIR and insoluble fraction data generated suggested that the first peak observed in mixing torque represents a combination of melting and partial reaction between anhydride and amine functionality. Whereas, the second peak in the mixing torque represents the initiation of crosslinking. The slower kinetics observed in the current investigation was found not to be a consequence of immiscibility of polyether diamine and polyethylene or the relatively higher molecular weight of diamines utilized in some reactions since using a low molecular weight aliphatic diamine, hexamethylenediamine, produced similar trends. FTIR and gel content (insoluble fraction) data generated on the prepolymers by processing them at high temperatures, suggested residual anhydride presence in products which could not be assessed using FTIR. This observation renders the popular monitoring of anhydride peak in such systems to assess the degree of reaction highly questionable. Cured thermosets from the prepolymers produced showed gel fractions of the same scale as in traditional crosslinked products. DSC heat scans on the thermosets showed separate crystal populations for polyethylene in cured and uncured fraction. Dynamic mechanical analysis result showed the thermosets withstood temperature up to 200 °C without failure and a crosslink plateau could be observed following the melting transition. Tensile properties of the thermosets were observed to be promising and composition dependent.

These thermosets are expected to extend the polyolefins applications in areas like sealant, adhesive and coatings. The low viscosities of starting materials could also lead to new processing routes for polyolefins.

ACKNOWLEDGEMENT

First and foremost I want to thank my advisor Prof. David Potter for his guidance, encouragement and generous support during my PhD. I would have never completed this work without his innovative inspiration and constant support. It has been an honor to be his first Ph.D. student.

I would like to thank my supervisory committee members Prof. Shiping Zhu and Prof. Harald Stöver for their constructive advice and remarks.

I take this opportunity to mention those who have been helpful during this thesis work. Elizabeth Takacs for her constant support during my research. I am extremely grateful to Paul Gatt for helping me build some of the experimental setups and always being there for help whenever needed. Prof. Shiping Zhu and Santiago Faucher for sharing a lot of specialized laboratory equipment when I started with an empty laboratory. Hermann Koch (Clariant, Canada) and David Alexander (Huntsman Chemicals, USA) for supplying materials for the experimental work.

My appreciation goes to all the undergraduate students (Steffi, Hilary, Tanja, Rima, Rohan, Patrick, Rummana) who helped in the experimental work. I would like to thank my colleague Giang Li for her company and advice.

Finally, I would like to thank my wife, Saima, and my daughters, Maryam and Fatima, for their patience, love and support that was so much needed during this endeavor.

PUBLICATIONS

This thesis is organized in a sandwich style based on the following publications as of December 2011.

1. **Reactions of low MW highly functionalized maleic anhydride grafted polyethylene with polyetherdiamines** *Journal of Applied Polymer Science* 2010, 116, 2285-2297
2. **Melt reactions between functionalized polyolefin and diamines** submitted to Advances in Polymer Technology 2011
3. **Study of reaction between a low molecular weight highly functionalized polyethylene and hexamethylenediamine** *Macromolecualr Materials and Engineering* 2011. In Press
4. **Thermal, mechanical and thermo-mechanical properties of thermosets produced using low Mw functionalized polyolefins and polyamines** *Journal of Applied Polymer Science* 2011. In Press

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Chapter 1 Introduction, Research Background and Objectives

1.1 Introduction

1.1.1 Polyolefins

Global production of plastics has increase tremendously in the last few decades. Polyolefins constitute the major share in the world commodity polymers [1,2]. The key applications include liquid containers (bottles, drums, tanks), pipes, sheets, films and cable insulation [2,4]. They are widely used in these applications owing to their adequate physio-chemical properties and cost. Advances in the catalyst technology over the years have enabled the production of polyolefins of controlled molecular structure and composition satisfying the desired end use properties [1-10]. Most of these acclaimed properties are related to the molecular architecture (molecular weight, molecular weight distribution, branching, comonomer insertion and distribution) of these polymers [2-9]. When a specific molecular architecture leads to a set of properties it is sometimes referred to as a structure-property relationship. For example, tailoring the molecular weight of polyethylene can be used to produce product ranging from highly rigid ultra high molecular weight polyethylene to very low viscosity polyolefin wax. Whereas, high molecular weight polyolefin products find their applications in areas where considerable strength is required e.g. containers, sheet pipe etc. the low molecular weight waxes are used as compatabilizers, in toner ink, polymer processing aids, and aqueous dispersions to name a few [11-13].

Modern single site metallocene catalyst systems allow production of polymers with narrow molecular weight distributions compared to products generated using high pressure autoclave and Ziegler-Natta catalyst technologies [2,3,4,14,15]. Molecular weight distribution has implications on the mechanical performance and processing of these products with broad MWD showing increased shear-thinning behavior [2,3,5,6]. Tailoring of short chain branching characteristics using α-olefin comonomers can be used to obtain rigid high density polyethylene to very low density rubbery materials [16-19]. Long chain branching on the other hand has been reported to enhance melt strength, environmental stress crack resistance as well as improving the processibility by providing increased shear thinning [2,3,5,20-22]. Hence, introduction of long chain branching has been exploited as a way of overcoming the difficult processibility of narrow MWD polyolefins synthesized by single-site metallocene catalyst without scarifying their superior mechanical properties. Presence of long chain branching also induces superior extensional characteristics desirable for blow molding and foaming processes [6].

Low molecular weight polyolefins are referred to as polyolefin waxes. They are produced both by controlled degradation of high molecular weight polyolefins [23-25] as well as polymerization using Ziegler-Natta and metallocene catalyst systems [26-27]. These materials are used as additives and find applications in aqueous dispersions, polymer processing aids, ink toners, compatibilizers in polymer wood and clay composites and hot melt adhesive formulations. In many of these applications the virgin waxes cannot be used owing to their inert nature. Hence these waxes are functionalized to make them polar or reactive to interact as desired in an application [27,28].

1.1.2 Functionalized polyolefins

Polyethylene and polypropylene are in principal chemically inert as a result of their chemical constitution, being composed of methylene and methyl groups. Whereas, this chemical inertness renders them a material of choice in certain applications, this very characteristic is a drawback in other application where a certain degree of interaction with other materials is desired e.g. paintability [28,29,30], interaction with other polymers e.g. in polymer blends [31-33] and inorganic substrates [11,34-36] in polymer composites. Functionalization or chemical modification of polyolefins is an inexpensive route to obtain value added products with a degree of functionality when it is necessary. Polymer modification using an extruder sometimes referred to as reactive extrusion is a very attractive option since functionalization can be achieved using existing processing equipment in an economical way. The most popular technology to achieve this is grafting using free radical chemistry [37-44]. The free radical grafting process is composed of three main players: the polyolefin to be grafted, an unsaturated grafting monomer (reactant), and a free radical initiator. Free radicals are generated by dissociation of free radical initiator (mostly organic peroxides) which then attack the polymer backbone and form macroradicals by hydrogen abstraction. The macroradical thus formed can result in crosslinking, chain scission or grafting of the desired monomer depending on the structure of the chain. In the case of grafting the macroradicals provide active sites for the unsaturated monomer to attach to the polymer chain. By far, the most popular monomer for polyolefin functionalization is maleic anhydride (MA) [27,38-45]. Grafting of MA on polypropylene is associated with chain scission that could be detrimental to the mechanical properties of the functionalized material [39,42,47]. On the other hand, the grafting of MA to polyethylene is accompanied by some degree of crosslinking which has its implications on the processibility and final properties [41,43,44]. The degree of functionality that could be achieved is limited by both the residence time in the extruder as well as the acceptable degree of chain scission/chain extension of the product.

Gaylord et al. [41] investigated the grafting of MA onto LLDPE in the presence of organic peroxide using a batch melt blender at 160 °C. The product was reported to contain 0.6 wt% of grafted MA. As a result of melt grafting the melt index dropped from 20 for the starting LLDPE to 0.9 for the grafted product. Based on the solubility of the product in xylene (90% soluble) it was concluded that the polymer underwent chain extension (increase in M_w) rather than crosslinking.

On the other hand De Roover et al. [40] investigated the grafting of MA onto polypropylene using organic peroxides. The grafting was carried out in a melt blender. Based on the experimental results a reaction mechanism was proposed in which free radicals, generated by organic peroxide dissociation, abstract a tertiary hydrogen from the PP backbone resulting in a macro radical. This macroradical then underwent β-scission creating a chain end radical to which a MA molecule can be grafted. The MA thus grafted was suggested to be capable of further homopolymerization leading to oligomeric MA grafts. In fact two different peaks were assigned to the succinic and oligomeric MA grafts in the FTIR spectra of the grafted product.

Russell and coworkers [48,49] investigated the grafting of maleic anhydride to model linear and branched hydrocarbons, eicosane and squalane, at 160 C. ^{1}H and ^{13}C NMR analysis of the products was explained to suggest grafts of single anhydride units. However, the presence of very low concentrations of oligomeric anhydride was not ruled out. In a later work [50], using similar model hydrocarbons and quantitative NMR analysis, grafting of exclusively single anhydride unit was claimed. The observation was explained to be in conformity with the low ceiling temperature of maleic anhydride (100 °C for homogeneous solutions of maleic anhydride in hydrocarbons where concentrations are 0.2-0.5 M). It was argued that there was no possibility of homopolymerization of maleic anhydride above 100 °C for solutions of maleic anhydride in hydrocarbons [51].

Functionalized polyolefin products are widely used as compatibilizers in polymer blends and composites [11,52-54]. Polymer blending is an inexpensive and quick way to achieve desired properties from existing polymers [14,15,54]. However, due to unfavorable thermodynamics of polymer mixing most industrially useful blends are immiscible. Fine dispersion of the minor phase in matrix phase and a strong interfacial adhesion between the phases is critical to achieve useful properties. Morphology achieved during blending is a function of blend components, composition, viscosity ratio of the components and presence of a compatibilzer. Morphology development during blending is driven both by thermodynamics and kinetics. Thermodynamics drives phase separation but the kinetics of phase separation can be exploited to achieve useful morphology. For example a fast reaction between the immiscible phases can be used to stabilize a finer morphology which would, if given enough time, otherwise result in phase separation. This is usually achieved by using block or graft copolymer such that each block has an affinity for one of the phases. These block copolymers can be produced separately and then added to the blend or can be produced insitu during blending (reactive compatibilization). In both cases the block or graft copolymer produced helps in emulsification and stabilization of the desirable morphologies. Although the first method has been widely investigated it did not achieve much industrial success due to the cost of block copolymers and the difficulty of carrying the block copolymer to the interface [52-54]. The industrial choice is usually the reactive compatibilization. It means the generation of block and graft copolymers at the interface insitu during blending. This could be achieved in conventional extruders and mixing devices. In order to achieve significant emulsification and phase stabilization the reaction to form insitu copolymers should be fast and the products stable [52-54]. The most popular interfacial reactions include: acid/amine, hydroxyl/acid or anhydride, aromatic amine/epoxy, aliphatic amine/epoxy, aromatic amine/anhydride, and aliphatic amine/anhydride [52-55]. The reaction rate for aliphatic amine/anhydride pair in melt phase was reported to be comparable to reactions of small molecules and the high viscosity in the melt was found to have little effect on reaction rate [55-56].

Other commercially important functionalization of polyolefin includes grafting of silane groups, widely used to produce crosslinking polyethylene [42,57-59]. Using free radical chemistry vinyl tri-methoxy and tri-ethoxy silane monomer are grafted to the polyolefin chains using a reactive extrusion process.

1.1.3 X-linked polyolefins

In some applications in order to achieve enhanced mechanical properties and suppress flow at elevated temperatures, crosslinked polyolefin products are used. Crosslinking enhances impact strength, thermal performance and chemical and environmental stress crack resistance [2,57,59,60]. Currently, there exist three methods to achieve this namely; moisture curing of silane groups, electron beam irradiation and free radical chemistry. In the first case, silane groups are grafted to polyolefin by reactive extrusion in the melt state or copolymerized into the polyolefin backbone during polymerization [37,42,57]. The silane grafted polymer resin is shaped using extrusion or injection molding and the product is then treated with moisture in the presence of a suitable catalyst to generate Si-O-Si bridges (crosslinks) between the polymer chains. Moisture curing is a slow process lasting from a few hours to several days. Further, the diffusion of moisture limits the thickness of the articles that could be created using this method.

In the second method, an electron beam is irradiated on the finished article to generate reactive sites on the polymer backbone, which leads to C-C crosslinks [2,60-62]. Once again the penetration of electron beam limits the shape and thickness of the articles that can be produced using this method. The high cost of an electron beam is an added drawback.

Crosslinking by using free radical chemistry could be achieved in polyethylene by addition of a suitable peroxide free radical initiator during melt processing. The peroxide dissociates at high temperatures into free radicals that generate macroradicals by hydrogen abstraction from the polyethylene chains. These macroradicals can then form C-C crosslinks. However, in order for the process to be viable, the peroxides should slowly decompose at the extrusion temperature i.e. they should possess longer half life than the residence time in the extruder. Once an article is shaped heat treatment is applied to decompose the remaining peroxide which results in the crosslinking of the material [2,42,60,63].

1.1.4 Reactions between anhydride and amine groups in polymeric systems

Reaction between maleic anhydride and amine in polymeric systems has been a popular topic [52-56, 64-72]. The reaction has been successfully used for blend compatibilization [31-33,54], adhesion promotion [56,64], encapsulation [65], amination of polyolefins [56], and surface modification [66]. Vermeesh and Groeninckz [67] studied the chemical modification of poly(styrene-co-maleic anhydride) with primary amines using reactive extrusion. The maleic anhydride content in the copolymer was 25 wt%. A twin-screw extruder was utilized for the reaction with temperatures exceeding 220 °C. Ammonia and alkyl amines with different carbon chain length (C1-C12) were used to study the imidization behavior. High conversion (> 90 %) of maleic anhydride during the course of reaction in the extruder was confirmed by titrations. These conversions were supported by elemental analysis of the reaction products for nitrogen content. However, no mention was made whether residual amines were purged from the product or not. Systematic increase in M_w was suggested to be a consequence of coupling of the amines as side chains on the polymer backbone. The FTIR spectra presented showed a decrease in both the 1858 and 1779 cm^{-1} vibration bands due to anhydride carbonyl, and the development of peaks at 1770 and 1716 cm^{-1} associated with the carbonyl stretching of imide as a result of the reaction. No peaks for amide were observed suggesting complete imidization within the residence time of extruder.

On the other hand, Schmidt et al. [66] investigated the modification of poly(octadecene-alt-maleic anhydride) (POMA) films with a variety of amines. The FTIR data reported contained no acid peak in the POMA and little change in spectra due to conversion of anhydride to acid was observed after immersion in water for 20 hours at room temperature. However, treatment with steam (120 °C; 2 bar) for 20 minutes resulted in significant decay in the anhydride response and the appearance of the acid peak (1710 cm^{-1}). The change was shown to be easily reversed by annealing at 120 °C for 2 hours.

Reaction between amine (3-dimethylamino-propyl amine) in aqueous media with POMA films was reported to be fast. The FTIR spectra suggested both the formation of amide (1652 and 1544 cm^{-1}) and of imide (1770 and 1700 cm^{-1}) as a result of this reaction.

Song and Baker [68] studied the reaction between several amines (primary, secondary and tertiary) and anhydride in polymeric systems. Styrene maleic anhydride copolymer (SMAn) and small molecule diamines were melt mixed in a melt blender at 180 °C and a rotor speed of 100 rpm. The torque variation during the mixing was recorded to understand reaction kinetics. Reaction was observed to be fastest between anhydride and primary-diamine followed by secondary and tertiary-diamine. Based on the torque data, the reaction between anhydride and primary diamine was concluded to be complete within two minutes in the blender. The reaction product in this case was a powdery material which was insoluble in refluxing toluene. This was suggested to be a consequence of formation of a highly crosslinked product. On the other hand, SMAn-secondary diamine product showed a relatively late increase in mixing torque signal (10-17 min). The product was reported to be a gel-like material at high temperature and showed 92% gel fraction by soxhlet extraction in refluxing toluene for 24 hours. This was suggested to be a lightly crosslinked product. The SMAn-tertiary diamine melt mixing did not show any significant change in mixing torque due to crosslinking suggesting little reaction. The product was soluble in toluene and had a melt index not very different from the starting SMAn. FTIR spectrum of the SMAn-primary diamine product presented suggested a significant degree of reaction between anhydride and amine groups evident from the disappearance of anhydride response at 1780 and 1858 cm^{-1}. The new peak developed in the product at 1700 cm^{-1} was attributed to acid or amide. However, due to the amine absorption around 3450 cm^{-1} it was concluded that amide was present in the product instead of acid. Imide formation was confirmed by a strong response at 1770 cm^{-1}. For SMAn-secondary diamine product, a new peak appearing at 1700 cm^{-1} was suggested to be a result of amide formation. Significant response at 1780 and 1858 cm^{-1} were concluded to come from residual maleic anhydride in the product. FTIR spectra for the SMAn-tertiary amine reaction product was very similar to the parent SMAn suggesting little reaction between anhydride and tertiary-amine groups.

In a separate study Orr et al. [55] investigated the reaction kinetics of different coupling reactions widely used to increase interfacial adhesion in immiscible polymer blends. The reactive functional groups were present as terminal groups on polystyrene (PS) and poly (methyl methacrylate) chains. Polymers containing different functional groups were melt blended at high speed (320 rpm) in a mini-mixer at 180 °C for 20 min. Samples were withdrawn from the mixer at regular intervals. These samples were analyzed using gel permeation chromatography for change in molecular weight and MWD, which were then utilized to infer the reaction kinetics. No reaction was observed between terminal carboxylic and primary amine groups. However, very a fast reaction was observed between anhydride and aliphatic-amine groups. The reaction was claimed to be complete in less than a minute. The kinetics of the anhydride reaction with amine group was suggested not to be diffusion controlled.

In a different study, Lu et al. [56] tried to obtain amine-grafted-polypropylene by reacting maleic anhydride grafted polypropylene (MA-g-PP) with several diamines. Both an extruder and a melt blender were used to carry out the modification. PP-g-MA was melt mixed with diamines at different amine to maleic anhydride (NH_2/MA) molar ratios. Using FTIR analysis of the reaction products it was shown that significant conversion of anhydride and generation of imide occurred during the course of reaction. No mention was made of amide present in the products although broad peaks could be seen around 1550 cm^{-1}. A gradual decrease in anhydride absorption (1780 cm^{-1}) with an accompanying increase in imide (1702 cm^{-1}) with increasing NH_2/MA molar ratio was also reported. From the torque data obtained during mixing it was suggested that reaction between anhydride and amine was practically complete within 90 seconds in the melt blender consistent with the earlier findings of Orr et al. [55] and Song and Baker [68]. The melt viscosity was reported to be highest at NH_2/MA molar ratio 1.0 consistent with the crosslinking statistics. Dynamic rheological measurement data presented showed significant increase in viscosity of the modified products which was attributed to extensive branching. However, presence of a macroscopic network (crosslinks) was not observed.

Model experiments to understand the mechanism and kinetics of the reaction between anhydride and amine in polymeric systems were conducted by Scott and Macosko [71]. Reactions were conducted in well mixed systems in which polymers with anhydride and amine functionality were dissolved in a common solvent. Styrene-maleic anhydride copolymer and amine terminated butadiene-acrylonitrile copolymer were reported to react in toluene at room temperature forming a weak gel within 30 seconds. The FTIR spectra generated using this gel was reported to show consumption of anhydride and formation of amide salt. This amide salt intermediate was suggested to generate cyclic imide on application of high temperature. However, when the gel was processed at higher temperatures to study the reaction kinetics, the amide salt hypothesis could not be verified.

Shearer and Tzoganakis [69] performed model reactions between maleic anhydride and amine. A low molecular weight polypropylene terminally functionalized with maleic anhydride and hexadecylamine were each blended into a unique polypropylene resin. Thin films of the two blends were later stacked and FTIR spectra were collected continuously using a heated infrared cell. The spectra presented showed the anhydride disappeared faster than the growth of cyclic imide. This was suggested to be a result of a relatively fast conversion of anhydride into amic acid/amide followed by the dehydration of amic acid into cyclic imide. The reaction scheme presented showed amic acid/amide as an intermediate instead of amide salt as suggested by Scott and Macosko [71]. However, no evidence was provided for the presence of amic acid/amide intermediate in the FTIR spectra.

In another study, Colbeaux et al. [70] attempted the crosslinking of maleic anhydride grafted polyethylene with 1,12-diaminododecane by melt mixing in a polymer melt blender. Once again, reaction between amine and anhydride was reported to be fast and thought to proceed via. an amide intermediate to form cyclic imide. Although the degree of maleic anhydride grafting of the polyethylene utilized was low compared to that reported by Lu et al. [56], a maximum of 32% gel content was reported for the product when the amine to maleic anhydride molar ratio (NH_2/MA) of the reaction mixture was 2.0. This result is in contrast to no crosslinking reported by Lu et al. [56]. The complex viscosity from dynamic viscoelastic measurements also showed a maximum at the NH_2/MA 2.0.

From the above literature review it can be concluded that polyolefins are one of the most widely used and very versatile family of plastics. They can be used in applications as thermoplastics, thermosets and their chemical inertness can be altered by available functionalization processes to produce value added functionalized products. Reactions between anhydride and amines are widely used in polymer blends and composites. Although disagreements exist regarding the reaction mechanism, the reaction is reported to be extremely fast. This provided the motivation to exploit the reaction between maleic anhydride and amine to produce useful thermoset materials by combining commercially available highly grafted polyolefins and polyether diamines. The thermosets are expected to extend the polyolefins applications in areas like sealant, adhesive, coatings and molding compounds. The low viscosities of starting materials could also lead to new processing routes for polyolefins.

1.2 Motivation, research objectives thesis outline

Conventional polyolefins are high molecular weight polymers that are processed in the melt phase and are associated with high viscosity and elasticity [2,5,6]. Processing equipments used for these materials are thus designed to handle such rheology. Typically, extruders and injection molding machines are used to process these polymers. These equipments work at elevated temperatures, high shear rates and pressure. These are capital and energy intensive machines and are usually located in a factory because of their size. Very high viscosities of these materials also warrant heavy molds and extremely high clamping forces [73]. This limits the molding of intricate designs and size of the molded products. On the other hand, the low molecular weight polyolefins are mainly used as additives, compatibilizers and coupling agents.

However, a very different processing route is available for the polymer family called polyurethanes. Molded polyurethane products can be produced right from the oligomeric raw materials at relatively low temperatures, efficiently using a process called reaction injection molding (RIM). RIM is a promising process to manufacture intricate and large polymer parts at high production speed using lighter molds and low clamping force compared to injection molding process [73,74]. This process exploits the fast reactions between hydroxyl groups with isocyanate moieties at relatively low temperatures. Although very popular, these products have the disadvantage owing to the handling of isocyanate due to their potential toxic nature. Research efforts are already under way to find alternate routes to produce polyurethanes without isocyanate [75-78]. Further, increasing petroleum prices make these products economically less attractive.

Recent advances in catalyst technology have enabled the production of low-M_w polyolefins with narrow MWD and controlled comonomer insertion and distribution. These polymers have been tailored to cover a wide range of melting points and viscosities. These materials are now commercially available from Clariant® [12,13,27]. The low-viscosities and melting points allow the grafting of these materials in batch processes without significant degradation [27]. As a result, polyolefins containing ~5% grafted maleic anhydride are now available in the market. These polyolefin products are principally used as polymer processing aids, compatibilzer in wood-polyolefin composites, melt adhesive formulations and day-care products. However, low viscosities and the high degree of functionality of these materials open opportunities for novel processing routes and applications for polyolefins. Reaction between amine and maleic anhydride groups has been reported to be fast [55,56,68]. However, little attention has been directed towards exploiting such reactions to generate useful high molecular weight polymer products from low molecular weight functionalized polyolefins.

More specifically the goal of this research was to exploit the fast reaction between amine and maleic anhydride to generate useful thermoset materials using commercially available low viscosity and highly grafted maleic anhydride polyolefins and polyamines. The design (molecular architecture and composition) of the proposed novel material could be controlled by selecting the proper starting materials and processing conditions. These materials are anticipated to offer unique properties desirable for applications in sealants, coatings, adhesives and molding applications. An offshoot of this research would be the development of potential technology to process low molecular weight oligomers into high molecular weight materials without using conventional energy and capital intensive polymer processing machinery.

The objectives of the research could be summarized as: (1) To understand the reaction between anhydride and amine groups in low molecular weight highly functionalized polyethylene and various commercial polyamines; (2) investigate the synthesis of the crosslinked material as a result of reactions between low molecular weight highly functionalized polyethylene and polyamines and (3) thermal, rheological and mechanical characterization of the crosslinked product obtained as a result of reactions between low molecular weight highly functionalized polyethylene and polyamines

Chapter 2 details the reactions carried out between low molecular weight polyethylene and polyamines in a solvent medium. The products were then analyzed using various techniques to establish the chemistry and physical properties.

This was followed by reactions in the melt state as detailed in Chapter 3. The products from the melt reaction were also characterized using different techniques to understand their physical properties and chemistry.

Next, reactions between a relatively small and compatible polyamine were studied by reaction with the functionalized polyethylene in a melt blender as described in Chapter 4. This helped to compare the reaction kinetics as reported in earlier studies.

Finally, the work in Chapter 5 was dedicated to understanding the thermal and physical properties of the thermosets generated using reaction between functionalized polyethylene and polyamine.

Significant findings and recommendations are summarized in Chapter 6.

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Chapter 2. Reactions of low MW highly functionalized maleic anhydride grafted polyethylene with polyetherdiamines

This chapter is based on the paper published in *Journal of Applied Polymer Science* **2010**, 116, 2285-2297 by Tayyab Hameed, David K. Potter and Elizabeth Takacs.

2.1 Abstract

Reactions between low molecular weight highly functionalized maleic anhydride grafted polyethylene and several diamines were carried out using xylene as a reaction media. The influence of varying the amine to maleic anhydride (NH_2/MAH) molar ratio and chain length of diamine on reaction was investigated. It was shown that the reactions of these materials cannot be followed by FTIR measurements alone. In these examples, colorimetric titrations were used to assess residual acid/anhydride content that was not detected by FTIR. The reaction between anhydride and amine was observed to be fast. The degree of reaction and crosslinking in the reactor was observed to depend on the concentration of the reaction mixture and the NH_2/MAH molar ratio. In some cases, a gelatinous insoluble mass was produced in the reactor and this material was not easily processed for further characterization. All soluble reaction products obtained were observed to be thermoplastic and could be melt processed at elevated temperatures. However, further reaction and crosslinking of these materials occurred during processing

to produce thermosets, as demonstrated by rheological measurements and sintering experiments.

2.2 Introduction

Polyolefins (polyethylene and polypropylene) constitute the most widely used commodity plastics because they are inexpensive and chemically inert and because they posses adequate physical properties for many applications. Over time, advances in catalyst technology [1-3] has resulted in the ability to exert more control over the molecular architecture of these polymers so that material engineered for the desired end use application is possible. Materials with a wide range of molecular weights (polyolefin waxes to ultra high molecular weight high density polymers), controlled degree of long and short chain branching and varying degree of isotacticity are now available in the market [3].

Polyolefins are very inert and hydrophobic materials. Whereas this property is an advantage in many applications, these same characteristics limit the use of polyolefins in applications where interaction with other materials is desirable. Modification of polyolefins by chemical functionalization is a well established practice [4-10]. In commercial settings it is typical to add this functionalization to the readily available commodity polyolefin polymers. This is often carried out using reactive extrusion processes in which free radical chemistry is used to “graft” small molecule functionality to the polyolefin polymer molecule. The most commonly used grafting material is maleic anhydride (MAH) [4-10]. This functionality renders the polyolefin more hydrophilic and enhances its compatibility with systems containing basic functionalities. The amount of MAH functionality that can be added to the polyolefin in a reactive extrusion process is limited by the residence time in the extruder and by the polymer degradation associated with processing at high temperatures in the presence of free radicals [6,7].

Low MW polyolefin waxes are widely used in toner inks [10], as compatibilzer in wood polymer composites [11], hot melt adhesive formulations and in personal care products [12]. These waxes are usually generated by degradation of high MW polyolefins [13] and more recently synthesized using Ziegler Natta and metallocene catalyst technology [14]. The metallocene catalyst technology enables the control of molecular weight and molecular weight distribution, as well as comonomer placement in the polymer molecule. Some commercially available waxes are designed to have low melting temperatures, compared to “normal” polyolefin materials, and a significantly reduced melt viscosity. These materials can be functionalized in a batch reactor process, rather than in the conventional extrusion process. The use of a batch process eliminates limitations due to the residence times associated with a reactive extrusion process. Lower melting temperatures also facilitate processing at temperatures that are considerably lower than those used in the extrusion processing of conventional polyolefins. Free radical chemistry can therefore be used to achieve a much higher degree of functionalization with these materials in a batch process, compared to the extrusion processes [10,12]. The relatively high degree of functionality and low viscosities of these functionalized polyolefin products enable the potential use of these materials in applications that were not previously considered.

Reaction between maleic anhydride and amines in polymeric systems has been extensively studied [14-22]. The reaction is an important interfacial reaction widely used in the compatibilization of immiscible polymer blends [15;16;21;22]. Song and Baker [16] studied the reaction between MAH groups and different types of amines (primary, secondary, tertiary) in polymeric systems. Reactions were conducted between styrene/MAH copolymer and diamines in a melt blender at 180 °C. Fast reaction between MAH and primary amine was reported and the generation of imide reaction product was confirmed by FTIR.

Lu et al. [20] investigated the reaction of amine groups to a PP-g-MAH. Reactions were performed over a range of amine/maleic anhydride (NH_2/MAH) molar ratios and were conducted both in a melt blender and an extruder. The mixing data suggested that the MAH-amine reaction was complete within 90 seconds and this was supported with FTIR analysis. The dynamic rheological measurements presented did not show any evidence of crosslinking in the reaction products at the different NH_2/MAH molar ratios studied. However, the complex viscosity and storage moduli were influenced by addition of diamine and ascribed to the increased branching in the products as a consequence of reaction.

Colbeaux et al. [17] explored the generation of an interfacial coupling agent to compatiblize polyethylene and polypropylene using PE-g-MAH and a diamine. The degree of MAH grafting of the PE was very low (0.18%). The reactions were carried out in a melt blender at 150 °C using two diamines and various NH_2/MAH molar ratios. For reaction between PE-g-MAH and 1,12-diaminododecane, the extent of reaction in the blender was observed to be a strong function of the NH_2/MAH molar ratio. Based on the FTIR spectra, complete conversion of anhydride was reported for NH_2/MAH molar ratio of 2 and above. Solvent extraction and rheological measurement suggested the products to be coupled to varying degrees.

Most of the studies conducted to date involving maleic anhydride functionalized polyolefin reactions with polyamines have utilized traditional polyolefins with high MW and low degrees of functionalization. Reactions of these materials with a polyamine are expected to yield branched reaction products that have utility as compatibilizers in immiscible blends or as modifiers of polymer properties such as melt rheology or mechanical performance. The reaction products are thermoplastics because the extent of reaction is limited by the low level of functionalization of the polyolefin. The work described here is a preliminary study of the reactions of highly functionalized low molecular weight polyolefin with polyamines. It is anticipated that the increased functionality of the polyolefin should allow for the synthesis of crosslinked thermoset materials. In the current investigation reactions between highly functionalized, MAH grafted low MW polyethylene and polyether diamines in are carried out in solution. The reaction products are analyzed to assess the degree of reaction using titration and FTIR techniques. Rheological and thermal characterizations tools are used to assess the properties of the reaction products.

2.3 Experimental

2.3.1 Materials

The maleic anhydride grafted (PEMA4351) and ungrafted polyethylene wax (PE4201) were commercial grade Licocene® PEMA4351 and PE4201 provided by Clariant GmBH, Germany. Properties of these materials are provided in Table 2.1. The molecular weight data (M_w, M_n, and MWD) was obtained by high temperature GPC at 135 °C (using PE standards for calibration) and was kindly provided by the manufacturer. The maleic anhydride (MAH) content in the grafted products were measured by colorimetric titration. The colorimetric titration technique was verified using grafted polyethylenes; PE-g-MA (Sigma Aldrich) and Epolene G2608 (Eastman Chemicals, USA) and polypropylene; PPMA6252 (Clariant, Germany). Diamines EDR176, ED600 and D2000 were commercial polyetherdiamines supplied by Huntsman Chemicals, USA. The diamines had molecular weights of 176, 600 and 2000 g/mol respectively. The molecular structures of the diamines are presented in Table 2.2. All diamines were supplied as liquids and used as received. Antioxidant stabilizers Irgafos 168 and Irganox 1010 were obtained from Ciba Specialty Chemicals, Basel, Switzerland. Solvents xylene and methanol were reagent grade and used as received.

Table 2.1 Characteristics of polyolefin waxes

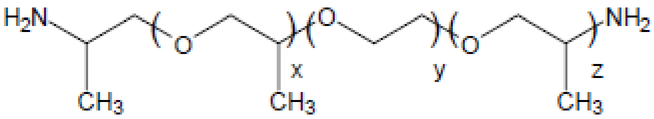
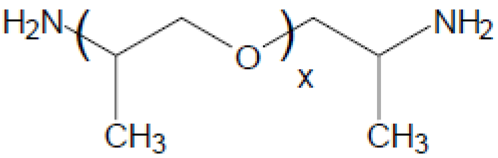
	M_w	M_n	M_w/M_n	Viscosity[3] (mPa.s)	MAH content[2] (wt%)
PE4201	-	-		60	0.0
PEMA4351	3000	1200	2.5	300	5.20

[1] Measured by high temperature GPC at 135 °C; [2] Measured by titrations; [3]measuresd at 140 °C

2.3.2 Reactions

All reactions were carried out in a 500 ml glass resin kettle equipped with a thermometer, drop bottle, condenser and an overhead stirrer. The impeller was a high-speed dispersion blade made of stainless steel. A stirrer bearing was used to ensure no solvent escaped the reactor during reaction. PEMA4351 was vacuum dried overnight at 100°C. Measured amounts of PEMA4351, and xylene were added to the clean and dried resin kettle. Approximately 0.01% of antioxidant, a 50/50 mixture of Igafos 168 and Irganox 1010, was added to protect the polymers against possible degradation. The condenser, thermometer, stirrer bearing and stirrer were then placed and the whole assembly was lowered in an oil bath maintained at 200 °C or a heating mantle fitted with a feedback temperature controller. Stirring was maintained above 500 rpm for 10 min to ensure complete dissolution of polymer. Measured amounts of diamine were then added as a 40% v/v solution using the drop bottle in one shot. The rotational speed of the stirrer was always ≥500 rpm before the amine addition. On addition of amine, if the viscosity of the reaction mixture increased, the input voltage to the motor was manipulated to maintain the stirrer speed above 500 rpm if possible. The reaction time was 10 minutes unless the reaction mixture turned into a gelatinous mass, in which case the reaction had to be terminated earlier. At the end of each reaction, the reactor contents were casted into a rectangular mold. These were then dried overnight in a fume hood and then vacuum dried overnight at 100 °C to remove trace amounts of solvent left over.

Table 2.2 Molecular structures of the polyetherdiamines

EDR176	 $x = 3.0$
ED600	 $y = 9; x+z = 3.6$
D2000	 $x = 33$

2.3.3 Titrations

The MAH content of the grafted polyolefins and reaction products was assessed using colorimetric titrations. Approximately 0.2 g of the sample was dissolved in 60 ml of xylene under reflux. The hot solution was then titrated against a standard ~0.01 N KOH in methanol. The alcoholic KOH solution was standardized against a standard HCl (0.01 N) aqueous solution. Thymol blue in methanol was used as an indicator. When the blue coloration persisted for a minute titration was stopped. The method was verified by titrating a standard solution of succinic acid.

2.3.4 FTIR

FTIR spectra were collected using a Thermo Nicolet IR300 spectrometer fitted with a Pike Technologies Diffuse IR™, diffuse reflectance accessory. The accessory was purged by a continuous flow of nitrogen. At least 64 scans were applied and data between 400 and 4000 cm^{-1} were recorded. Approximately equal amounts of sample and potassium bromide (KBr) were ground using a mortar and pestle. This mixture was then transferred to a small cup. Spectra were then collected at room temperature. For quantitative analysis absorbance at 1460 cm^{-1} representing the methylene groups in the PEMA4351 backbone was used as the internal standard peak.

2.3.5 Rheological measurements

Dynamic viscoelastic measurements were performed in Rheometric Scientific, Advanced Rheometrics Expansion System (ARES) controlled strain rheometer equipped with a transducer capable of measuring torque values ranging from 0.2-200 g-cm. In all measurements parallel plate geometry with 25 mm platens was used. Sample discs of 1.5 mm thickness were prepared by compression molding in a mechanical press at 140 °C to conduct rheological measurements. All measurements were carried out within the linear viscoelastic region established by a strain sweep. Dynamic time and frequency sweeps were performed at 140 °C using a hot air convection oven. Stress relaxation measurements were also performed to verify the presence of a network in the reaction products.

2.3.6 DSC measurements

Thermal properties of the compression molded reaction products and neat polymer were conducted using a Q2000 Differential Scanning Calorimeter (DSC), TA Instruments, USA. Approximately 5 mg of sample was encapsulated in aluminum pans for testing. The first heating cycle from room temperature to 160 °C at 10 °C/min was used eliminate the thermal history. It was followed by a cooling cycle and the second heating cycle at similar rates.

2.3.7 Sintering

Sintering behavior for selected reaction products were studied to confirm the evidence of flow on heating in the reaction products. The sintering experiments were performed on vacuum dried reaction products. The apparatus consisted of a heating chamber and an optical microscope equipped with a video camera. The camera was connected to a videorecorder and television, which in turn was connected to a personal computer with a frame grabber board, where the images were processed. The heat chamber had glass windows on the top and bottom for inspection and video recording of the process. The temperature of the oven was controlled by the thermocouple sitting in the wall of the heat chamber. All observations were recorded at 150 °C.

2.4 Results and Discussion

2.4.1 Assessment of Degree of Grafting

For grafted polyolefin products, the assessment of the degree of grafting is an important characterization parameter. Several techniques including NMR [9;23], FTIR [5;9;16-20;25-28], and colorimetric titrations [9;24-27] have been reported in the literature to assess the MAH content in functionalized polyolefins. Titration and FTIR techniques are most popular since they are easy to perform and relatively quick. Several titration procedures, with some variation in the use of solvent and indicator, are reported in the literature [6;9;24-27].

Titration results for the four MAH grafted polyolefins are presented in Table 2.3. These include both polyethylene and polypropylene products functionalized to varying degrees. Some studies [26] reported poor reproducibility of the titration results with standard deviations as high as 40%. Very good reproducibility (< 0.2%) in the titration results were observed in the current investigation. The degree of functionalization measured for the MAH functionalized metallocene waxes (PEMA4351 and PPMA6252) is 3 to 5 times higher than the 1% to 1.5% that is typically observed with functionalized commodity polymers.

Table 2.3 MAH assessed through colorimetric titrations for various grafted polyolefins

	Average MAH content (wt %)	**Standard deviation (%)**
PEMA4351	5.15	0.18
PPMA6252	4.32	0.12
PE-g-MA	2.15	0.02
Epolene G2608	0.92	0.11

The reported assessment of MAH grafting using the titration method assumes that all of the grafted MAH exists in the anhydride form. Since polyolefins have a tendency to slowly absorb moisture during storage, which results in the conversion of anhydride into acid groups, not all of the functionality reported will be in the anhydride form. It is well known that the kinetics of reaction between amine and anhydride are quite different from amine and acid reactions [16;20]. It is therefore important to understand how much of the anhydride is in the hydrated state.

FTIR has been extensively used to characterize the maleic anhydride functionality of grafted products. The FTIR absorbance spectra of non-grafted PE4201 and MAH grafted PEMA4351 (vacuum dried at 100 °C for 24 hours) used in this study are shown in Figure 2.1. Three distinct absorbance peaks at ~1715, 1780 and 1860 cm^{-1} are present in the PEMA4351 spectrum while they are absent in the non-grafted PE4201. The 1780 and 1860 cm^{-1} absorptions are responses from symmetric and asymmetric stretching of the

MAH carbonyl [5]. The absorption at 1715cm^{-1} arises from the carbonyl stretching of a carboxylic acid group.

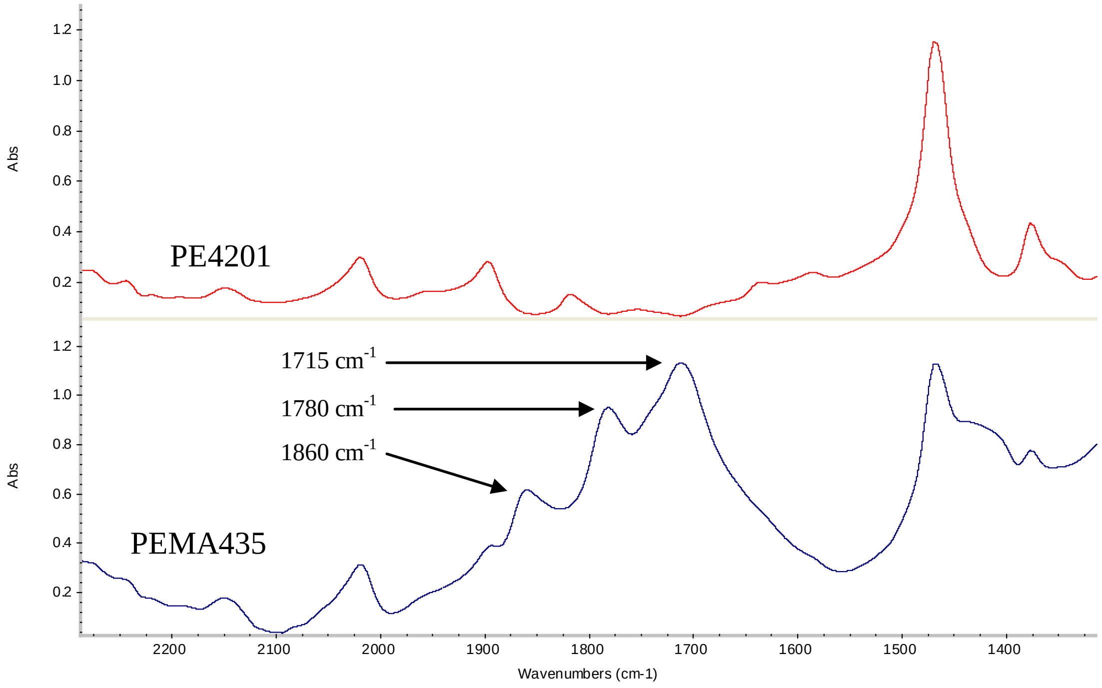


Figure 2.1 FTIR spectra of PEMA4351 and PE4201

The carboxylic acid absorbance at 1715 cm^{-1} in the PEMA4351 spectra is very strong indicating that a significant portion of the maleic anhydride functionality is present in the hydrated form despite the vacuum drying process employed. This result is quite different from some of the work described in the literature where either a relatively weak acid response or no response was observed [5;18-20]. Vacuum drying of the grafted products to convert carboxylic acid functionality back to the anhydride form by removal of water is commonly practiced [5;20;25;28]. For example, Scmidt et al. [28] used FTIR spectra to demonstrate complete conversion of the anhydride into acid by steam sterilization and back again to anhydride by annealing at 120°C for 2 hours, in their work with poly(octadecane-*alt*-maleic anhydride) thin films. On the other hand, Battinni and Agnelli, [25] observed little influence of vacuum drying on the conversion of acid groups into anhydride in MAH-g-PP samples vacuum dried at 130°C for 96 hours. Our experience here is consistent with the observations of Battinni and Agnelli [25].

More intense processing of the maleic anhydride grafted PEMA 4351 in the melt state did not lead to a complete conversion of acid functionality to anhydride either. The PEMA4351 was melt processed with constant stirring in an open cup at 150 °C (the peak melting temperature of PEMA4351 by DSC is 120°C) for different time intervals. The FTIR spectra for these melt processed samples are presented in Figure 2.2. The relative intensity of the acid and anhydride absorbances are altered by this treatment and a decrease in the acid absorbance with a concomitant increase in anhydride response is observed with melt processing time. For clarity the relative absorbance intensities for these functionalities are plotted as a function of melt processing time in Figure 2.3 using the methylene absorbance at 1460 cm^{-1} (C-H stretching) as the reference peak. The conversion of acid to anhydride appears to be linear with mixing time under these conditions but complete dehydration of all of the acid functionality was not achieved.

Following the work of others [5;25], blends were prepared by melt mixing MAH with ungrafted PE4201 in order to construct a calibration curve for the measurement of functional group content. Measurements of the anhydride content of these blends were performed by FTIR and compared to the known stoichiometry. The FTIR spectra of these blends in Figure 2.4 show strong anhydride absorbances at 1780 and 1860 cm^{-1} but no significant carboxylic acid absorbance (1715cm^{-1}). The anhydride absorbances (relative to methylene at 1460 cm^{-1}) are plotted in Figure 2.5 against the known stoichiometry and a linear trend is observed. The 1780 cm^{-1} absorbance is more sensitive than the 1860 cm^{-1} absorbance in agreement with earlier reports [16].

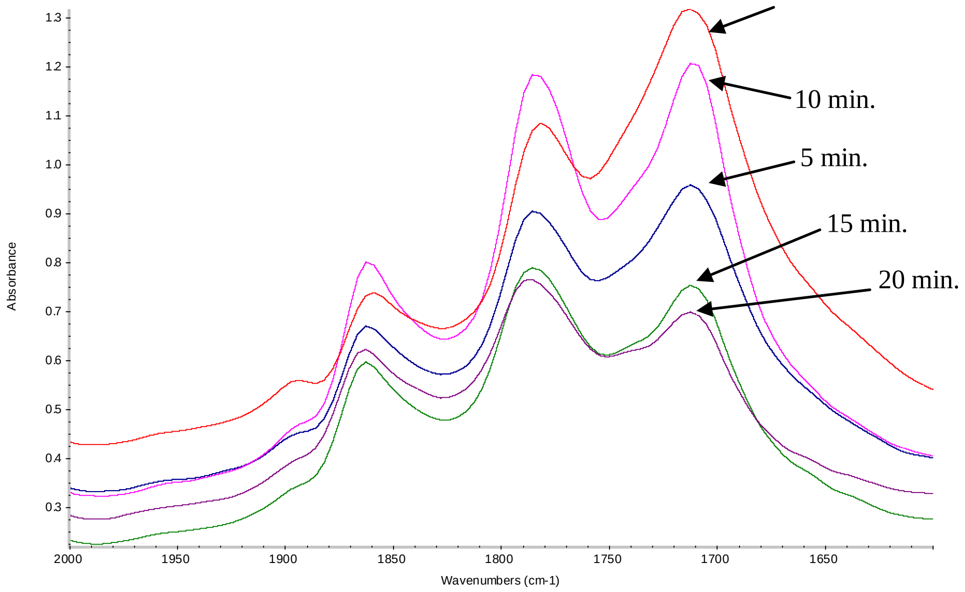


Figure 2.2 Overlaid FTIR spectra for PEMA4351 melt processed for different time intervals at 150°C

The calibration plots in Figure 2.5 provide estimates of MAH content that are higher than the MAH content measured by titration (~20%). This is likely a consequence of the significant baseline shift that is observed in the spectra between 1550-1900 cm^{-1} for the PEMA4351 compared to the calibration blends (Figure 2.6). The cause of this shift is

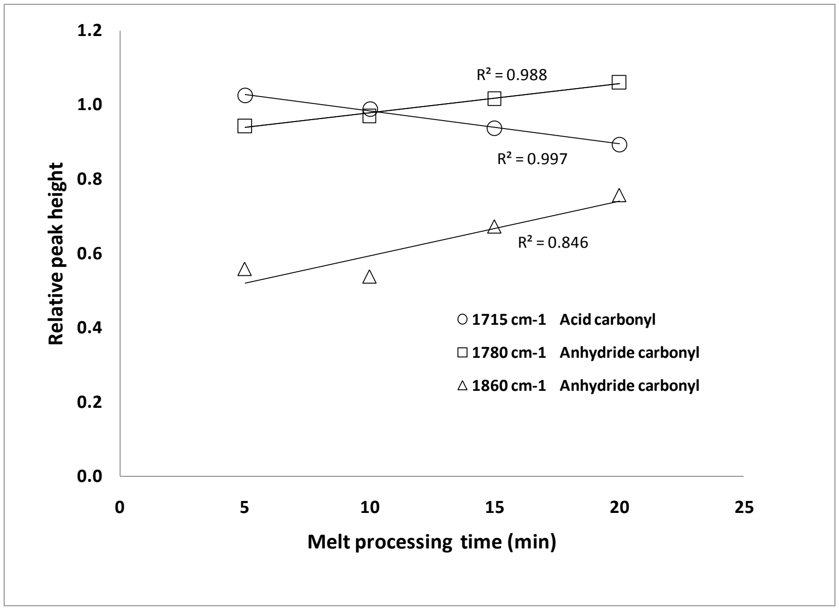


Figure 2.3 Relative peak height vs. melt processing times for PEMA4351

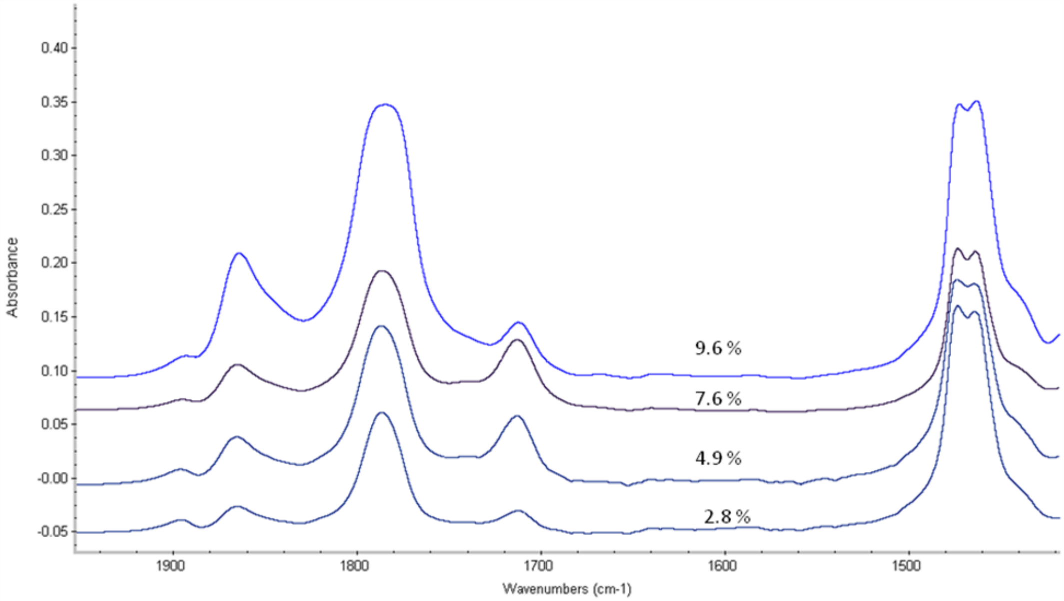


Figure 2.4 FTIR spectra of standard blends of dodecenyl succinic anhydride and PE4201 at various compositions

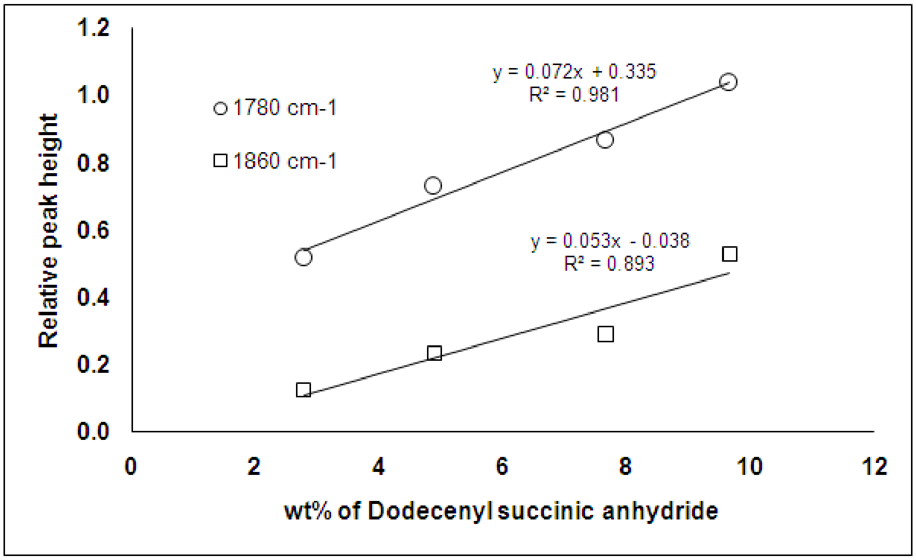


Figure 2.5 Relative peak heights of 1780 and 1860 cm^{-1} peaks vs. wt% of dodecenyl succinic anhydride in the blend

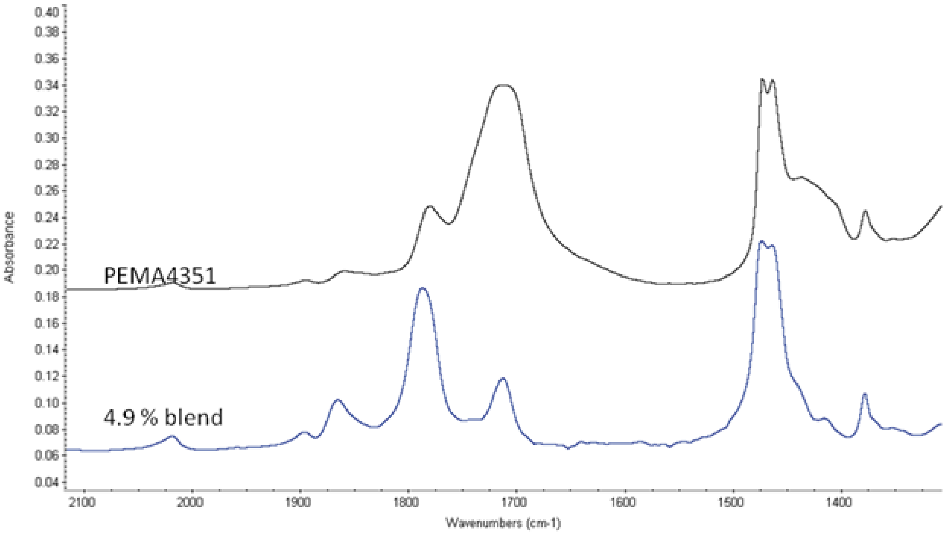


Figure 2.6 FTIR spectra for PE4201 blend containing 4.9 % dodecenyl succinic anhydride and PEMA4351

unclear. Earlier reports [5;25] where such calibration plots were successfully generated did not present any FTIR spectra for the standard blends.

2.4.2 Reaction of MAH Functionalized Polyolefin with Diamines

Reactions of the highly functionalized MAH grafted low MW polyethylene (PEMA4351) with diamines of different molecular were carried out in xylene solution. These experiments are summarized in Table 2.4. In all of these experiments, visual evidence of the reaction between the anhydride and diamine were manifest as soon the amine was dropped in the solution containing grafted polymer. This was not surprising since, the MAH-primary amine reactions have been reported to be extremely fast [16;20]. Lu et al. [20] working with high MW PP-g-MAH reported complete conversion of MAH into imide within 90 second in an extruder or a melt blender. Similar evidence was reported by other investigators [15;16].

Frothing in the reaction mixture and a decrease in the rotational speed of the stirrer due to viscosity build up were obvious. The reaction mixture would "climb" the agitator shaft as mixing proceeded. This is evidence of the formation of sufficient higher molecular weight polymer to develop a Weissenberg effect. In some cases, the reaction mixture turned into a gelatinous mass which was sometimes torn into small chunks due to shearing by the high speed dispersion blade. In those experiments where gelation (not in the sense of crosslinked polymer product as no assessment of insolubility was made) was observed, the recovered reaction product could not be processed into films or discs for further characterization.

Table 2.4 Summary of composition and critical observations during the reactions of PEMA4351 and diamines of varying MWs

Diamine	**Concentration g of polymer/ml of solvent**	**NH_2/MA molar ratio**	**Observation during reaction**
EDR 176	0.25	0.33	No gelation
	0.25	0.5	No gelation
	0.25	0.66	No gelation
	0.25	1.0	No gelation
	0.25	1.33	No gelation
	0.25	1.5	No gelation
	0.25	2.0	No gelation
	0.5	0.5	No gelation
	0.5	1.0	Gelled
	0.5	1.5	No gelation
	0.5	2.0	No gelation
	1.0	0.5	Gelled
	1.0	1.0	Gelled
	1.0	1.5	Gelled
	1.0	2.0	Gelled
D 2000	0.25	1.0	Gelled
	0.20	1.0	Gelled
	0.16	1.0	Soft flowing gel
	0.13	1.0	No gelation
	0.13	0.75	No gelation
	0.13	0.5	No gelation
	0.13	0.25	No gelation
D600	0.16	1.0	No gelation
	0.16	0.75	No gelation
	0.16	0.5	No gelation
	0.16	0.25	No gelation

The formation of a gelled materials depended on the concentration of reactants and on the molecular weight of the diamine used. An inspection of the data in Table 3 reveals that the concentrations at which gelation occur varies inversely with the molecular weight of the diamine used as coreactant. All the reaction products that were soluble at the end of the reaction time were casted into rectangular aluminum molds. The solvent was allowed to evaporate in the fume hood. Samples were then vacuum dried overnight at 100 °C to remove trace amount of solvents. The vacuum dried products from these reactions were thermoplastic and could be easily formed into thin films and discs by compression molding at elevated temperatures. These findings suggest that the extent of reaction and hence degree of crosslinking in the reaction products could be controlled by varying the concentration of the reaction mixture.

FTIR spectra were used to qualitatively follow the changes in chemistry and assess the extent of reaction between amine and MAH. Figure 2.7 shows the overlaid FTIR spectra for the recovered reaction products of PEMA4351-EDR176 reacted at a concentration of 0.25 g polymer/ml of xylene. A consistent decrease in absorbance at 1860 cm^{-1} and the disappearance of absorbances at 1780 and 1715 cm^{-1} due to the consumption of MAH and the development of new absorbances at 1700, 1770, 1550 and 1645 cm^{-1} suggest significant reaction between MAH and amine. New absorbances at 1700 and 1770 cm^{-1} are ascribed to the formation of imide [16;18;20;29]. Peaks developing at 1645 cm^{-1} are likely due to amic acid [19] or residual amine groups [29]. The response at 1645 cm^{-1} grows steadily with the increase in NH_2/MA molar ratio in the reaction products (see Figure 2.8) which suggest it is more likely to be an amine absorption.

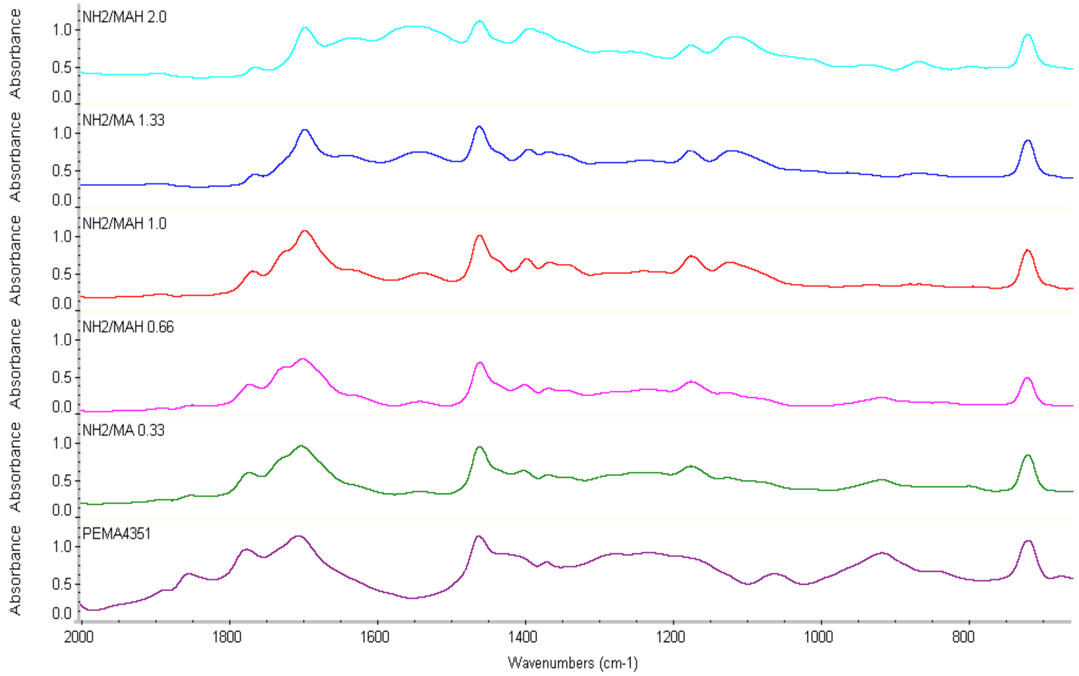


Figure 2.7 Overlaid FTIR spectra for PEMA4351 and its reaction products with EDR176

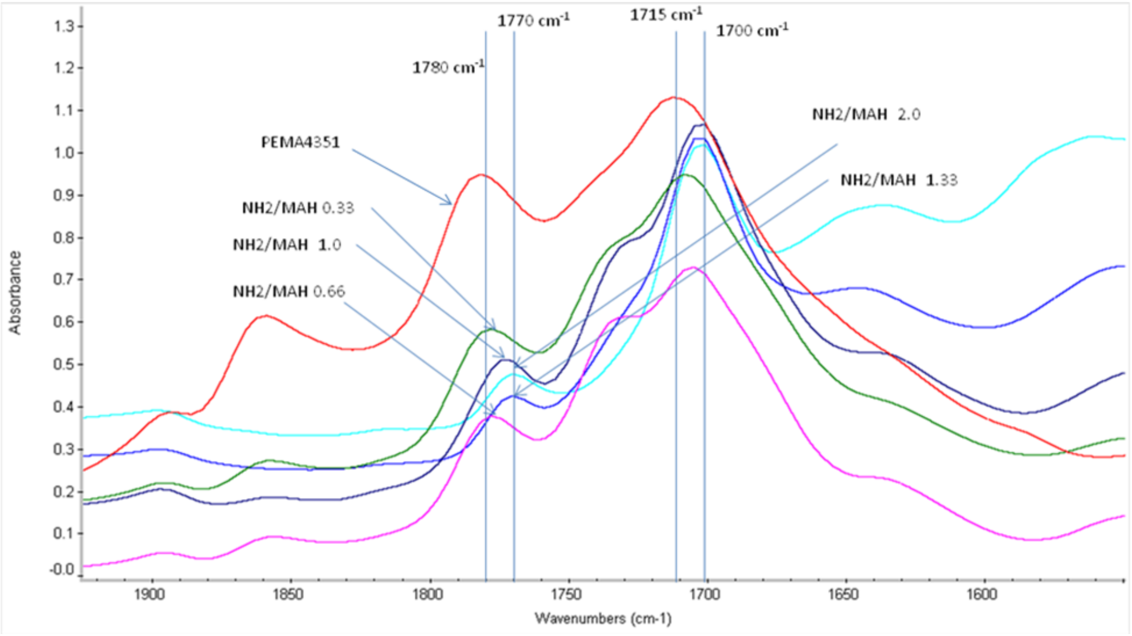


Figure 2.8 Development of imide peak (1700 and 1770 cm^{-1}) with NH_2/MAH molar ratio

Although these spectra qualitatively describe the change in chemistry as a result of reaction, quantitative assessment of the extent of reaction was made difficult due to two factors. First, as discussed in the previous section the grafted MAH in PEMA4351 was present both in the form of anhydride and acid. Hence, no unique absorption can be used to track the extent of reaction. Secondly, the imide absorptions generated as a result of reaction between anhydride and amine are observed at 1700 and 1770 cm^{-1} and are very close to the acid (1715cm^{-1}) and MAH (1780cm^{-1}) absorptions. In fact the responses for MAH and acid around 1780 and 1715 cm^{-1} are merged with those of the developing imide response at 1700 and 1770 cm^{-1}. The generation of imide as a consequence of the reaction is therefore manifested as shifting absorbance from 1780cm^{-1} to 1770cm^{-1}, and from 1715cm^{-1} to 1700cm^{-1} as the imide is generated and the acid and anhydride is consumed.

These observations are quite different from those reported by Lu et al. [20]. Working with a similar system (PP-g-MAH and diamines) their FTIR spectra show a very strong imide response around 1700cm^{-1} but surprisingly no significant imide peak is observed at 1770 cm^{-1} as a result of reaction between anhydride and amine. Further, a very weak absorption peak for carboxylic acid in the PP-g-MAH they used, allowed quantification of the extent of reaction in terms of a decreasing MAH absorption with NH_2/MAH molar ratio. Similar responses were observed in the FTIR spectra for the reaction products of PEMA4351-D600 and PEMA4351-D2000 reactions and these spectra are not reproduced here.

Since the extent of reaction could not be quantitatively assessed by measuring the residual MAH by FTIR, titration of the reaction products were carried out to assess the residual MAH groups. The measured MAH content in the reaction products are plotted as a function of the NH_2/MAH molar ratio in the Figure 2.9 for the PEMA4351-EDR176 reaction products. The decreasing level of residual MAH with increasing amine mole ratio that is observed in Figure 2.9 is generally observed for all of the reaction products studied and is consistent with the trends observed in the FTIR data for increasing imide concentration. Significant MAH (> 1%) in reaction product in which the molar ratio of NH_2/MAH > 1 are particularly surprising since no anhydride or acid absorption could be

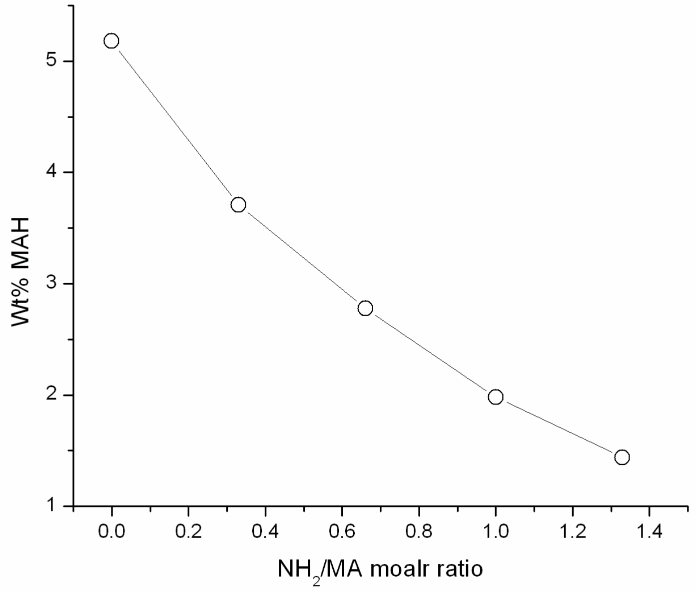


Figure 2.9 MAH content in PEMA4351 and its reaction products with EDR176 assessed by colorimetric titrations as a function of NH_2/MA molar ratio

detected in the FTIR spectra for these products. The reason for this observed discrepancy is not clear yet but may be related to the limits of sensitivity of the FTIR technique.

2.4.3 Properties of Reaction Products

All of the reaction products that did not gel in the reactor could be formed into disks for rheological evaluation by compression molding at elevated temperatures. Although significant reaction did take place in the reactor, as evident by FTIR and titration results, the material was still thermoplastic.

The thermal behavior of a semi-crystalline polymer can sometimes provide an indication of changes in polymer architecture as a consequence of reactions that lead to branching. For example, short chain branching hinders the chain folding mechanism in polymer crystals and hence suppresses the degree of crystallinity [30]. On the other hand, the presence of multi-phases is manifested in the characteristic melting peaks for each phase. Figure 2.10 shows the second heating DSC scans for PEMA4351 and melt processed reaction products of PEMA4351 and EDR176 at different NH_2/MA molar ratios. A unique melting peak is observed for PEMA4351 whereas a new developing shoulder is seen in all reaction products. The peak melting temperature for PEMA4351 and the major melting peak in reaction products was always around 120 °C. However, a significant drop in the intensity of the major peak was observed as the NH_2/MA molar ratio increased. The decrease in peak intensity may be a result of an increasing number of branches and crosslinks in the reaction products which hinder chain folding and consequently lower crystallinity. The development of a shoulder around 110 °C with increasing NH_2/MA molar ratio might be ascribed to the development of a separate crystal population as a consequence of weaker interactions due to sterically hindered branches or crosslinks.

The viscosity of the PEMA4351 starting material was too low to be measured using our instrument. Hence, the first evidence of molecular weight build up as a result of reaction

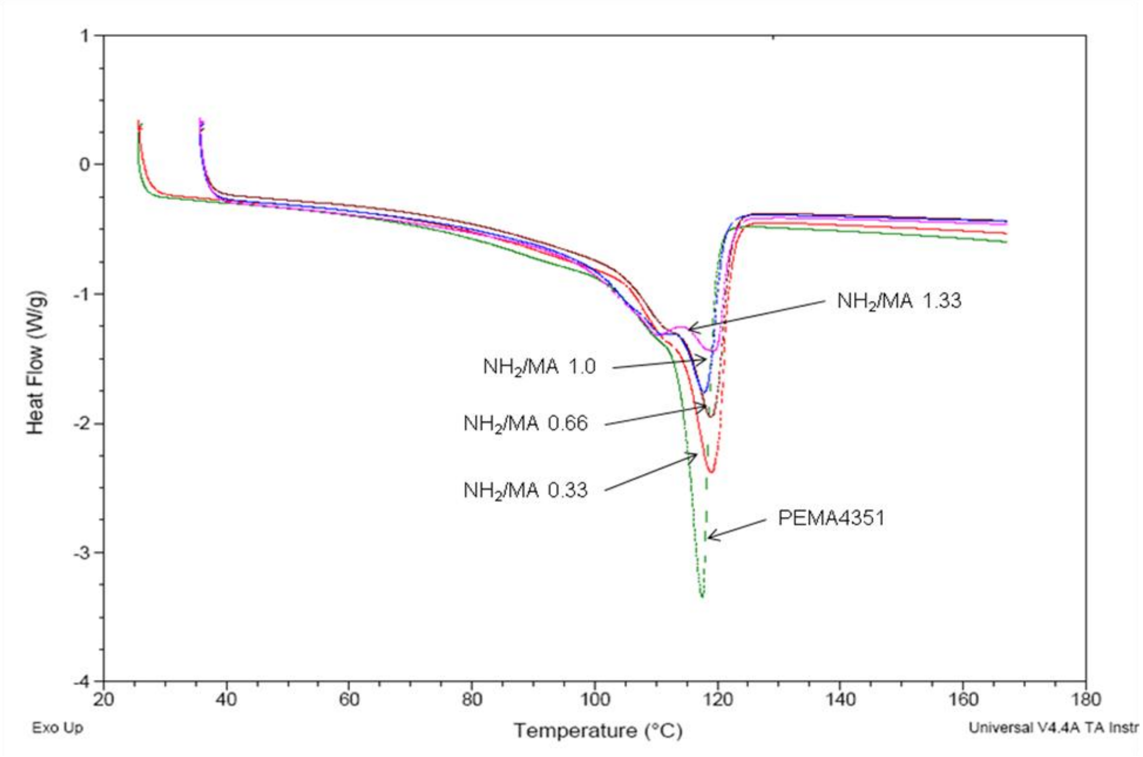


Figure 2.10 Second heating scan for PEMA4351 and its reaction products with EDR176

and processing is the fact that unlike the starting material (PEMA4351), the reaction products have viscosities that are high enough to be measured by the equipment. Results of a dynamic mechanical time sweep, shown in Figure 2.11 for the PEMA4351-EDR176 reaction products reveals that G’ is invariant over the course of time sweep for all of the reaction products. The G’ values are always orders of magnitude larger than the G″ values (not shown). These measurements would indicate that the material properties are not changing further as a consequence of the conditions of measurement.

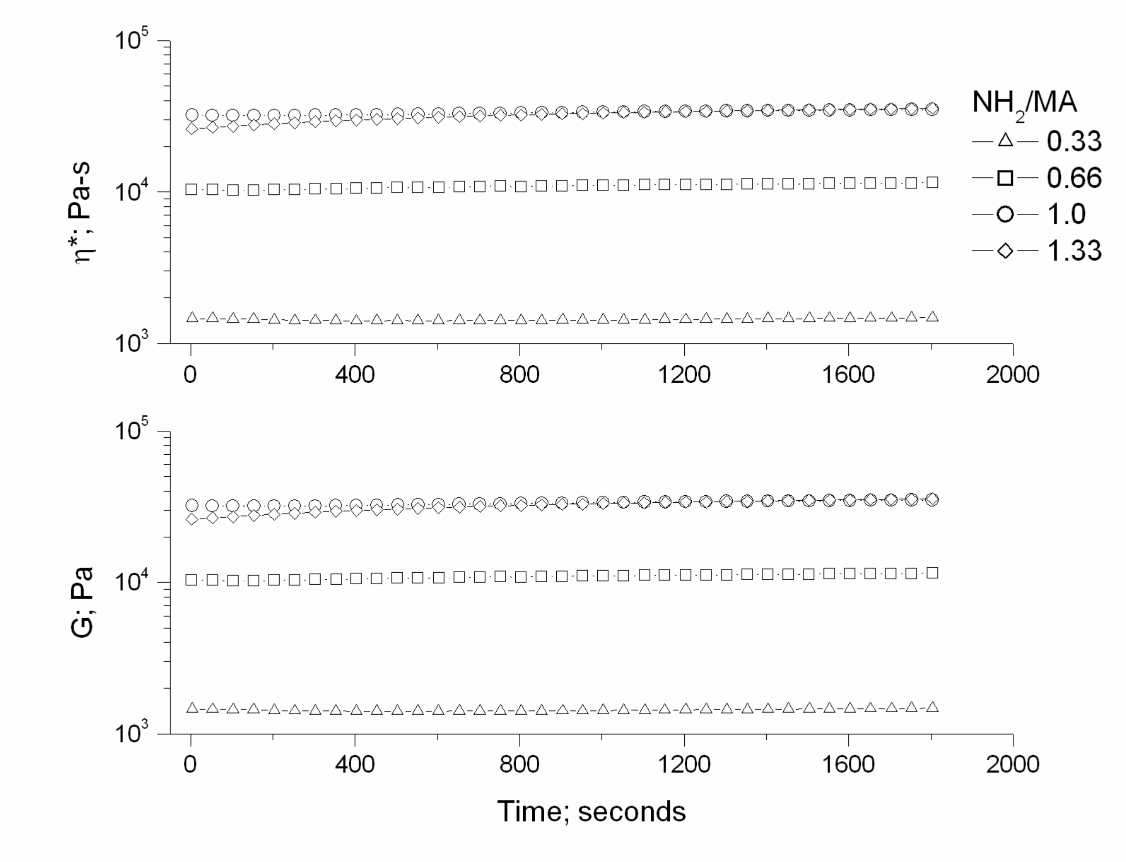


Figure 2.11 G’ and η* data from dynamic time sweep for PEMA4351-EDR176 reaction products at different NH2/MA molar ratios. (Ttest = 140 C; γ° = 0.05; ω= 1 rad/sec)

Dynamic frequency sweeps followed the time sweep measurements. Data from these frequency sweeps for processed PEMA4351-EDR176 reaction products are shown in

Figure 2.12. Almost no dependence of G’ on frequency was observed and the G’ curves for all products investigated are flat over the whole frequency range studied. This behavior is very different from the typical thermoplastic response in which G’ shows a strong dependence on frequency, especially at low frequencies where a typical slope of about 2 has been reported (terminal zone behavior) [31-33]. However, this frequency

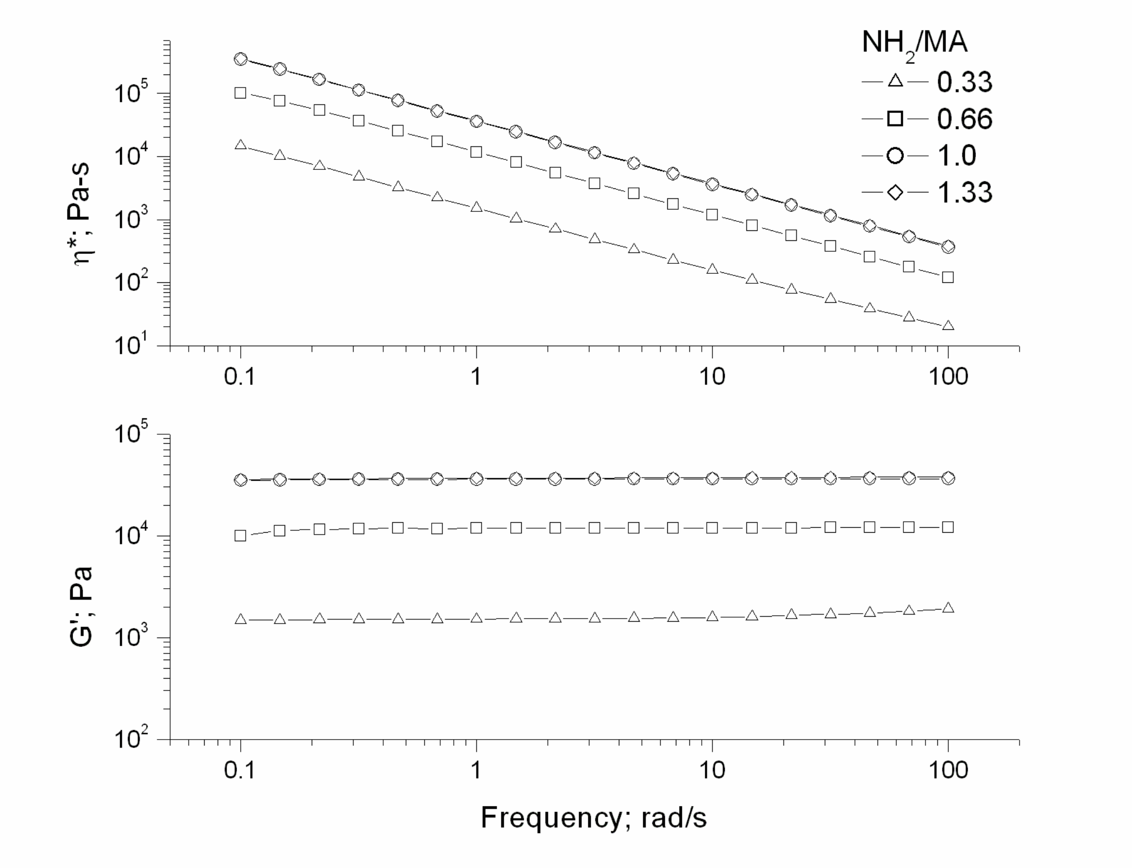


Figure 2.12 G’ and η* data from dynamic frequency sweep for PEMA4351-EDR176 reaction products at different NH_2/MA molar ratios. (T_{test} = 140 °C; $\gamma° = 0.05$)

dependence has been reported to decrease with introduction of long chain branching [31;33] and crosslinks [32;33] which introduce additional modes of relaxation, absent in the linear polymers of equivalent molecular weight. These observations suggest that the reaction products are either very high molecular weight branched polymers, or that a crosslink network is present. The observed behavior is typical of rubbery plateau behavior associated with chain entanglements in high molecular weight polymers, or the molecular weight between crosslinks in network polymers. The plateau value of G' increases with the increase in the NH_2/MAH molar ratio from 0.33 to 1.0. Dynamic frequency sweeps for the PEMA4351-ED600 are presented in Figure 2.13 and show very similar results.

The nature of this plateau zone was further explored with stress relaxation experiments. At elevated temperatures, samples capable of significant flow in order to relieve an applied strain, will exhibit a rapid decay in the stress relaxation modulus with time. The stress relaxation modulus for network polymers will decay to a value of modulus that is characteristic of the degree of crosslinking of the material. Stress relaxation tests were conducted at 140 °C and the results are shown in Figure 2.14 for the PEMA4351-EDR176 reaction products. The sample with 0.33 NH_2/MAH molar ratio exhibits thermoplastic behavior characterized by a rapid decay of modulus to zero after imposition of a strain. The other materials exhibit a plateau zone that is more characteristic of a thermoset.

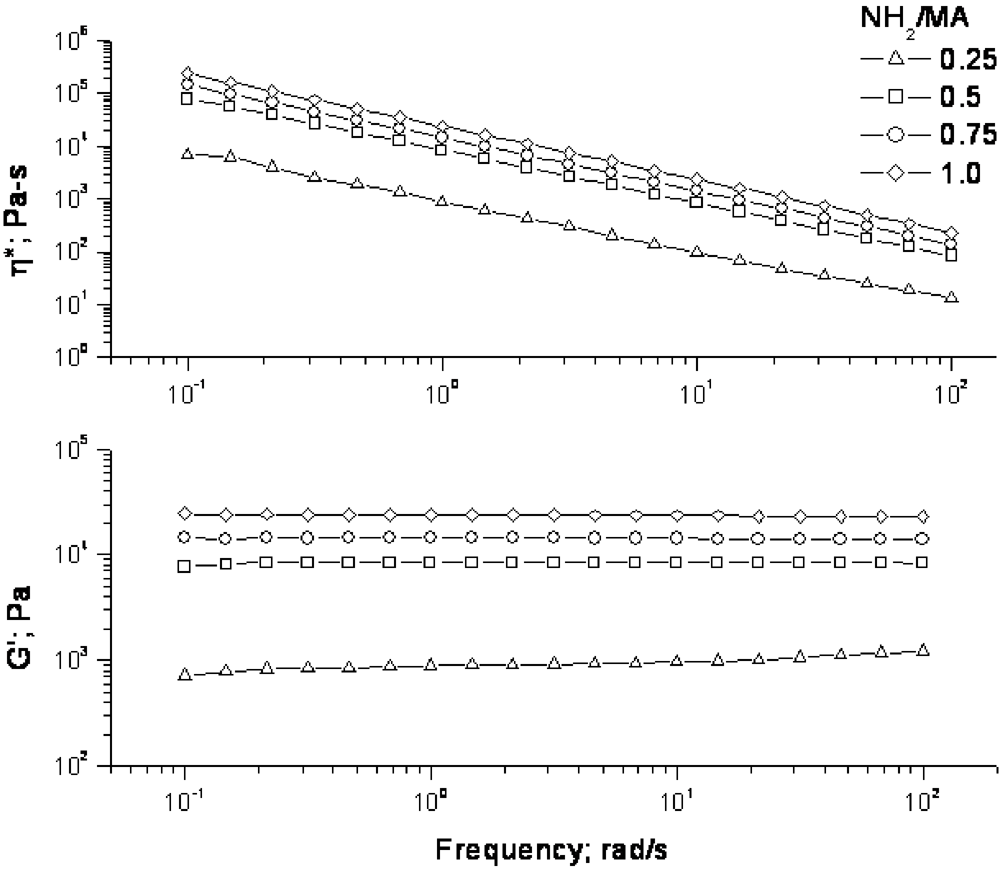


Figure 2.13 G' and η* data from dynamic frequency sweep for PEMA4351-ED600 reaction products at different NH_2/MA molar ratios. (T_{test} = 140 °C; $\gamma° = 0.05$)

The evidence of plateau behavior that is more consistent with a thermoplastic material seemed contradictory to the fact that these materials were moldable at elevated temperature by compression molding. The contradiction suggests that the degree of crosslinking of the material is altered with molding processes or by the measurement processes themselves. This hypothesis was tested by observing the ability of the material to flow as a function of time at elevated temperatures. Specifically, the propensity of the material to sinter was used as a gauge of thermoplasticity.

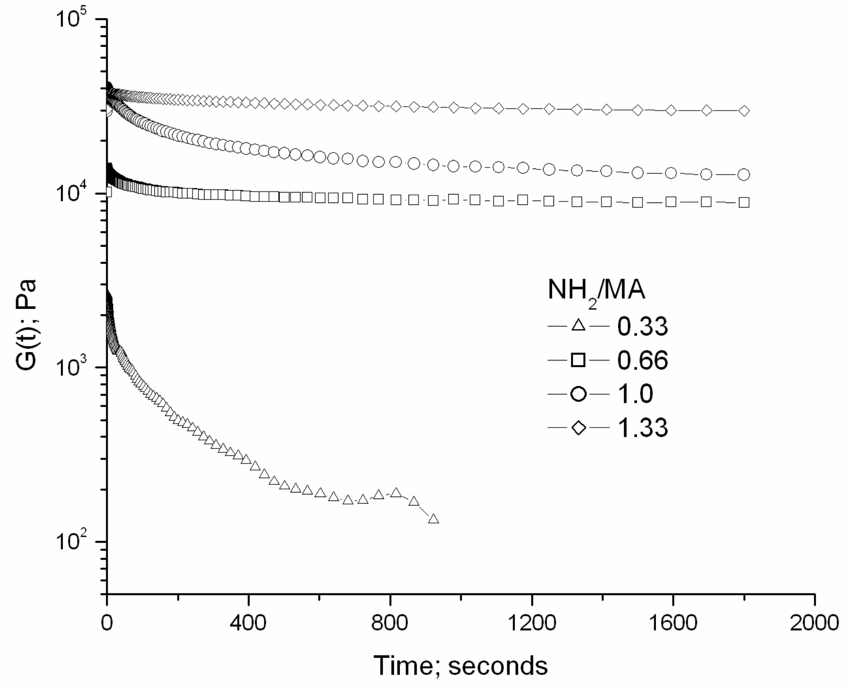


Figure 2.14 Relaxation modulus as a function of time for PEMA4351-EDR176 reaction products at different NH_2/MA molar ratios. (T_{test} = 140 °C; $\gamma°$ = 0.05)

In sintering experiments, two small pieces of powdery material are placed in contact at temperatures above the melting range of the material. With typical thermoplastics, surface tension effects will cause the two particles to flow into each other to eliminate the boundary between the two particles, resulting in one larger particle with no remnant of the boundary visible. Figure 2.15 shows this experiment for the PEMA4351-EDR176 reaction products for NH_2/MA ratio 1.0. The optical micrograph clearly shows that flow occurs to eliminate particle boundaries within a time frame of 75 seconds. This is consistent with the observed moldability of this material.

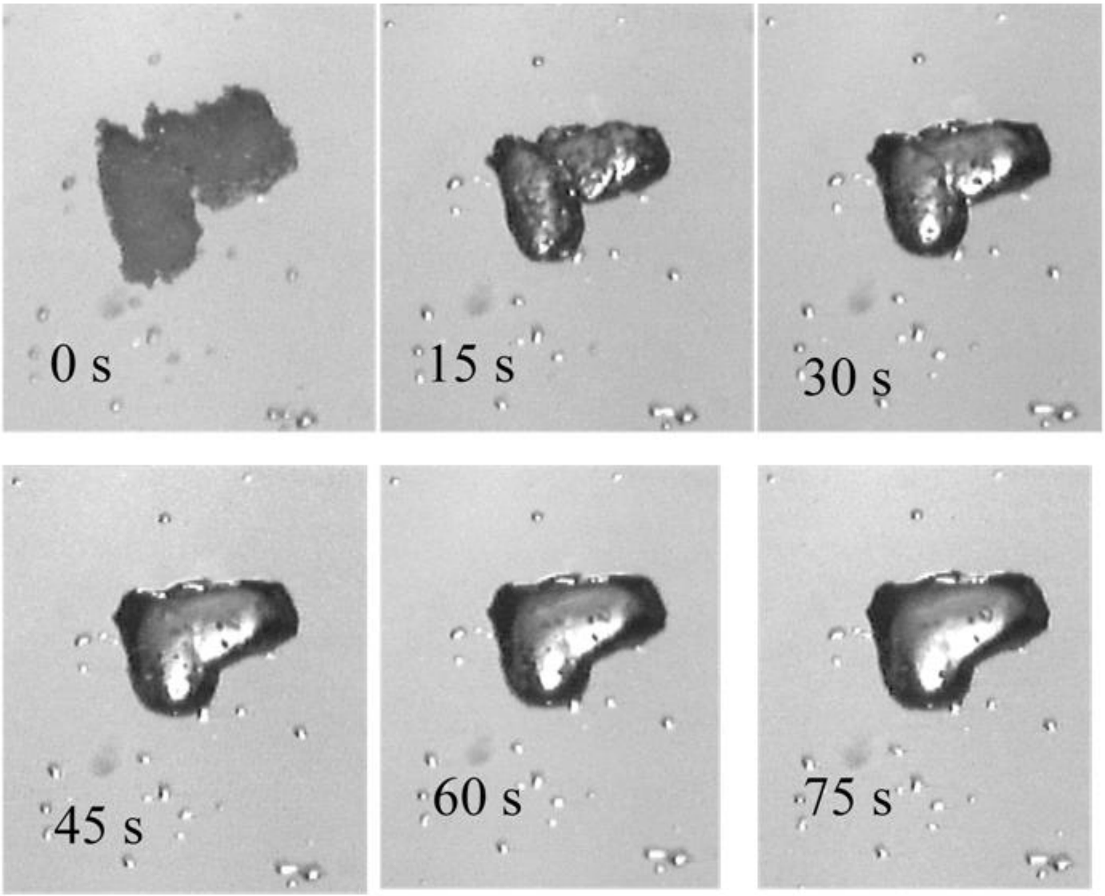


Figure 2.15 Sintering of PEMA4351-EDR176; NH2/MA 1.0 reaction product with time.

Similar behavior is observed in Figure 2.16 for PEMA4351-EDR176 reaction product NH_2/MAH of 1.33 that has been exposed to elevated temperature for a period of 1 minute before the sintering experiment. In fact, this same behavior is repeated for material that has been maintained at elevated temperatures for 2 minutes and for 3 minutes (not shown). When particles of this same material are placed side by side in a sintering experiment after being exposed to 150°C for 6 minutes, different behavior is observed (Figure 2.17). No sintering is observed at the interface of the two pieces over an extended period of time. This suggests that the material is in a state in which it cannot readily flow after a period of 6 minutes at 150°C. This is the behavior expected of a thermoset material and these observations reinforce the hypothesis that the material converts to a thermoset after extended periods of time at elevated temperatures. The dynamic mechanical frequency sweep data and the stress relaxation data discussed earlier would be characteristic of the material after such a time and temperature history.

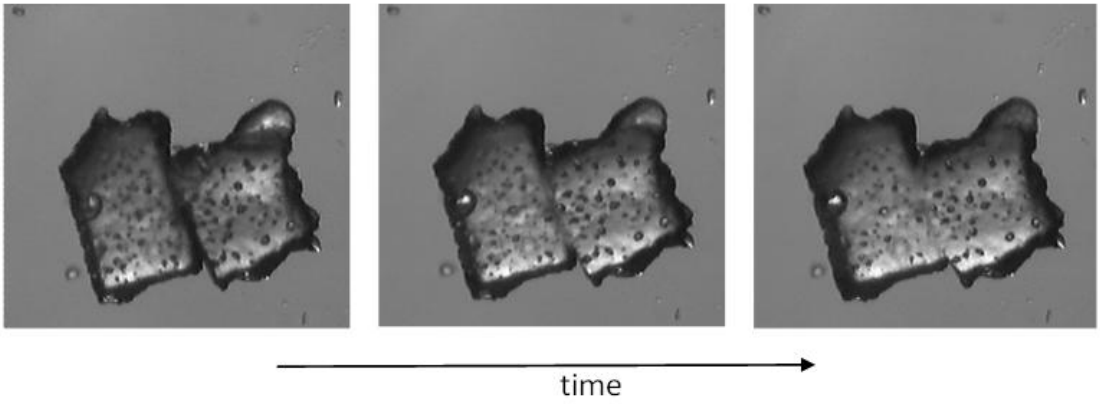


Figure 2.16 Sintering of PEMA4351-EDR176 raction products NH_2/MA 1.33; left in the melt state at 150 °C for 1 minute

This evidence of a delayed reaction to yield thermosetting material is interesting since no residual anhydride or acid was detected in the FTIR spectra although the titration data clearly shows that there ought to be residual anhydride or acid. The anhydride-amine reaction has been observed to proceed at a much faster rate than the acid-amine reaction. Perhaps residual acid in the reaction product is converted to anhydride when exposed to elevated temperatures for a sufficient time span. The newly available anhydride would react quickly with residual amine to generated new crosslinks, ultimately leading to sufficient crosslinking to produce a thermosetting material.

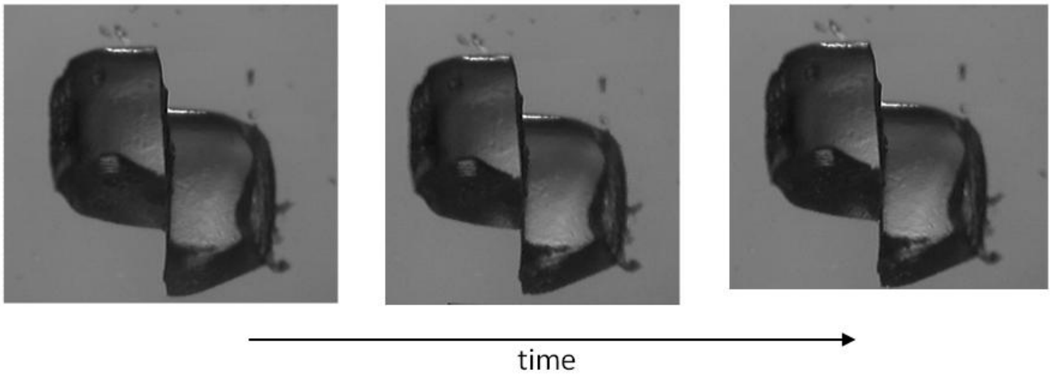


Figure 2.17 PEMA4351-EDR176 raction products NH_2/MA 1.33; left in the melt state at 150 °C for 6

2.5 Conclusions

Thermosetting materials were produced by reacting a highly functionalized maleic anhydride grafted low molecular weight polyethylene with diamines in xylene as a reaction media. The reaction in solution was observed to occur within seconds to minutes, as indicated by visual changes in the rheology of the reaction mixture. The completeness of the reaction in solution was observed to depend on the molar ratio of amine to maleic anhydride, the chain length of the diamine, and the concentration of the reactants in solution. Recovered reaction products, for which gelation did not occur in the reactor, were observed to be thermoplastic and could be melt processed at elevated temperatures. Dynamic mechanical data combined with sintering experiments show that these thermoplastic materials become thermosets when maintained for sufficient time at elevated temperatures.

Disappearance of the anhydride or acid absorbance in the FTIR spectra for the reaction products for which the NH_2/MAH molar ratio was greater than one, suggested complete conversion of anhydride. However, significant residual anhydride/acid content was assessed in the same reaction products using colorimetric titrations. Other measurements, such as rheological and thermal analysis, suggest the melt processed products were crosslinked to varying degrees depending on the molar ratio of functional groups in the reaction mixture. This suggests that FTIR analysis alone is inadequate in establishing the extent of reaction in such products and should be complemented by other analytical techniques.

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Chapter 3. Melt reactions between functionalized polyolefin and diamine

This chapter is based on the paper submitted to *Advances in Polymer Technology* 2011 by Tayyab Hameed, David K. Potter and Elizabeth Takacs.

3.1 Abstract

Reactions between low molecular weight maleic anhydride grafted polyethylene and a polyether diamine were carried out at different stoichiometric ratios of amine to maleic anhydride in the melt state. Reactions were performed both in a resin kettle and melt blender. In all cases a well mixed, thermoplastic product was recovered from the processing equipment. Titration and FTIR spectroscopy of these products suggested that some reaction between anhydride and amine functionalities did occur although the reactant conversion was not complete. When these thermoplastic products were further melt processed at elevated temperatures, they converted into thermosets containing a high degree of insoluble gel. Analysis for anhydride groups, by FTIR, in the reaction products was observed to be composition dependent. No anhydride response was observed in the product when amine was in excess, although titrations and post processing confirmed the presence of residual anhydride groups in the product. FTIR analysis seems misleading in establishing the extent of reaction in these systems in the absence of corroborating data.

3.2 Introduction

Polyolefins are among the most widely used commodity plastics. At relatively low cost, these plastics provide adequate mechanical properties for many applications, and are chemically inert. Advances in catalyst technology have enabled tailoring of the molecular structure of these materials enabling the production of polyolefins with desired physical properties [1-4]. As a result polyolefin products are available with a range of molecular weights and molecular structures. Low molecular weight polyolefin products are marketed as waxes and find applications as polymer processing aids, hot melt adhesive formulation components, in personal care products [5] and as compatibilzers in polymer composites [6].

While it is desirable to have chemically inert materials in many applications, this property of polyolefins can limit the utility of these materials in other applications where interaction with other materials is desired. Introduction of polar groups or even chemically reactive groups in the polyolefin polymer chain is carried out in practice by reactive processing of these materials. Chemical grafting of small molecules onto the polyolefin chain using a free radical source during an extrusion operation is a common technique that is used to provide additional functionality. Grafting of reactive functional groups like maleic anhydride and silane is a very popular way to make polyolefins adaptable to a specific application [7].

Anhydride grafted polyolefins are widely used as compatibilizers in polymer composites and blends [6,8,9]. They enhance the interfacial strength by interacting with the filler surface like clay or wood in composites whereas in immiscible polymer blends they improve the compatibility between the different phases by *insitu* coupling reaction. One of the most widely used and studied coupling reaction is the reaction between anhydride and amine groups [8,9]. Orr et al. [9] investigated the kinetics of functional groups widely used for *insitu* compatibilization of polymer blends. Reactions were carried out between polystyrene and poly(methyl methacrylate) (PMMA) with terminal functional groups in a high speed mini melt mixer at 180 °C. Products were then analyzed using GPC to quantify the extent of reaction. Among the nine different reactions investigated, the aliphatic amine reaction with anhydride was found to have the fastest kinetics with complete conversion of amine and anhydride groups observed within 30 seconds. Interestingly, although the reactions were carried in very viscous polymeric systems, the reaction between amine and anhydride functionalities was found not to be diffusion controlled. Increasing the molecular weight of the polymers or decreasing the speed of the mixer (shear rate) was reported to have little influence on the reaction kinetics.

In another study, Lu et al. [10] investigated the possibility of grafting amine groups on polypropylene. To achieve this, stoichiometry and differences in the relative reactivity of primary and secondary amine groups were exploited. Hexamethylene diamine (HMDA) and N-hexylethylenediamine (HEDA) were melt mixed with maleic anhydride grafted polypropylene at 180 °C in a melt blender as well as in an extruder. A fast reaction between amine and anhydride functionalities as reported earlier by Orr et al. [9] was claimed based on mixing torque data and FTIR analysis of the products. The reaction was suggested to be complete within 90 seconds. The dynamic viscoelastic measurements of the aminated polypropylene indicated the presence of extensive branching, which was a strong function of stoichiometry. However, no evidence of significant crosslinking was observed in any of the products.

Song and Baker [11] studied the reactivity of different amine groups (primary, secondary and tertiary) with maleic anhydride and acid groups in polymeric systems. Styrene maleic anhydride copolymer (6% anhydride) and a reactive polyethylene (9% acrylic acid) were reacted with different diamines. Fastest reaction kinetics were reported for reaction between primary amine and anhydride groups, although significant reaction was also observed between secondary amine and anhydride groups. All reactions were carried out at one stoichiometric ratio in which the reactive groups were equimolar. Based on the melt blender torque data, they concluded the reaction between primary amine and anhydride was complete within 2 minutes at 180 °C. Based on the melt flow index (MFI) measurements and dissolution behavior of the product in xylene, it was concluded that functionalized polystyrene-primary diamine product was completely crosslinked. The crosslinking of the product was suggested to be a result of a combination of imide as well as amide linkages.

In another study, Colbeaux et al. [12] attempted the crosslinking of maleic anhydride grafted polyethylene with 1,12-diaminododecane by melt mixing in a polymer melt blender. Once again, reaction between amine and anhydride was reported to be fast and suggested to proceed via. amide intermediate forming cyclic imide. Although the degree of maleic anhydride grafting of the polyethylene utilized was low compared to that used by Lu et al. [10], a maximum of 32% gel content was reported for the product when the amine to maleic anhydride molar ratio (NH_2/MA) of the reaction mixture was 2.0. This result is in contrast to no crosslinking reported by Lu et al. [10]. The complex viscosity from dynamic viscoelastic measurements also showed a maximum at the NH_2/MA 2.0.

In summary, most of the earlier studies suggested extremely fast kinetics for reaction between amine and anhydride groups and that the reaction could be used for polymer modification. However, almost all of these reports employed high molecular weight anhydride grafted materials and low molecular weight amine molecules [10-12]. Reactions between a low molecular weight anhydride grafted polyolefin and polyamines have never been explored to the best of our knowledge.

Further motivation to explore these reactions comes from the recent commercialization of low molecular weight highly functionalized polyolefins [5,7]. These polyolefins with tailored architectures and melt temperatures have been synthesized using advanced catalyst systems. With lower melting temperature and significantly lower melt viscosities, these materials can be reactively processed in the melt in a batch reactor rather than using conventional extrusion equipment. Consequently, grafted versions of these waxes could be functionalized to a much higher degree in a batch reactor compared to that achieved in conventional reactive extrusion operations [7].

In this article, an attempt has been made to study the reaction between functionalized polyethylene and a polyether diamine. Reactions were performed by melt mixing commercially available maleic anhydride grafted polyethylene wax and polyether diamine in a resin kettle or a melt blender. Changes in viscosity of the reaction mixture and analysis of the reactor products using several techniques was used to understand the reaction kinetics, the reaction path and crosslinking mechanism. This publication focuses on understanding the mechanism of the formation of thermosets. Detailed characterization (thermal, rheological, mechanical) of the thermosets so obtained will be presented in a later publication.

3.3 Experimental

3.3.1 Materials

Licocene® PEMA4351 (maleic anhydride grafted polyethylene) was kindly supplied by Clariant® Canada, Inc. Maleic anhydride grafting is carried out in a batch process using a free radical mechanism with this material, as described in the patent literature [7]. The grafts are believed to be distributed randomly based on the free radical mechanism utilized to achieve them. PEMA4351 received as fine grains was vacuum dried overnight at 100 °C before use. Polyether diamine (ED600) was obtained from Huntsman Chemicals, USA. It is a liquid at room temperature and was used as received. The polyether backbone constitutes predominantly polyethylene oxide units although some propylene oxide units are also present. The important characteristics of the materials are presented in Table 3.1. Molecular weight, viscosity and density values were obtained from the supplier. Titrations were performed in our lab.

Table 3.1 Characteristics of reactants

	M_w g/mol	M_n (g/mol) g/mol	M_w/M_n	Viscosity mPas	Density g/cm^3	MA content %
PEMA4351	3000	1200	2.5	300[1]		5.2[3]
ED600		600		77.6[2]	1.035	

[1]measuresd at 140 °C; [2]measuresd at 20 °C

[3]assessed by colorimetric titrations

3.3.2 Procedures

Reactions were carried out at different NH_2/MA using a resin kettle (NH_2/MA 1.5, 2.0 3.0) and a melt blender (NH_2/MA 0.66 and 1.0).

Reactions carried out in the resin kettle, utilized a 500 ml glass kettle equipped with an overhead stirrer (2 inch diameter high speed dispersion blade from McMaster Carr USA) and a thermocouple. The kettle was heated using a heating mantle. To initiate the reaction, a premixed PEMA4351-ED600 mixture was added to the resin kettle at room temperature, which was then heated with continuous stirring using the overhead stirrer. The power to the stirrer motor was fixed to give a rotational speed above 1000 rpm at the start of the experiment. Temperature and rpm data over the course of the reaction were recorded using a thermocouple and digital tachometer. The reaction was continued until the reaction mixture wrapped around the stirrer and started to climb along the shaft (Weissenberg effect). At this point it was immaterial to continue reaction since no more mixing could be achieved. Reaction was terminated and the reaction mixture removed from the resin kettle. The time required to reach this endpoint varied with the composition of materials in the kettle and never exceeded 20 minutes. The final temperature reached by the reaction mixture was in the range between 150°C and 160°C in all experiments.

Reactions performed in the melt blender used a Haake PolyLab system (Rheomix 3000p) equipped with roller rotors. PEMA4351 was premixed with ED600 and the mixture added to a preheated blender operating at 150 °C and 50 rpm. Reaction time was 15 minutes. Mixing torque and temperature data were recorded over the course of the reaction.

Throughout the rest of this paper we refer to the materials that are produced as a consequence of the melt mixing operation both in resin kettle and melt blender as “reactor products”.

These reactor products were analyzed using titration, FTIR and assessed for the degree of gel content to establish the extent of reaction during the melt mixing. These reactor products were further melt processed by compression molding using a hydraulic press (Carver Press) at different temperatures and lengths of time to probe changes in chemistry and possible crosslinking as a consequence of further processing.

Reactor products were analyzed for maleic anhydride content by titration. Approximately 0.2 g of the sample to be analyzed was allowed to dissolve in 60 ml of xylene under reflux in a 500 ml round bottom flask fat at least 10 minutes. The hot solution was then titrated against standard KOH solution (~0.02 M) prepared in methanol. Thymol blue dissolved in methanol was used as indicator. When the blue color persisted for one minute the titration was stopped and degree of grafting assessed as mg KOH/g of polymer. These values can be used to calculate the percentage of maleic anhydride grafted using simple stoichiometric calculations provided elsewhere [15].

The gel content of the reactor products were analyzed using the extraction method described in ASTM D2765. Approximately 0.2-0.3 g of finely cut polymeric sample was enclosed in small pouches made of 120×120 mesh Type 304 stainless steel wire cloth. These pouches were then left immersed in refluxing xylene for more than 12 hours to extract the soluble fraction. At the end of extraction period, the samples were removed from the solvent, washed with acetone and allowed to dry. The loss in weight was used to calculate the degree of gel content.

FTIR spectra were collected using a Nicolet® 510 FTIR spectrometer, USA. Data was collected and processed using EZOminic software. Thin films of the samples were prepared by compression molding at elevated temperatures. Spectra were recorded between 400-4000 cm^{-1}. At least 32 scans were performed to generate a spectrum.

3.4 Results and Discussion

Reactions were carried out in a resin kettle for compositions with NH2/MA > 1.0. The rotational speed of the stirrer dropped to a minimum and then started to increase again during processing. The drop in stirrer speed was associated with the initiation of melting of the PEMA 4351 wax. Speeds above 1000 rpm were regained once the wax was melted. This was accompanied by a vortex (signifying good flow and mixing) and the formation of a visually homogenous mixture. As mixing continued, the mixture was observed to wrap around the agitator and climb along the agitator shaft (Weissenberg effect). The build up in the elasticity of the mixture was probably a consequence of reaction between anhydride and amine functionalities resulting in an increase in the molecular weight/crosslinking of the material. Stirring and heating were terminated at this point, and the reactor products collected for further analysis.

Mixing torque data for the two reactions (NH_2/MA 0.66 and 1.0) performed in the melt blender are presented in Figure 3.1. Two peaks in the mixing torque data were observed for both reactions. Based on earlier reports for similar systems [10,11] the first peak is ascribed to the melting of PEMA4351, whereas the second peak is associated with the reaction of maleic anhydride and amine resulting in formation of viscous, high molecular weight product. The magnitude of the stabilized mixing torque values after the reaction peak is higher for the NH_2/MA=1.0 reaction mixture. This is presumably a consequence of the development of a higher viscosity signifying more crosslinking/branching and is consistent with crosslinking theory [10]. The drop in mixing torque after the second peak, associated with reaction/crosslinking, is due to physical break up of the network polymer due to shear force of the blades at high temperature. Similar trend in mixing torque have been reported in published literature [10-12]. In earlier investigations [10,11] either a single or two closely associated peaks were observed for polymer melting and reaction. However, the peaks for melting and reaction were separate in the current study. The delay in the appearance of the reaction peak in this work may be a consequence of the reaction conditions or the low molecular weight of the functionalized polyethylene utilized. Reaction conditions (temperature and rotor speed) used in the current study are milder than that utilized in the referenced studies. The molecular weights of diamine used in the previous studies were much smaller. The larger diamine molecules used here could be expected to affect the rate of diffusion of reactive groups towards each other during the mixing process. Immiscibility between the polyethylene and polyether might be another possible reason for the delayed reaction peak.

To understand the extent of reaction achieved in the reactor, the reactor products were analyzed using several techniques. Colorimetric titrations were used to assess the extent of reaction that occurred in the reactor (melt blender/resin kettle) by measuring residual anhydride content in the reactor products. Table 3.2 presents the residual maleic anhydride content assessed in all the reactor products (both from melt blender and resin kettle). Significant portion of the initial maleic anhydride content (5.2%) was still unreacted and complete conversion of reactants did not take place. The lowest residual

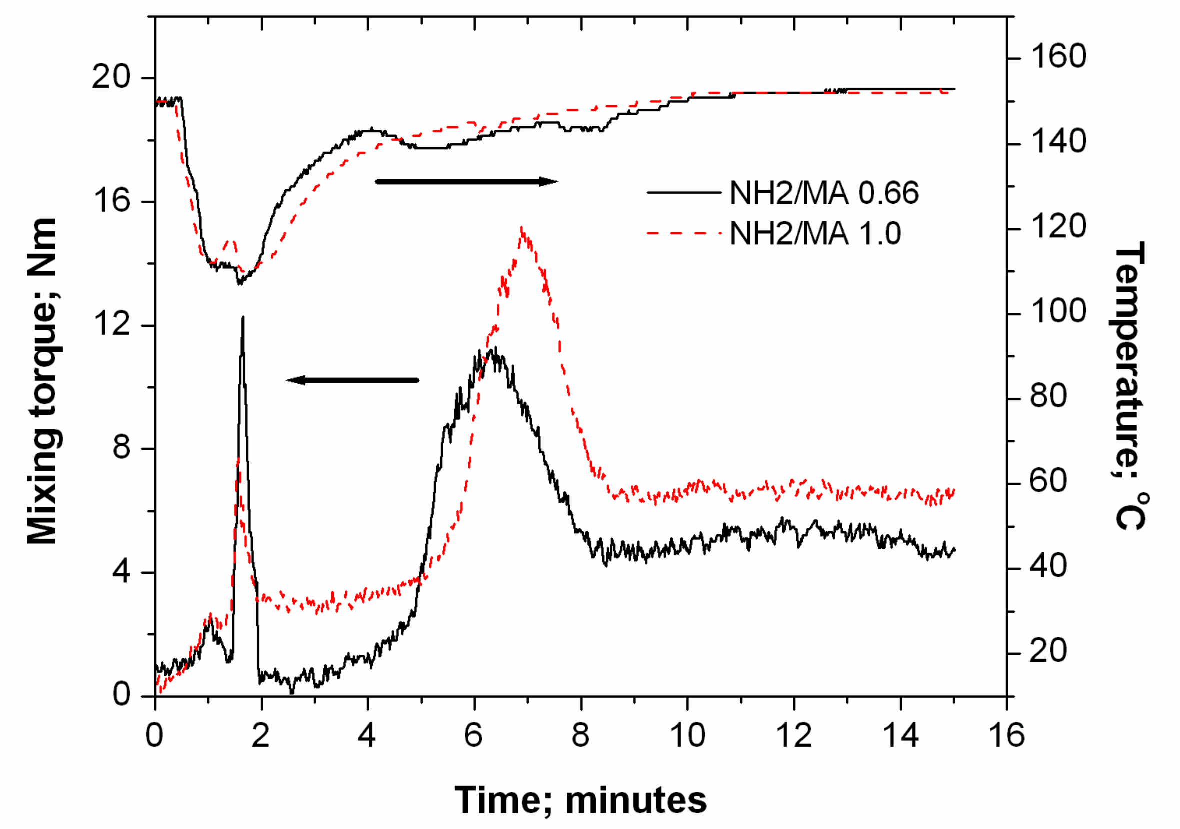

Figure 3.1 Mixing torque data for reactions performed in the melt blender at 150 °C; 50 rpm.

maleic anhydride was assessed in reactor product NH_2/MA=1.0 which could be due to the combination of stoichiometry and intense reaction conditions in the melt blender compared to resin kettle. This material did not completely dissolve prior to titration which is likely a consequence of a high degree of crosslinking in this reactor product. Due to these observations, the reported residual anhydride at best reflect the anhydride content in the "sol" soluble fraction of this reactor product. Although this confirms the presence of residual anhydride suggesting incomplete reaction, the information is not complete to find a relationship between NH_2/MA molar ratio and the degree of reaction (residual anhydride content).

Table 3.2 Residual maleic anhydride content using titration method in the reactor products

NH_2/MA molar ratio	Residual MA content (%)
0.66	2.9±0.1
1.0	1.74±0.3
1.5	2.72±0.04
2.0	2.68±0.07
3.0	2.65±0.09

To further understand the degree of reaction and the associated chemistry, FTIR spectra were collected for all reaction products and the reactant PEMA4351 (Figure 3.2). Reactor products NH_2/MA 2.0 and 3.0 showed spectra similar to reactor product NH_2/MA 1.5 and hence the spectra not presented. In the PEMA4351 spectrum, strong responses at 1715 cm^{-1} and 1780 cm^{-1} are assigned to the carbonyl stretching vibrations of carboxylic acid and anhydride respectively. The weak response at 1860 cm^{-1} is due to the asymmetric carbonyl stretching of anhydride. Absorptions around 1460 and 720 cm^{-1} are due to the C-

H stretching of methylene groups in polyethylene chain. Strong response at 1715 cm^{-1} suggest that significant anhydride is present in the form of diacid even after vacuum drying overnight at 100 °C [17].

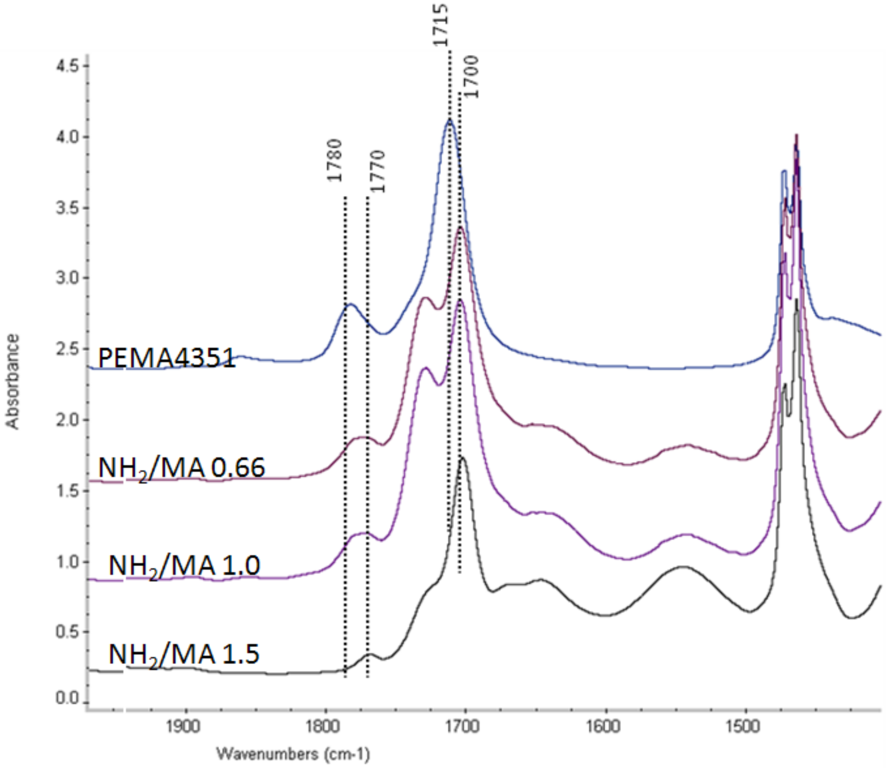

Figure 3.2 Overlaid FTIR spectra for PEMA4351 and reactor products. Films prepared in a hot press at 160 °C and 2 minutes.

Spectra for the reactor products NH2/MA ≤ 1.0 were observed to be different than those > 1.0 and will be discussed separately. In the spectra for reactor product NH_2/MA 0.66 and 1.0 the anhydride absorbance at 1780 cm^{-1} is observed to be relatively broad and slightly shifted to a lower wave number. The 1860 cm^{-1} response is also weak in these reactor products compared to that in the reactant. The decrease in the peak height is due to the consumption of anhydride due to reaction with amine as signified by cyclic imide peak ~1700 cm^{-1}[10-12,16]. However, broadness and slight shift in the 1780 cm^{-1} peak in the reactor products NH_2/MA 0.66 and 1.0 is interesting. This broad response is ascribed to a merged response from decreasing anhydride (1780 cm^{-1}) and a developing cyclic imide (1770 cm^{-1}) absorbance. To confirm the hypothesis this broad peak in spectra for reactor product NH_2/MA 0.66 was deconvoluted and the results are presented in Figure 3.3. As seen the observed broad response was deconvoluted into two peaks around 1780 and 1770 cm^{-1} representing anhydride and cyclic imide. Other peaks of interest in the reactor product include those around 1640 and 1550 cm^{-1}. They are assigned to the carbonyl stretching of the amide intermediate [11,16].

On the other hand, reactor products NH_2/MA 1.5 showed no broad response around 1780 cm^{-1}, instead showed a sharp peaks at 1770 cm^{-1} due to cyclic imide. This is accompanied by another peak at 1700 cm^{-1} also representing cyclic imide common to all reactor products irrespective of NH_2/MA. The authors have observed very similar spectra for similar products prepared in the presence of solvent [17]. In fact, Lu et al [9] presented very similar FTIR spectra although the interpretation of the results was different than in the current study. Again, peaks around 1640 and 1550 cm^{-1} are observed and assigned to the carbonyl stretching of the amide intermediate

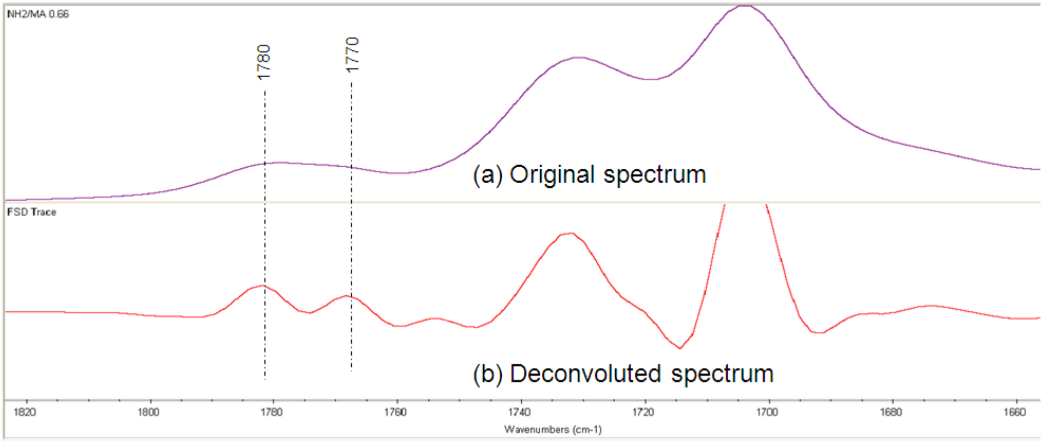

Figure 3.3 FTIR spectrum of reactor product NH2/MA 0.66 (a) original and (b)deconvoluted response around 1780 cm-1

In such reactions, the decrease in anhydride response 1780 cm^{-1} has been taken as a measure of the degree of conversion of anhydride due to reaction [10-13]. However, anhydride response in FTIR spectra observed in the reactor products investigated in the current study is rather unusual and seems to be a function of the NH$_2$/MA. Spectra for reactor products NH$_2$/MA $\leq$ 1.0 show carbonyl peak for anhydride but no such peak is observed in the spectra of reactor products NH2/MA $\geq$ 1.0 suggesting absence of residual anhydride in the products which is contrary to the titration results presented earlier (Table 3.2).

It was reasoned that if the products did contain residual anhydride functionality, as suggested by titration measurements, the reaction should continue under favorable conditions. All reactor products were further melt processed for different time periods using a hot press. The products so obtained referred to as "**melt processed products**" were analyzed for the extent of reaction using FTIR and gel content measurements. The processing schemes for these melt processed products used temperature regimes that would be more typical of the reactive processing conditions found in the literature [10,11]. The reactor products were melt pressed at temperatures of 160°C, 180°C and 200°C for time intervals of up to one hour. It is interesting to note that all the reactor products flowed and completely filled the molds on application of pressure at elevated temperatures. This suggested that all reactor products were thermoplastic and could be easily shaped by injection or compression molding.

Typical gel content data for the melt processed product $NH_2/MA=1.5$ is presented in Figure 3.4. The data at zero minutes in the figure represents the gel content in the reactor product. A value less than 1% suggested the extent of reaction that occurred in the reactor did not result in the formation of a network polymer. Gel content for the reactor product $NH_2/MA=2.0$ and $NH_2/MA=3.0$ were also similar. However, the gel content assessed for the melt processed products was very different. Within 10 minutes of melt processing at 160 °C more than 30% of the material converted to insoluble gel. The quantity of insoluble gel increased to almost 45% within 30 minutes. The maximum gel content observed is ~60%. Extent of gel content in the investigated system is limited by the degree of grafting of the functionalized polyethylene used. Based on the M_w and degree of MA grafting of PEMA4351, there are on average 1.6 MA groups per chain of functionalized polyethylene. Since the grafting is random, some PE chains would have two or more MA groups whereas some will have one and some will have none. It is this ungrafted fraction that can never become part of the network polymer and controls the degree of maximum achievable gel content assuming a complete reaction. The extent of crosslinking was even higher at higher temperatures suggesting that the crosslinking is not only a function of time but temperature too. This suggests that reactor products did contain residual anhydride functionality that underwent reaction with the excess amine resulting in crosslinking of the product. These observations are in agreement with the residual anhydride assessed using titration of the reactor products (Table 3.2).

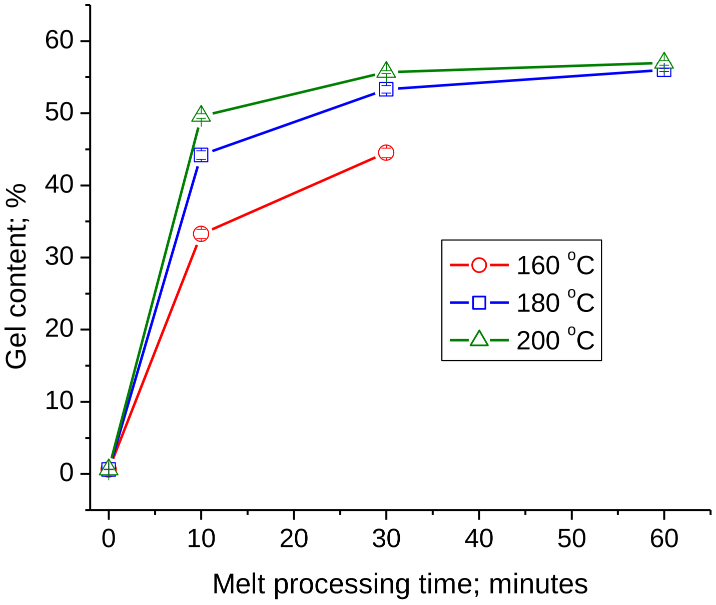

Figure 3.4 Gel content of reactor product NH_2/MA 1.5 as a function of melt processing time at different temperatures

To further elaborate the chemistry associated with the crosslinking mechanism during melt processing, reactor products were melt processed into thin films under similar conditions as used for gel content assessment. Figure 3.5 shows the overlaid spectra for the reactor product NH_2/MA 1.5 melt processed for different lengths of time at 180°C. No reactant peak; anhydride (1780 cm^{-1}) or acid (1715 cm^{-1}) could be seen in any of the melt processed products. However, the cyclic imide absorption at 1700 and 1770 cm^{-1} are clearly seen developing with increasing melt processing time. This is accompanied by a decrease in amide absorption at 1550 and 1640 cm^{-1}.

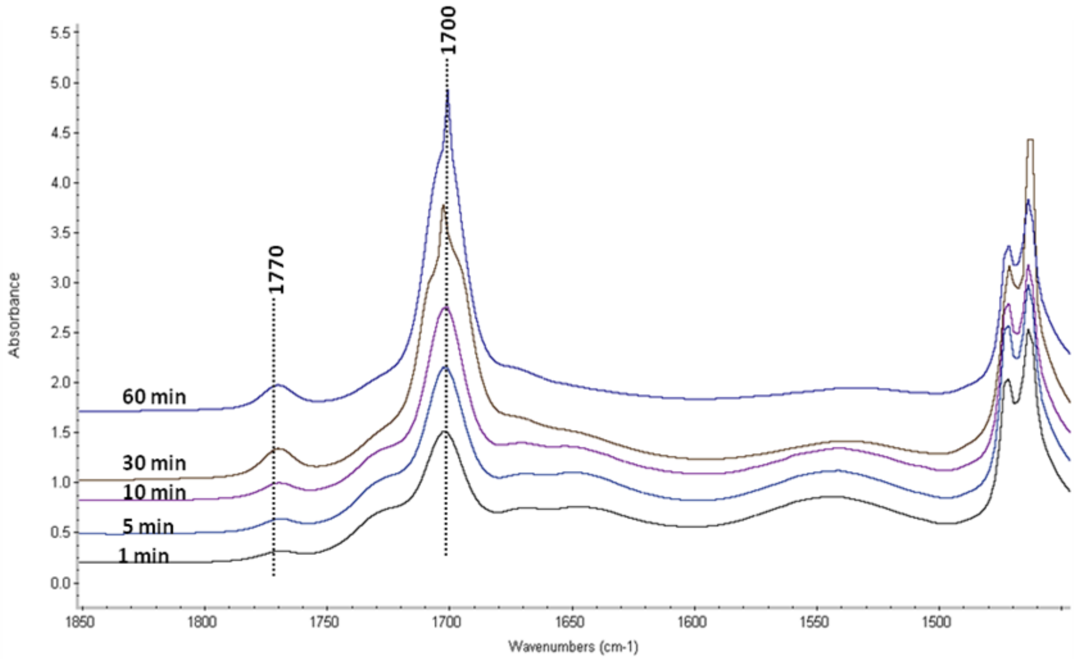

Figure 3.5 Overlaid FTIR spectra for reactor product NH2/MA 1.5 melt processed for different times at 180 °C

These result are quantified in Figure 3.6 where the relative cyclic imide and amide absorptions are plotted as a function of compression molding time. The cyclic imide responses could be seen growing with melt processing time while the amide absorptions decrease. Peak height of amide is plotted vs. the imide peak height in the inset in Figure 3.6. A linear relationship suggests cyclic imide being formed as a result of conversion of amide by dehydration. A cursory look these observations might seem consistent with the reaction mechanism widely accepted [Figure 3.7] suggesting fast formation of amide intermediate which then slowly converts to cyclic imide on dehydration [9-12,18,19]. Shearer and Tzoganakis [19] while performing model experiments between anhydride and amine functionalities in a polymeric system reported a fast disappearance of anhydride peak compared to the development of cyclic imide response. A similar mechanism was suggested by Scott and Macosko [18] claiming the dehydration of amide intermediate into cyclic imide being the slower and hence the rate controlling step. However, this hypothesis does not seem valid when the FTIR results presented in Figure 3.5 and 3.6 are considered in conjunction with the gel content results reported in Figure 3.4. The observed increase in cyclic imide response cannot be a consequence of conversion of amide intermediate as suggested by the decrease in amide peak presented alone. Conversion of amide into cyclic imide is a mere change in chemistry of an existing linkage and cannot account for the increase in the gel content observed in the melt processed products. Hence, the increase in gel content with melt processing time must be attributed to the reaction of residual anhydride and amine. Presence of residual anydride was confirmed by titrations although no MA peak was observed in FTIR. These results suggest that the analysis of the degree of reaction in these systems using FTIR analysis alone could be very misleading.

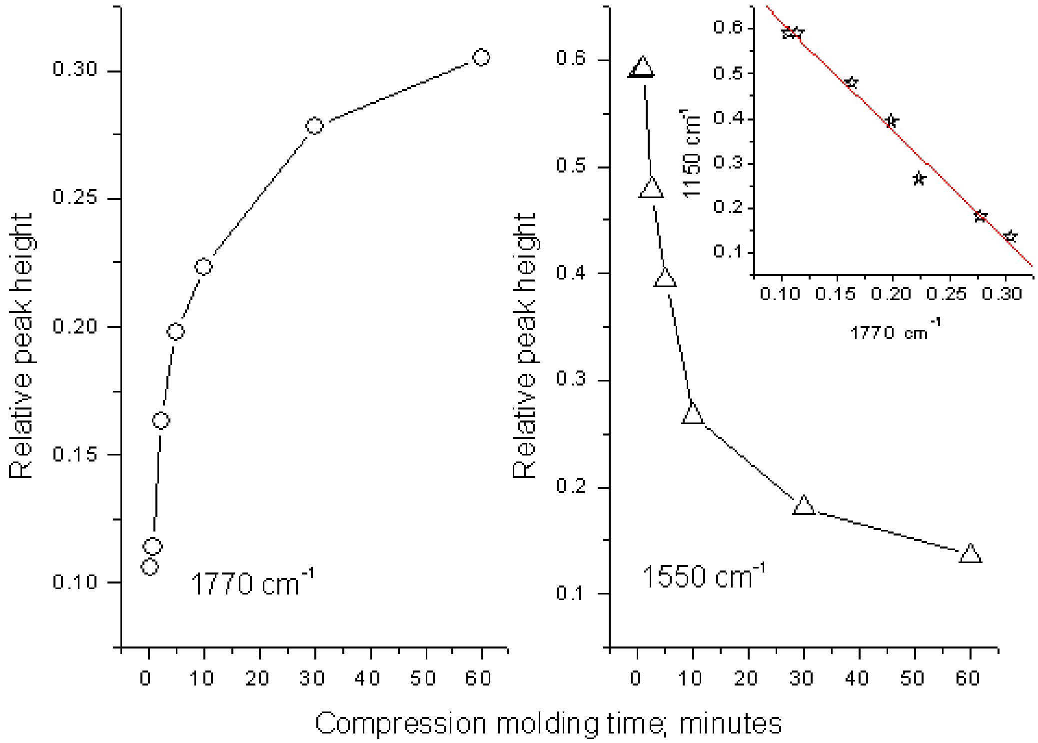

Figure 3.6 Relative peak height of for reactor product with NH2/MA molar ratio 1.5 melt processed for different times at 180 °C

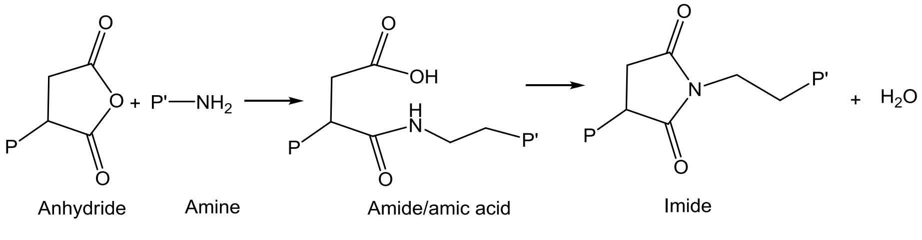

Figure 3.7 Anticipated reaction between anhydride and amine [9-12,18,19]

3.5 Conclusion

Reactions between low molecular weight maleic anhydride grafted polyethylene and a polyether diamine were carried out at different stoichiometric ratios of amine to maleic anhydride in the melt state. Reactions were performed both in a resin kettle and melt blender. In all cases well mixed, thermoplastic products were recovered from the reactor. Titration and FTIR spectroscopy of these products suggested that some reaction between anhydride and amine functionalities did occur although the reactant conversion was not complete. When these thermoplastic products were further melt processed at elevated temperatures, they converted into thermosets as evidenced by the presence of high degree of insoluble gel fraction in xylene. The FTIR analysis for anhydride groups in the reaction products was observed to be composition dependent. Titrations and post processing confirmed the presence of residual anhydride groups in these products. FTIR analysis seems to be misleading in establishing the extent of reaction in these systems in the absence of corroborating data.

Acknowledgements

This work was financially supported by the Ontario Centres of Excellence (OCE) and Clariant Canada Inc. The authors wish to thank Hermann Koch (Clariant Canada, Inc.) and David Alexander (Huntsman Chemicals, USA) for providing the Licocenes and diamines. We would like to acknowledge Giang Le for the processing work with the melt

blender and summer students T. Jakanovic and N. Childs for assisting in most of the experiments. Support extended by Paul Gatt is also appreciated.

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Chapter 4. Study of reaction between a low molecular weight highly functionalized polyethylene and hexamethylenediamine

This chapter is based on the paper published in *Macromolecular Materials & Engineering* **2010** by Tayyab Hameed, Patrick J. Quinlan, David K. Potter and Elizabeth Takacs. DOI: 10.1002/mame.201100117.

4.1 Abstract

Reactions were carried out between a low molecular weight, highly functionalized maleic anhydride grafted polyethylene and hexamethylenediamine in a melt blender at 150 °C. The reactions were investigated at various stoichiometric ratios of functional groups. At all compositions, two peaks were observed in the mixing torque data. The appearance of first peak, observed soon after introduction of the reactive mixture to the melt blender, was independent of composition while the second peak was composition dependent. Gel content and FTIR analysis suggest that the first peak is a result of melting of the functionalized polyethylene and some reaction of the anhydride and amine functionalities while the second peak was mainly a result of crosslinking. The reaction mixture is thermoplastic before the second peak and the time between the first and second peak defines a processing window, in which the reaction mixture is thermoplastic. Higher temperature melt processing of the thermoplastic reaction products converted these materials to thermosets. The progress of the anhydride-amine reaction was studied using FTIR during this conversion, as well as by measuring the generation of insoluble

crosslinked material. These FTIR results reveal that the reaction between anhydride and amine moieties results in the formation of an amide intermediate, which then converts to cyclic imide at higher temperatures. The analysis suggests that the use of the FTIR anhydride absorption to assess the degree of reaction is misleading in these reactions.

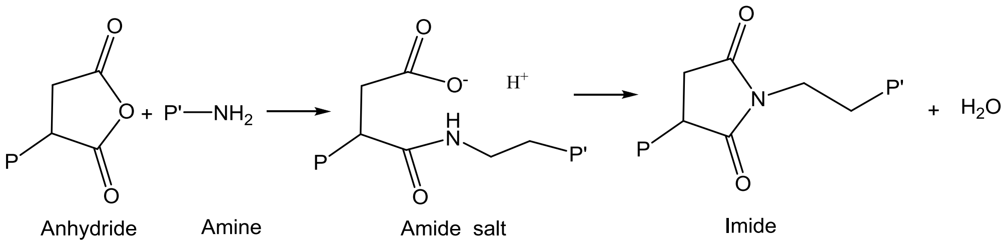
4.2 Introduction

Reactions between amine and anhydride moieties has been widely used in polymer modification [1-5] and interfacial phase compatibilization in immiscible polymer blends [1,5-9]. Kinetics of reactions between anhydride and amine in polymeric systems have been investigated [1,6-8,10]. In some studies reaction were carried out between anhydride functionalized polymers and polyamines to study the crosslinking behavior and chemistry of the resultant polymeric products [1,5,11] while other investigations utilized the anhydride-amine reaction to specifically crosslink the polyolefins [12]. However, all the cited literature utilized high molecular weight anhydride functionalized polymers and relatively short mono or polyamines. No attempt to date has been made to investigate the same reaction between amines and anhydride functionalities grafted to low molecular weight polymers until recently [13-15]. Low molecular weight polyolefins are widely marketed as waxes and used in diverse applications as polymer processing aids, aqueous dispersions, hot melt adhesive formulations [16] and compatibilizers in polymer-wood composites [17]. Grafted versions of these polyolefin are used for applications where interaction with another substrate is required.

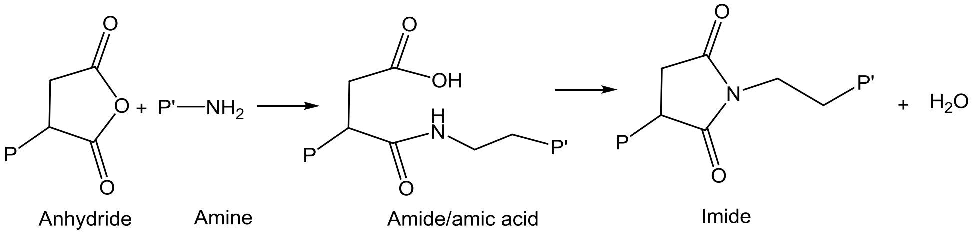
Recently, a range of polyolefin waxes with controlled molecular architecture have been synthesized using metallocene and Ziegler-Natta catalyst systems [16,18,19]. The low molecular weight and, associated low viscosities, enables functionalized versions of these materials to be obtained using free radical chemistry in batch processes [16,19]. This has enabled the production of functionalized products with grafting as high as 5.2 wt% [13-15]. Fast kinetics of the amine-anhydride reaction and the availability of highly functionalized low viscosity polyolefins and the oligomeric polyamines already in the market, provide motivation for the synthesis of novel olefin-based thermoset materials.

Model experiments to understand the mechanism and kinetics of the reaction between anhydride and amine in polymeric systems were conducted by Scott and Macosko [7]. Reactions were conducted in well mixed systems in which polymers with anhydride and amine functionality were dissolved in a common solvent. Styrene-maleic anhydride copolymer and amine terminated butadiene-acrylonitrile copolymer were reported to react in toluene at room temperature forming a weak gel within 30 seconds. The FTIR spectra generated using this gel was reported to show consumption of anhydride and formation of amide salt (Figure 4.1; Scheme 1). This amide salt intermediate was suggested to generate cyclic imide on application of high temperature. However, when the gel was processed at higher temperatures to study the reaction kinetics, the amide salt hypothesis could not be verified.

Shearer and Tzoganakis [6] also performed model reactions between maleic anhydride and amine. A low molecular weight polypropylene terminally functionalized with maleic anhydride and hexadecylamine were each blended into a unique polypropylene resin. Thin films of the two blends were later stacked and FTIR spectra were collected continuously using a heated infrared cell. The spectra presented showed the anhydride disappeared faster than the growth of cyclic imide. This was suggested to be a result of a relatively fast conversion of anhydride into amic acid/amide than the dehydration of amic acid into cyclic imide. The reaction scheme presented showed amic acid/amide as an intermediate instead of amide salt as suggested by Scott and Macosko [7]. However, no evidence was provided for the presence of amic acid/amide intermediate in the FTIR spectra.



Scheme 1. Amide salt intermediate [7]



Sheme 2. Amide/amic acid intermediate [1,5,6,8,10-12]

Figure 4.1 Proposed reaction mechanisms for reaction between anhydride and amine

In an attempt to produce amine functionalized polypropylene, Lu et al. [1] reacted maleic anhydride grafted polypropylene with different diamines. They exploited the stoichiometric ratio of functional groups and the difference in reactivity of various amines to achieve this goal. A set of reactions were performed between anhydride grafted propylene and hexamethylenediamne (HMDA) varying the amine to maleic anhydride molar ratio (NH_2/MA) in a melt blender and an extruder at 180 °C. The mixing torque data from both devices showed a single peak on addition of the mixture to the blender/extruder which was suggested to result from the combined effects of melting of the polymer and an increase in viscosity due to reaction of the anhydride and amine groups. Based on the width of the peak it was concluded that the reaction was complete within 90 seconds. This was supported by the disappearance of anhydride response at 1780 cm^{-1} and growth of cyclic imide response at 1700 cm^{-1} in the FTIR spectra. Melt viscoelastic measurements performed on the reaction products suggested little crosslinking however, changes in storage moduli (G') at low frequencies was explained to be a result of extensive branching in the reaction products.

Reaction between different amines and anhydride groups in polymeric systems were investigated by Song and Baker [11]. A styrene-maleic anhydride copolymer and several diamines (primary, secondary and tertiary) were reacted in a melt blender at 180 °C. Two closely associated peaks were observed on introduction of copolymer and primary diamine mixture into the blender. These were associated with the melting of the copolymer and the subsequent reaction between amine and anhydride functionalities. The powdery product removed from reactor was insoluble in xylene and was suggested be highly crosslinked material. FTIR spectra of the products showed a decrease in the anhydride response with the development of new peaks associated with amide and cyclic imide.

Recently, the authors investigated reactions between a low molecular weight highly functionalized maleic anhydride grafted polyethylene and polyether amines both in the presence of a solvent [13] and by melt mixing [14,15]. The reactor products showed little crosslinking, but significant reaction as assessed by titrations and FTIR measurements. Interestingly, no reactant (anhydride or acid) response could be seen in the FTIR spectra for products where the molar ratio of $NH_2/MA \geq 1.0$. Based on the earlier literature [1,3,6,11] this could have been taken as the complete conversion of anhydride functionality. However, when the same products were further melt processed at elevated temperatures, an increase in cyclic imide response was observed accompanied with a diminishing amide response and an increase in gel content (degree of crosslinking). It was not plausible to associate the absence of reactant peak in FTIR spectra to a fast conversion of anhydride into amide accompanied by slow conversion of the latter into cyclic imide as suggested in the literature [6,7] since it could not explain the accompanied increase in gel content (crosslinking). Conversion of amide into cyclic imide does not introduce new linkages, it merely changes the chemistry of an existing linkage. This suggested that the additional crosslinks were a consequence of reaction between residual anhydride and amine in the reaction mixture, although they could not be detected through FTIR analysis.

These recent studies revealed interesting results for polyolefin-polyether systems, which are very different than the earlier reports for systems that are compositionally different, and may be a consequence of the system composition.

The objective of the current research is to study the reactions between the low molecular weight highly functionalized maleic anhydride grafted polyethylene used in the recent studies [13-15] with a different co-reactant. Hexamethylenediamine (HMDA) is a small and more compatible molecule compared to the polyether diamines used in earlier investigations [13-15]. Hence, using HMDA as a co-reactant will allow more direct comparisons to the earlier literature [1-8,12].

4.3 Experimental

4.3.1 Materials

The maleic anhydride grafted polyethylene was Licocene® PEMA4351 acquired from Clariant®, Germany and was supplied as fine grains. It is a low molecular weight and low viscosity product. GPC and viscosity data as provided by the manufacturer is presented in Table 4.1. The degree of grafting was assessed to be 5.2 wt% using colorimetric titrations. Based on the M_w the product contains 1.59 maleic anhydride groups per chain. MA grafting is random as a result of the free radical mechanism used in the grafting process [19]. The hexamethylendiamine (99.5+%) was obtained from Acros Organics and used as received.

4.3.2 Procedure

A Haake Rheomix polymer blender equipped with roller blades was used as a reactor. The mixing parameters (rotational speed and temperature) were controlled through a microprocessor which recorded the mixing torque data during the reaction. PEMA4351 and HMDA were dry blended before being charged into the pre-heated polymer blender. The quantity of the reaction mixture charged in each case was such that 65% of the mixing chamber was filled. The time to charge the sample was approximately 1.5 minutes in all cases. The blender was operated at 150 °C and 100 rpm.

The reactions were carried out at NH_2/MA molar ratios of 1.0, 1.5 and 2.0. At each molar ratio, two reactions were carried out to enable the sampling of reactor product at different times.

Reaction products from the reactor were then melt pressed into discs (2mm thick and 25 mm diameter) and thin films for varying periods of time to understand the possible evolution of crosslinking and chemistry in these products.

Table 4.1 Characteristics of PEMA4351

M_w	M_n	M_w/M_n	Viscosity	MA content[2]
3000 g/mol	1200 g/mol	2.5	300 mPas[1]	5.20 wt %

[1]measuresd at 140 °C; [2]assessed by colorimetric titrations

Gel content was measured by assessing the insoluble content in refluxing xylene for more than 12 hours according to ASTM 2765. Approximately 0.2 g of sample were cut into small pieces and encapsulated in 120×120 mesh stainless steel type 304 wire cloth pouches, which were then left in refluxing xylene overnight. Samples were removed at the end of extraction period, dried and reweighed to calculate the insoluble fraction. All reported measurements are an average of at least five specimens.

FTIR spectra were collected in transmission mode using a Nicolet 510 FTIR spectrophotometer. All spectra were generated in a nitrogen-purged atmosphere using thin films. At least 32 scans were run to generate a spectrum. The spectra were collected and processed using Thermo Nicolet EZ Omnic software.

Dynamic viscoelastic properties were measured using a Rheometric Scientific, ARES rheometer. All properties were measured at 180 °C in dynamic mode using a parallel plate (25 mm diameter) geometry. Measurements were performed within the linear viscoelastic region for each reaction product, established using a strain sweep. Frequency sweeps were performed between 0.1-100 rad/sec at 1% strain amplitude. For stress relaxation measurements 1% strain was instantaneously applied to the sample and the stress decay was then monitored for 15 minutes.

Thermal properties were measured using a Thermal Analysis DSC Q100 operating under nitrogen purge. Approximately 5-6 mg of sample was encapsulated in aluminum pans. A heat-cool-heat cycle was then applied. The first a heating scan at 20 °C/minute up to 160 °C was to erase the thermal history of the material. This was followed by a cooling scan at 10 °C/min. up to 20 °C and the second heating scan at 10 °C/ minute to 160 °C.

4.4 Results and Discussion

The melt blender was used as a reactor in this study. Conventional high molecular weight polymers are processed in these blenders at high temperatures (>180 °C) owing to their high viscosities [1,8,11]. The low viscosity of the Licocene® polyolefin products provided the advantage of operating the blender at lower temperatures. Mixing torque data obtained for each reaction as well as the melting of straight PEMA4351 are presented in Figure 4.2. PEMA4351 showed a single peak in mixing torque whereas all the reaction mixtures showed two peaks. The single peak observed in PEMA4351 is ascribed to the melting of polymer. The intensity of first peak in the reactive mixtures is significantly higher than the intensity of the same peak in PEMA4351. The additional peak intensity is likely a consequence of some amine-anhydride reaction to build melt viscosity. A second peak was also observed in all reactive mixtures (see mixing torque curves with suffix A at each NH_2/MA molar ratio in Figure 4.2). Earlier studies on similar reactions [1,11] using high molecular weight polymeric reactants reported single or merged transitions in mixing torque combining the effects of both melting and reaction, and the reaction was deemed complete once the mixing torque stabilized.

In order to understand the significance of the two peaks observed in the current study, a second set of reactions was performed with similar composition such that the reaction was terminated before the appearance of the second peak in mixing torque. The sample was removed from the reactor for further analysis (mixing torque curves with suffix B in Figure 4.2). The products removed from the reactor hereto will be referred to as “reactor products”. The comparison of the two sets of reactor products (removed before and after

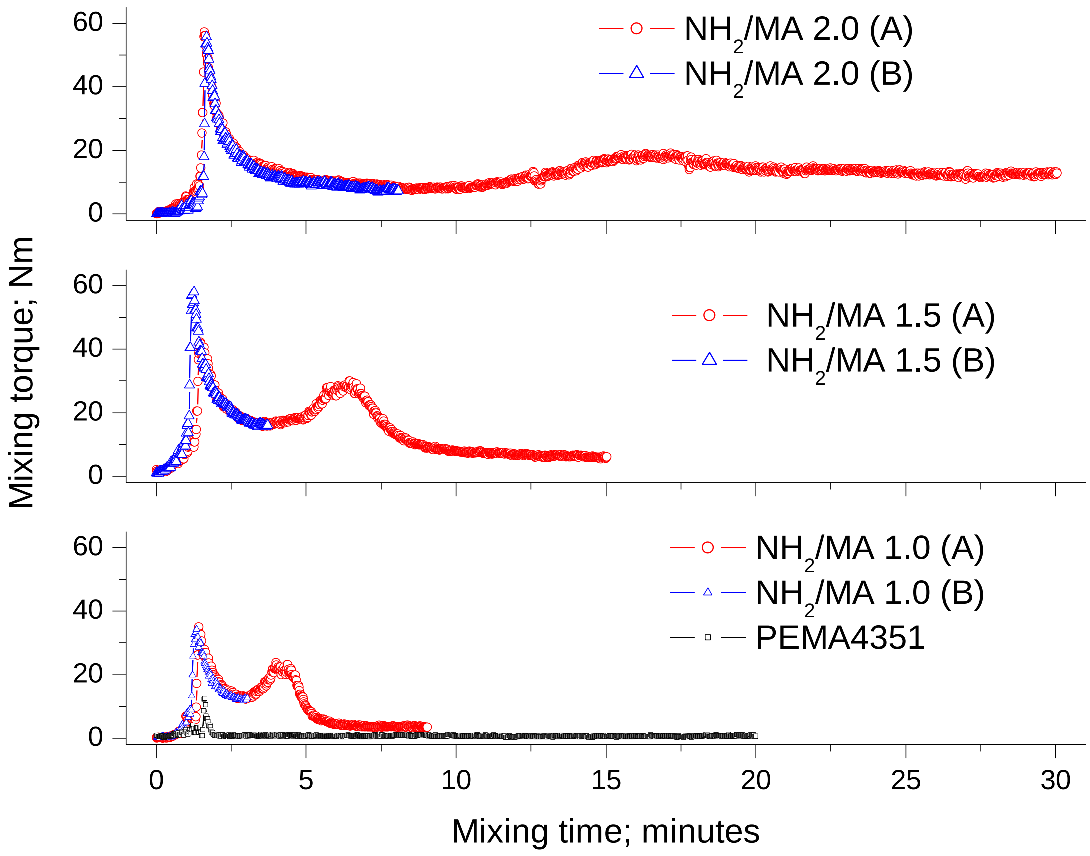


Figure 4.2 Mixing torque data from the reaction in the polymer blender

the second peak in mixing torque) was expected to provide insights into the significance of the two peaks. The texture of the reactor products removed from the blender after the first and second peaks were different. The reactor products removed before the second peak were soft and foaming for all NH$_2$/MA molar ratios studied. On the other hand, reactor product removed after the second peak had a grainy and friable texture for

NH_2/MA molar ratios 1.0 and 1.5, and a smooth texture for molar ratio NH_2/MA 2.0. Song and Baker [11] reported a powdery reactor product obtained on reacting styrene maleic anhydride copolymer with primary diamines. Inability of this product to either dissolve or swell in boiling toluene was suggested to be a result of the highly crosslinked network formed.

The significance of the two peaks in mixing torque was investigated by studying the characteristics of reactor products recovered from the mixer before and after the second peak in mixing torque. The gel content data for these samples are presented in Table 4.2. It is clear that the gel content for reactor products removed before the second peak are insignificant (<2%), whereas, the gel content for those removed after the second peak are significant. This suggests that the second peak in mixing torque is mainly associated with crosslinking. The reaction mixture is very much a thermoplastic before the second transition.

Song and Baker [11] reported two merged peaks representing melting and reaction when styrene-maleic anhydride copolymers were reacted with a primary diamine. Whereas, Lu et al [1] reported a single peak combining melting and reaction for reactive mixtures of maleic anhydride grafted polypropylene and HMDA. Both studies associated the width of the mixing torque peak with the completion of the reaction, which was suggested to be complete within 2 minutes. The results of the present study are completely different. The initiation of the second mixing torque peak, related to crosslinking, is composition dependent and varies from 2.5 to 10 minutes. When compared to earlier reports utilizing high molecular weight anhydride functional polymers and low molecular weight polyamines [1,11] these results suggest that the ability to form reactive prepolymers in recent studies [13-15] is not dependent upon the use of oligomeric polyether diamines. It appears to be related to the low molecular weight nature of the grafted polyethylene and the processing conditions that can be used as a consequence of these properties.

Table 4.2 Gel content and relative peak height of cyclic imide for samples removed before and after the second mixing torque peak.

	Gel content		FTIR cyclic imide relative absorption height at 1770 cm^{-1}	
NH_2/MA molar ratio	Before 2nd peak	After 2nd peak	Before 2nd peak	After 2nd peak
1.0	1.1±0.8	28.9±0.7	-	-
1.5	1.4±0.3	45.0±0.7	0.163	0.435
2.0	1.3±0.3	38.2±0.4	0.122	0.239

Although the gel content analysis clearly shows that the second peak is associated with crosslinking, this analysis does not offer any explanation for the higher torque intensity observed with the first peak in the torque trace of reactive systems compared to the processing of neat PEMA4351. The chemistry of the reactor products removed before and after the second peaks in the mixing torque trace were compared using FTIR analysis. Results for the reactor products with NH_2/MA molar ratios 1.5 are presented in Figure

4.3. Similar spectra were observed for reactor products with NH_2/MA molar ratio 2.0 and hence not shown. Spectra for reactor products NH_2/MA molar ratio 1.0 were different and will be discussed later. Spectra for samples removed before and after the second peak in the mixer torque data show strong cylic imide absorptions (1700 and 1770 cm^{-1}) and a broad absorption for the amide/amic acid intermediate (1550 cm-1). No anhydride or acid reactant absorption (1780 cm^{-1} or 1715 cm^{-1}) could be seen.

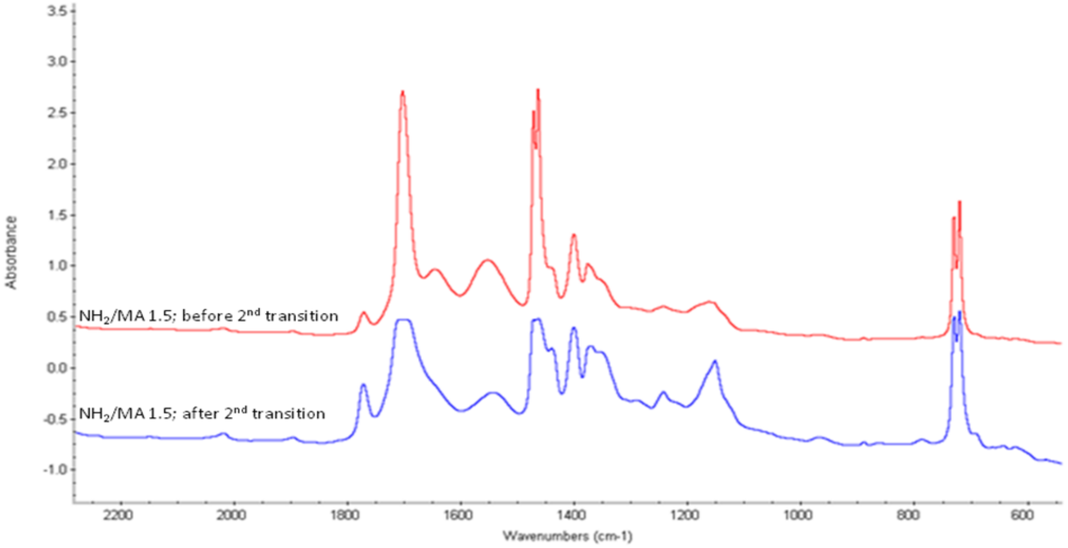


Figure 4.3 Spectra of reactor product NH_2/MA molar ratio 1.5 removed before and after the second transition

Table 4.2 displays the relative height of the cyclic imide absorption for reactor products removed before and after the second peak in mixing torque and it can be seen that the magnitude of the relative imide absorption changes proportionally with the gel content. The presence of significant cyclic imide and amide content in the reactor product removed before the second peak in the torque trace, indicates that reaction between anhydride and amine has occurred prior to this peak. This observation is consistent with the idea that the relatively high magnitude of the first peak in the mixing torque trace (compared to that for the mixing of the neat wax) may be due to the generation of higher molecular weight species during the initial stages of reaction.

FTIR and gel content data presented in Table 4.2 elaborate the extent of reaction with respect to the two peaks observed in mixing torque. The increase in reaction product functionality detected by FTIR is not corroborated in the FTIR spectra by a decrease in reactant absorptions since these absorptions are not detected. With systems studied in earlier reports, formation of amide and cyclic imide linkages is observed [1,6,7,11] however, the lack of reactant absorptions in the FTIR spectra is not reported.

The gel content results in Table 4.2 show that the degree of crosslinking of the reactor product progresses with mixing time. The crosslinking profile of reactor products that were removed from the mixer before and after the second peak in mixing torque, were studied by further melt processing these materials in an hydraulic press at 180°C. The evolution of reactor product gel content with melt processing time is presented in Figure 4.4. Initially, the reactor products that are removed from the mixer after the second peak in mixing torque are observed to have significantly higher gel content. The gel content of the thermoplastic samples removed before the second peak in mixing torque and those removed after this peak becomes coincident as the time of melt processing at 180°C increases. This last observation suggests the presence of residual reactants in the reactor products that undergo further reaction to produce further crosslinking.

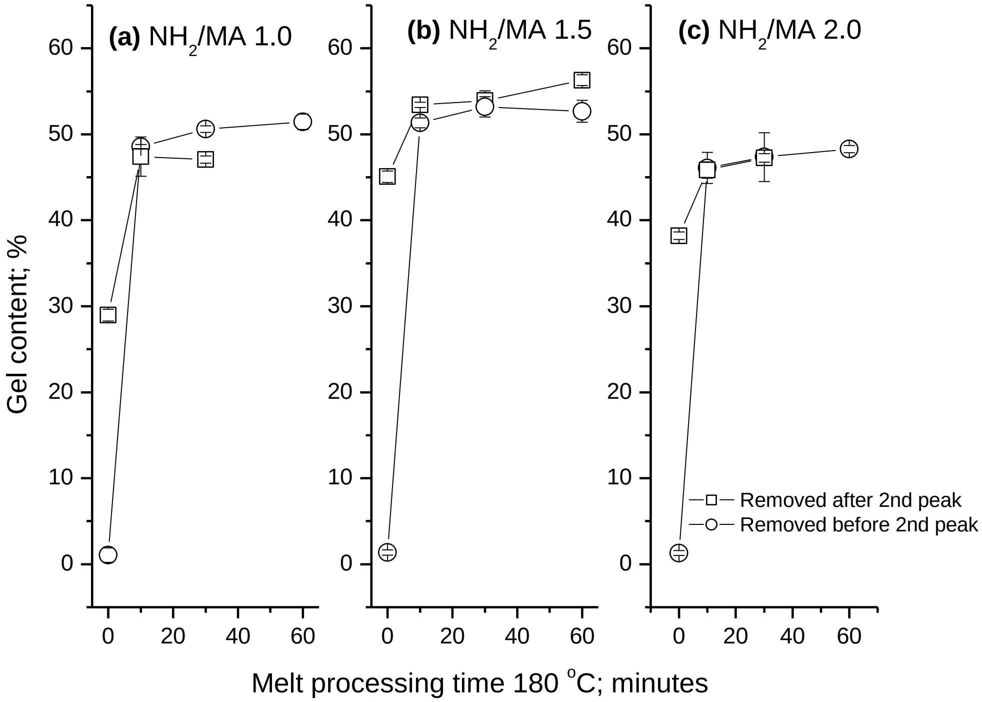


Figure 4.4 Gel content analysis of melt processed reactor products for different intervals of time at 180 °C

The corresponding FTIR spectra, for the reactor product (NH_2/MA molar ratio 1.5) removed before the second peak in mixing torque, are presented as a function of melt processing time at 180ºC in Figure 4.5. The overlaid are spectra for PEMA4351 and hexylamine (HMDA has a very similar spectra varying only in the intensity of some absorbances). None of the reactor product spectrum showed the anhydride (1780 and

1860 cm^{-1}) or acid absorbances (1715 cm^{-1}) observed in the PEMA4351 starting material. All of the reactor product spectra showed strong cyclic imide absorbances (1700 and 1770 cm^{-1}) which increase in intensity with melt processing time.

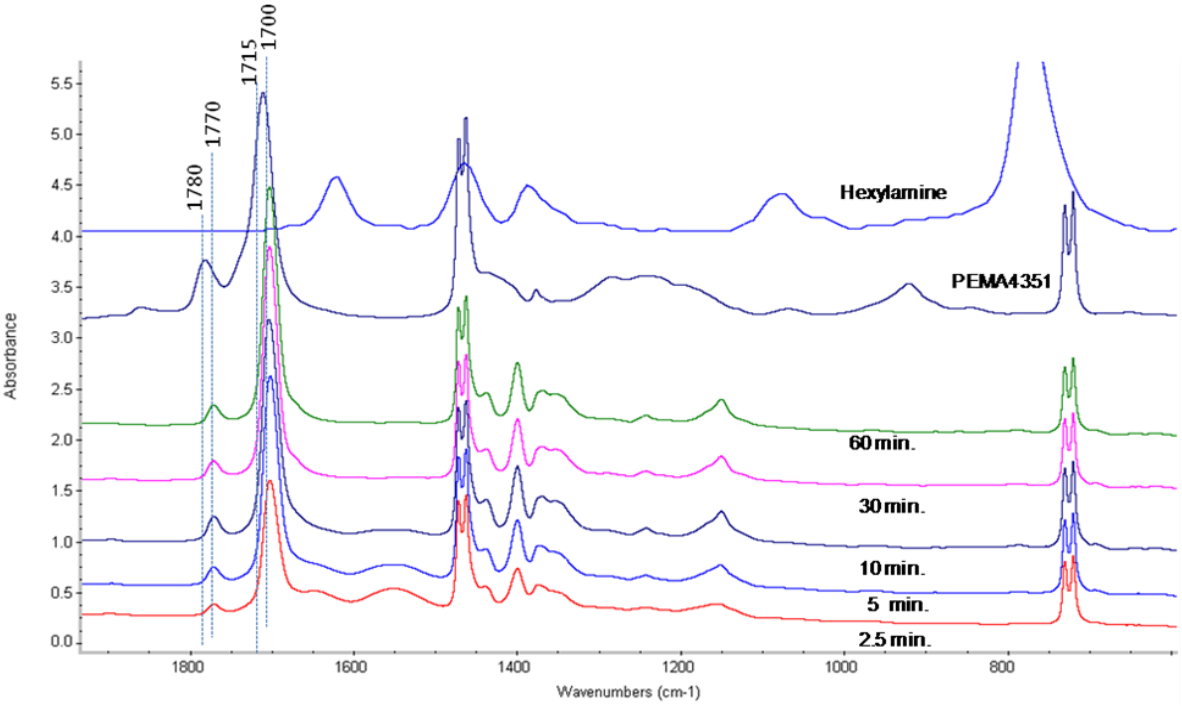


Figure 4.5 FTIR spectra of reactor product NH_2/MA=1.5; melt processed for different intervals of time at 180 °C

Further, the products melt processed for 2.5, 5 and 10 minutes also show broad response around 1550 cm^{-1} and weak response at 1640 cm^{-1} ascribed to amide/amic acid [11,20]. The intensity of the amide response decreases with increasing melt processing time. The relative peak height for cyclic imide (1770 cm^{-1}) and amide (1550 cm^{-1}) were calculated taking the methylene response at 720 cm^{-1} as an internal standard. Results are presented in Figure 4.6. For both NH_2/MA molar ratio 1.5 and 2.0, the cyclic imide (1770 cm^{-1}) response increases initially and then plateaus. On the other hand, the amide (1550 cm^{-1}) response decreases with increasing melt processing time. Although the initial amide response is relatively higher in the reactor product NH_2/MA = 2.0, the final concentration of cyclic imide in the two reaction products is similar, as could be expected since anhydride is the limiting reactant and the weight ratio of anhydride was very close in the two systems. The presence of amide in the products up to 10 minutes melt processing time suggests that the initial ($\leq$ 10 minutes) crosslinking is due to a combination of cyclic imide and amide linkages. However, at higher melt processing times all of the amide converted to cyclic imide which are the only linkages present in the product processed for longer times. These observations are in agreement with the earlier reports suggesting the reaction between anhydride and amine to form amide is faster than the dehydration of amide/amic acid into cyclic imide [6,7].

As discussed in earlier studies [14,15], the conversion of amide groups into cyclic imide cannot account for the observed increase in gel content. Figure 4.4 shows a significant increase in gel content within the first 10 minutes of melt processing at 180˚C. Conversion of amide into cyclic imide does not result in the formation of additional linkages/crosslinks, it only results in a change in the chemistry of an existing linkage

[Figure 4.1; Scheme 2]. Hence other possible chemistries that might produce additional crosslinks were investigated.

The formation of a salt (Figure 4.1; Scheme 2) intermediate, as suggested by Scott and Macosko [7], is a possible source of reactant for the observed increase in cyclic imide and gel content with melt processing time. Carboxylate ions show characteristic absorbances at 1550 cm^{-1} and 1400 cm^{-1} [7,11,21]. Since amide also shows an absorbance at 1550 cm^{-1}, the response at 1400 cm^{-1} helps to distinguish between the formation of an amide or an amide salt (Figure 4.1) [7,11]. The relative absorbance intensity for the response at 1400 cm^{-1} was quantified and the results for reactor product NH_2/MA 2.0 are presented in Figure 4.6. The possible carboxylate ion response remains unchanged over the course of melt processing. This observation together with the linear relationship observed between absorbances at 1550 cm^{-1} and 1640 cm^{-1} (an additional absorbance attributed to amide) response (Figure 4.6(a) inset) suggest that the reaction proceeds via formation of an amide intermediate rather than an amide salt.

Another alternative explanation for the observed gel content (insolubility in refluxing xylene) might be associated with the insolubility due to rigid imide groups, widely reported in polyimides [22-24]. The suggested phenomenon is observed when polyimide chains composed of stiff aromatic monomers are stacked up in layers giving rise to intermolecular interactions between carbonyl on one chain and nitrogen on the neighboring chain. However, this can only happen when the main chain contains rigid (composed of aromatic) groups in a regular geometry and there is a huge amount of

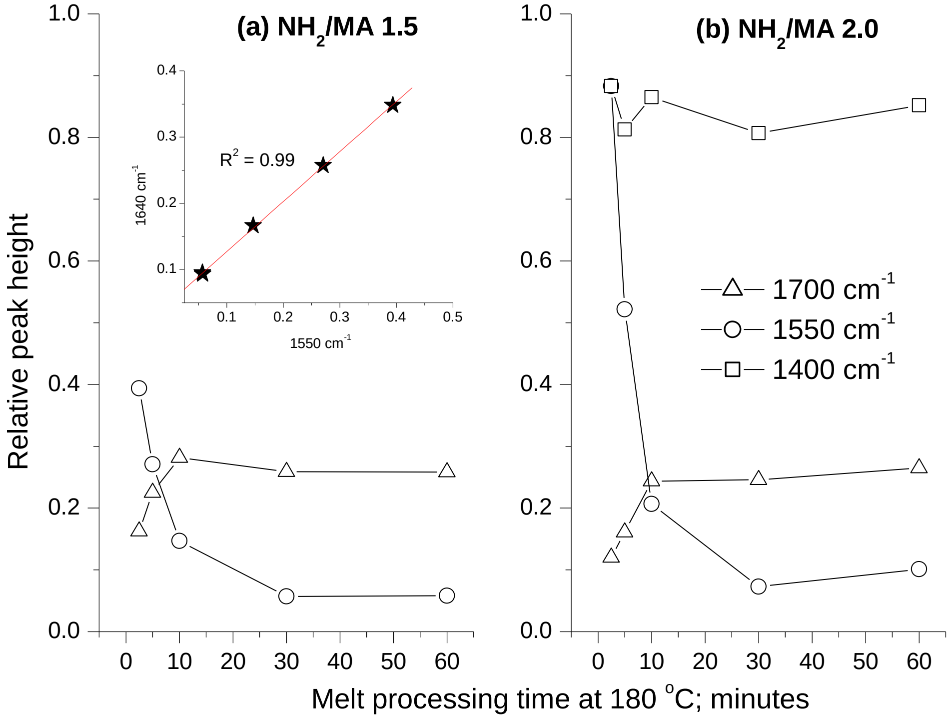


Figure 4.6 Relative peak heights for different reaction products as a function of melt processing time 180 °C

polyimide functionality as is the case with polyimide prepared from small aromatic monomers; dianhydrides and aromatic diamines [22-24]. The case in the current investigation is totally different. The anhydride grafting in polyethylene is 5.2%, which is far too low to induce such effects and this functionality is randomly dispersed over the available molecules so that the regular geometry that would be present in polyimide chains is not a factor here. Also amine and anhydride functional groups are attached to flexible polyether and polyethylene chains. Hence the observed insoluble fraction could only be a consequence of crosslinking as accepted in published literature [11-12].

The only plausible explanation for the new crosslinks is reaction between residual anhydride and amine in the reaction mixtures as discussed in earlier reports [13,15]. This explanation is supported by the observation in earlier work [15] that although the FTIR did not show any evidence of acid or anhydride response, colorimetric titrations confirmed the presence of acid groups in these reactor products.

The spectra for melt processed reactor product NH_2/MA molar ratio 1.0 were different from the other two compositions (NH_2/MA molar ratio 1.5 and 2.0) investigated. Spectra for reactor product NH_2/MA molar ratio 1.0 melt pressed for varying times are overlaid with PEMA4351 reactant, and with melt processed NH_2/MA 1.5 reactor product, in Figure 4.7. The spectra for reaction products NH_2/MA=1.0 show a strong absorbance around 1700 cm^{-1} ascribed to cyclic imide and a relatively broad absorbance between 1780 and 1770 cm^{-1}. This last absorbance is ascribed to a merged response from diminishing anhydride and growing cyclic imide. Very similar results were observed by the authors in earlier investigations [13-15] and were also reported by Lu et al [1].

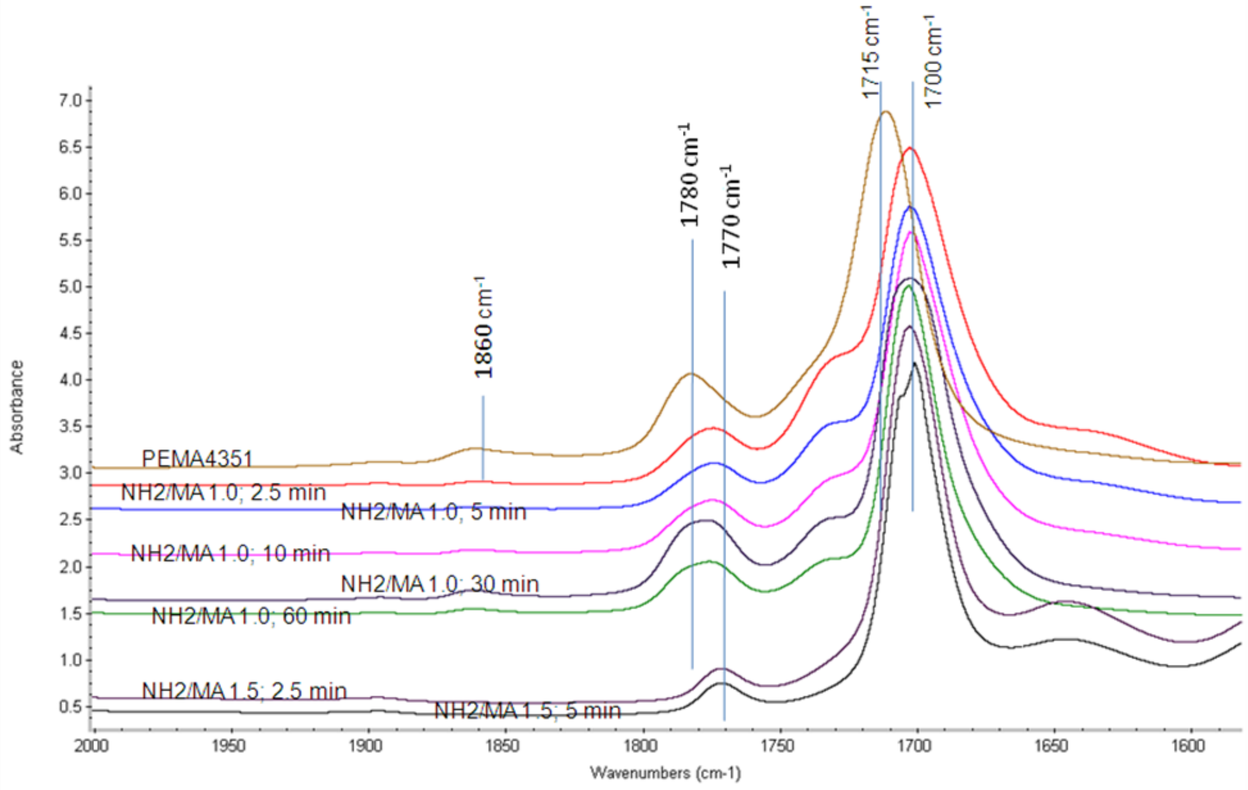


Figure 4.7 FTIR spectra of reactor product NH_2/MA=1.0; melt processed for different intervals of time at 180 °C

It is interesting to see, in the work of Lu and Macosko, a shift in the anhydride response at 1780 cm^{-1} in the unreacted grafted PP spectra towards a lower wave number in the reactive mixtures (see reference 1; Figure 1). The shift seems to be composition dependent. At NH_2/MA molar ratios ≥ 1.0 a distinct peak is seen at 1770 cm^{-1}. However, for NH_2/MA molar ratio ≤ 1.0 the peak is relatively broad and seems to be in transition towards 1770 cm^{-1}. No mention was made of the observation in the discussion and the peak was taken as an anhydride response. The extent of reaction assessed on the basis of this peak was suggested to increase with increase in the NH_2/MA molar ratio of the reactive mixture.

Figure 4.8 zooms in on the absorbance at 1700 cm^{-1} where it can be clearly seen that there is a "shoulder" absorbance at 1730 cm^{-1}. Song and Baker [11] reported an absorbance at 1740 cm^{-1} ascribed to polar interactions between anhydride and a tertiary amine. However, no such peak was observed when a primary amine was reacted with anhydride. The 1730 cm^{-1} response in the present study as well as in the earlier studies [15] was observed to be composition dependent. It increases with a decrease in the NH_2/MA molar ratio of the mixture. This observation together with unpublished work carried out in our lab involving reactions between and acid grafted polyethylene and a primary amine suggest that the 1730 cm^{-1} absorbance is in fact due to a an imide formed as a result of reaction between acid and a secondary amine. This reaction is favored at lower NH_2/MA molar ratios and hence in the current study is seen only at NH_2/MA molar ratio 1.0 and not at higher ratios.

The dynamic viscoelastic measurements of the polymer melt provide insight into the molecular architecture of the polymers. Molecular parameters like molecular weight, MWD, branching and

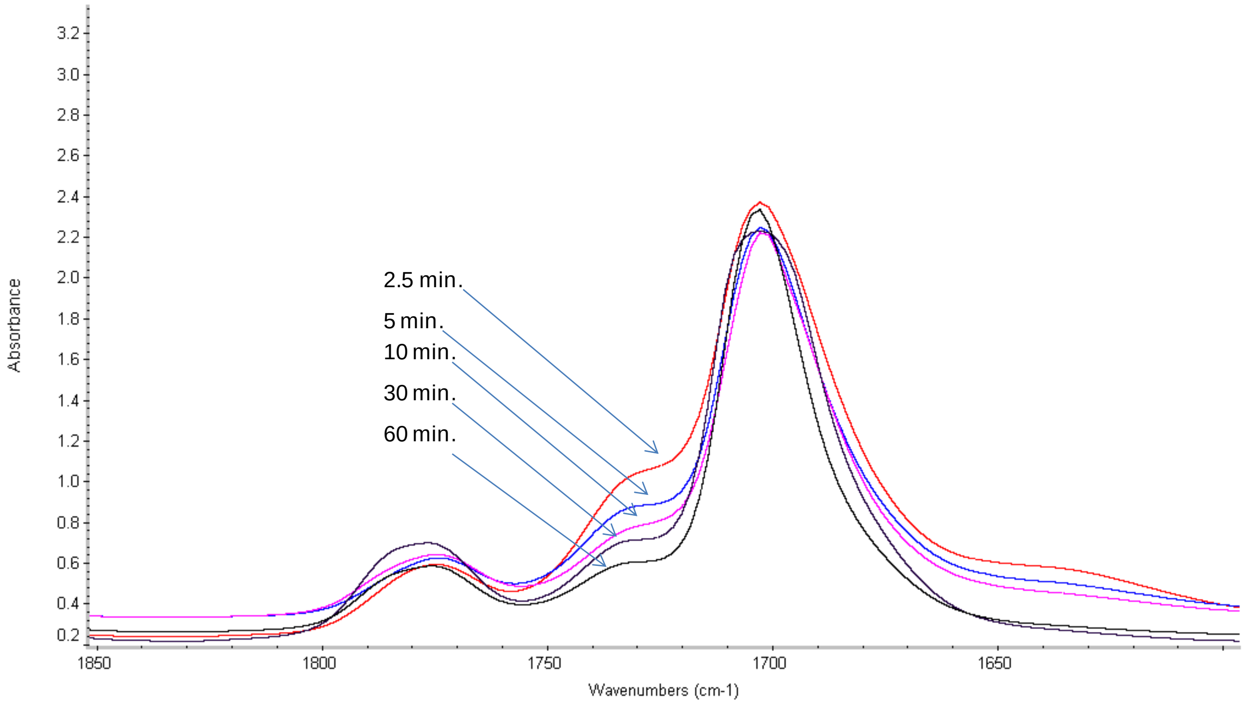


Figure 4.8 Cyclic imide response reactor product NH_2/MA=1.0; melt processed for different intervals of time at 180 °C

crosslinking are strongly reflected in viscoelastic parameters such as the storage modulus (G'). The complex viscosity, η*, and the storage modulus, G', are plotted in Figure 4.9, as a function of frequency, for the melt-processed reactor products. The flat storage modulus curve as a function of frequency is typical of the plateau zone behaviour associated with a crosslinked polymer [21]. The stress relaxation curves presented in Figure 4.10 are further evidence that a fairly extensive crosslink network has developed in the reactor product matrix as a consequence of crosslinking reactions. Thermoplastic, uncrosslinked polymers exhibit stress decay over time in the melt state after a deformation. The samples studied here relax to a plateau value since the crosslinks that have been formed prevent the free flow of molecules to accommodate the applied deformation. Little decay in the stress is observed over the 15 minute test time, as is expected for a thermoset material.

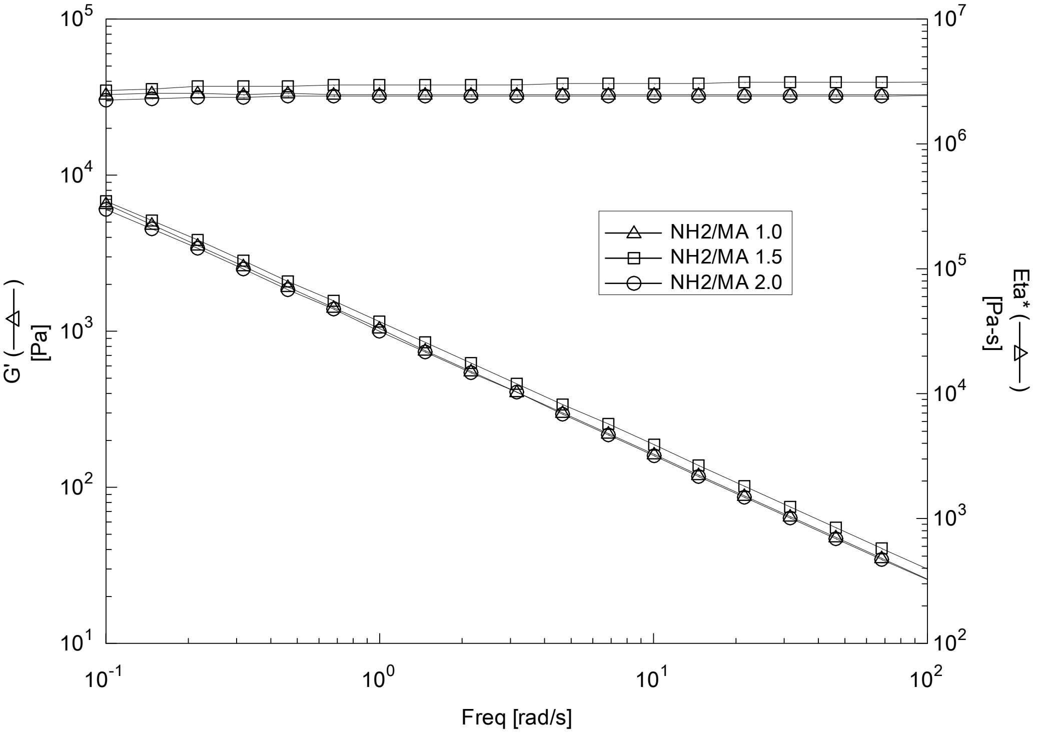


Figure 4.9 Frequency sweep for reactor products melt pressed at 180 °C for 60 minutes;

(T_{test} = 180 °C; γ= 0.01)

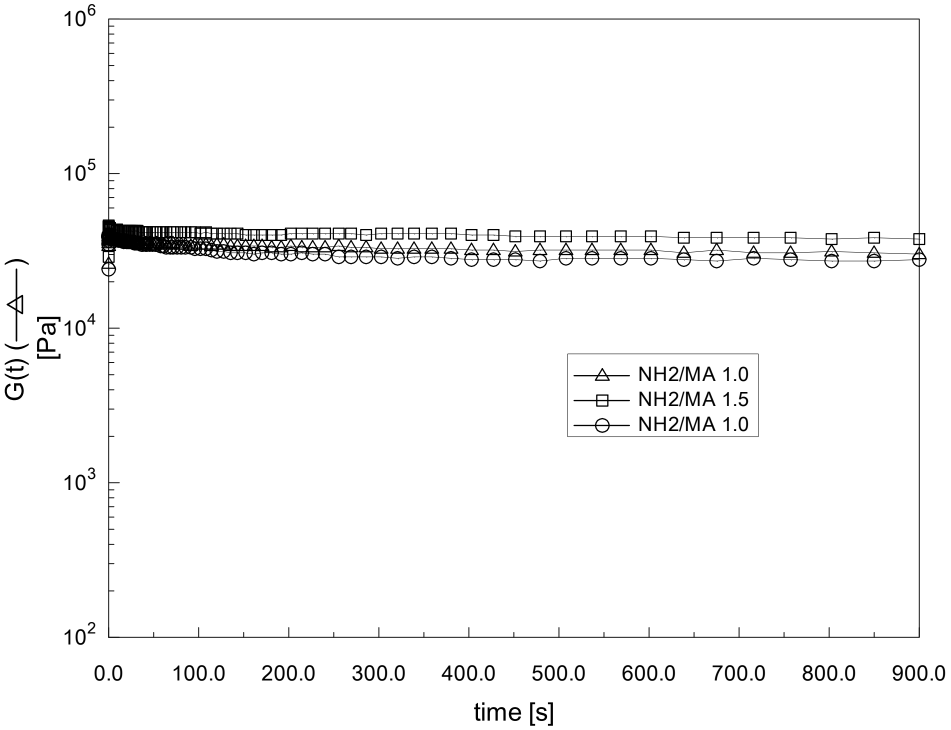


Figure 4.10 Stress relaxation curves for reactor products melt pressed at 180 °C for 60 minutes;

(T_{test} = 180 °C; γ= 0.01)

Thermal properties of the three reactor products removed prior to the second transition and their melt processed versions (180 °C; 60minutes) were assessed using DSC. The second heating curves for all the products together with straight PEMA4351 are presented in Figure 4.11.

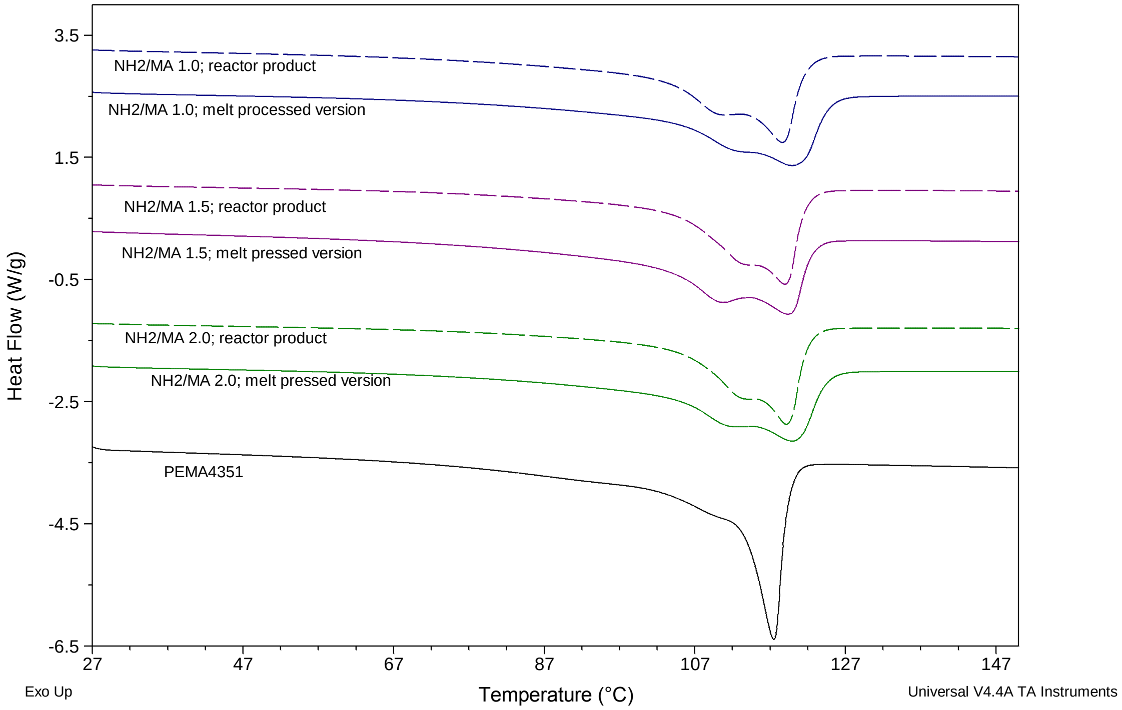


Figure 4.11 DSC heating curves for reactor products and their melt processed version (180 °C; 60 minutes)

Straight PEMA4351 shows a single sharp melting endotherm with a minor shoulder at a lower temperature. On the other hand, the reactor products removed before second transition as well as their melt processed versions show at least two well defined melting transitions. The higher temperature melting transition coincides with the peak melting transition observed for PEMA4351, whereas, the lower temperature transition is different for the reactor product and their melt processed versions. The two temperature transitions are suggested to represent two separate crystal populations. The higher melting temperature transition is associated with the

unmodified PEMA4351 in the reaction product. On the other hand, the lower melting transition in the reactor products are suggested to represent a new crystal population with hindered chain folding due to the branching, as these materials show little gel content (<2%). The lower melting transitions observed for melt-processed reactor products is ascribed to branching of the polymer chain due to the crosslinking reaction. Here, the crosslinks present significantly larger hindrance in chain folding leading to formation of defected crystallites with lower melting temperature then the unmodified PEMA4351 crystals. To confirm this hypothesis, DSC scans were performed on gel fractions obtained after solvent extraction for melt processed reactor products $NH_2/MA=1.5$. Results for this scan overlaid with the original scan for the melt processed reactor products are shown in Figure 4.12. Whereas, the original melt processed product shows two well-defined peaks, the gel fraction shows a single peak corresponding to the lower temperature.

The observed total heat of fusion for the two peaks for the two sets of reactor products together with the heat of fusion based on the wt% of PEMA4351 in the each sample were plotted as a function of composition and are shown in Figure 4.13. Although the heat of fusion is lower for all reaction products compared to the theoretical values, the heat of fusion for the melt processed crosslinked products is higher than the products removed

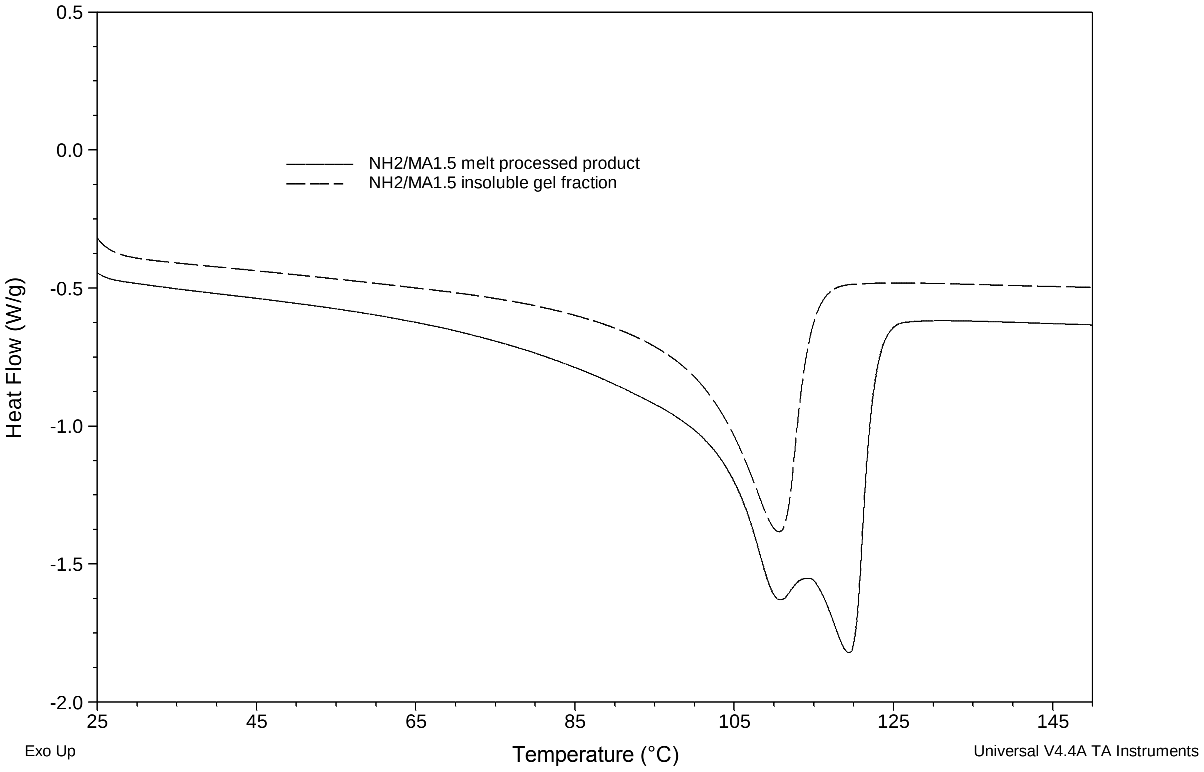


Figure 4.12 DSC heating curves for melt processed reactor product NH_2/MA 1.5 and its insoluble gel fraction.

from reactor. This is a bit unexpected since high degree of crosslinking is expected to hinder chain folding more and should result in suppressed crystallinity or heat of fusion. The reason for this unexpected increase seems to be the formation of a large quantity of low temperature melting, thin crystallites in the crosslinked products which is reflected in the significant decrease in the melt initiation temperature as shown in Figure 4.13.

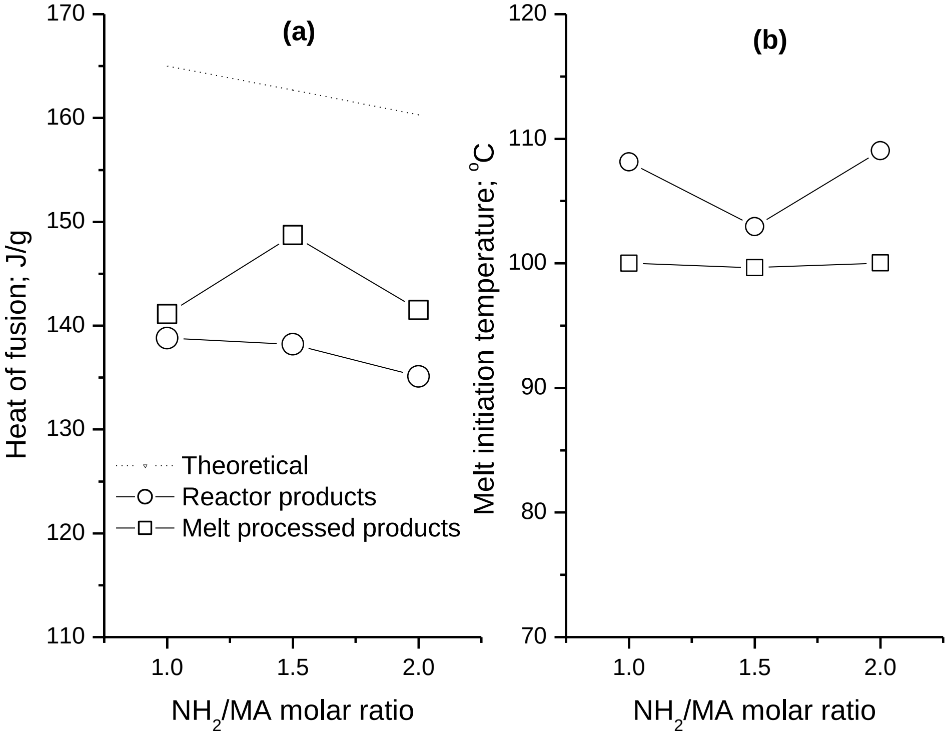


Figure 4.13 Heat of fusion and melt initiation temperatures as a function of NH_2/MA molar ratio of the reactor products

4.5 Conclusion

Reactions were carried out between a low molecular weight, highly functionalized maleic anhydride grafted polyethylene and hexamethylenediamine in a melt blender at 150 °C at various stoichiometric ratios of functional groups. Mixing torque data displayed two peaks at all compositions unlike a single peak reported in earlier studies. The first peak in mixing torque observed soon after the introduction of the reactive mixture to the mixer, was independent of composition. The second peak was composition dependent. Gel content and FTIR analysis suggest that the first torque peak is a result of melting and partial reaction between anhydride and amine functionalities to result in a molecular weight build. The second torque peak was a result of crosslinking. The reaction mixture is thermoplastic before the appearance of second torque peak.

Melt processing at high temperatures of the thermoplastic reaction products removed from the reactor before the second torque peak were used to understand the evolution of chemistry and crosslink development in the products. These results reveal that the reaction between anhydride and amine results in the formation of an amide intermediate, which then converts to cyclic imide at higher temperatures. Combination of FTIR and gel content analysis suggests the assessment of the degree of reaction based on the anhydride response in FTIR alone could be misleading in these reactions.

These results imply that a reactive polyethylene prepolymer could be obtained which is capable of undergoing curing/crosslinking on further melt processing. Use of HMDA confirms, that the capability to form a reactive prepolymer is not associated with the use of polyether amines in earlier studies, but is a result of the low molecular weight of the functionalized polyethylene utilized and the resulting processing conditions.

Acknowledgements

This research was financed by the Ontario Centre of Excellence (OCE) and Clariant Canada Inc. The authors wish to thank Hermann Koch (Clariant Canada, Inc.) for providing the Licocenes® materials. Support extended by Paul Gatt is also appreciated.

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Chapter 5. Thermal, mechanical and thermo-mechanical properties of thermosets produced using low M_w functionalized polyolefins and polyamines

This chapter is based on paper in press *Journal of Applied Polymer Science* **2011** by Tayyab Hameed, David K. Potter and Elizabeth Takacs.

5.1 Abstract

Thermosets obtained by reacting highly functionalized maleic anhydride grafted polyethylene and a polyetherdiamine at several NH_2/MA molar ratios were characterized for their gel content, thermal, mechanical and thermo-mechanical behavior. Gel content varied with composition and a maximum (57%) observed when NH_2/MA molar ratio was 1.5. Two melting transitions were observed for thermosets, representing the semi-crystalline polyethylene fraction in the gel and sol part of the material in contrast to a single transition for the starting polyethylene. Overall crosslinking suppressed the crystallinity of the polyethylene in the thermoset. A single T_g observed in the DMA analysis suggested phase mixing between the polyethylene and polyether chains. A shift in the T_g observed was related to the degree of crosslinking in the thermosets. Tensile properties of the thermosets were observed to be a strong function of composition and the degree of crosslinking and the optimum mechanical performance was shown by thermosets when NH_2/MA molar ratio was 1.5 and 2.0.

5.2 Introduction

In recent studies [1-3] the authors have shown the successful development of reactive prepolymers and thermosets by reacting low viscosity functionalized polyolefins and polyamines. Hameed et al. [1] investigated the reactions between highly functionalized low MW maleic anhydride grafted polyethylene with several diamines. When these reactions were conducted in a solvent media, the reactions were observed to be fast. However, reactive prepolymers were obtained in each case by adjusting the concentration of the reaction mixtures. The prepolymers could be later turned into thermoset materials by heat treatment. The crosslinking reaction was followed using FTIR and titration, while changes in physical characteristics were examined using rheological and sintering techniques.

In another investigation [2,3], similar reactions between a low viscosity functionalized polyethylene wax and a polyether diamine were carried out in the melt state. The products from these reactions were observed to be thermoplastic materials (prepolymers) which crosslinked when melt processed at elevated temperatures to produce thermosets. The evolution of chemistry (FTIR) and crosslinking (gel content) with melt processing time was studied at different temperatures. Crosslinking of the prepolymers was observed to be a function of both time and temperature. These observations were supported by an increase in cyclic imide linkages as revealed by FTIR. The combination of gel content and FTIR analysis suggested that the reaction between residual maleic anhydride and amine groups continued during the melt processing of the prepolymers, resulting in formation of thermoset materials.

To the best of our knowledge these recent studies are the first to explore such reactions using low molecular weight functionalized polyolefins and polyamines, however, several investigations exist where similar reactions were used to modify or crosslink high molecular weight polymeric systems [4-8]. Lu et al. [4] performed reactions between maleic anhydride grafted polypropylene and several low MW diamines in an attempt to generate polyolefins with amine functionality. The stoichiometry of the reaction mixtures were manipulated towards achieving this goal. Reactions were conducted using both an extruder and a melt blender at several amine to maleic anhydride (NH_2/MA) molar ratios. Reaction between anhydride and amine in the reactor was reported to be complete within two minutes based on the mixing torque data. This was further supported by FTIR analysis of the reaction products which was suggested to show increased conversion of anhydride with increasing NH_2/MA molar ratio. Dynamic viscoelastic measurements of the reaction products in the melt state were reported to suggest the reaction products were thermoplastic. However, the viscoelastic properties (G' and η^*) were strongly influenced by NH_2/MA molar ratio of the reaction mixtures, with maximum viscosity and storage moduli observed when the functional group stoichiometry was equimolar.

In another investigation, Colbeaux et al. [5] used diamines to crosslink maleic anhydride grafted polyethylene. The degree of grafting of the polyethylenes utilized was 0.16-0.18

%. Reactions were done in a polymer blender using two different diamines (aliphatic and aromatic) at several NH_2/MA molar ratios. Relatively faster reactions and higher extent of reaction was reported for aliphatic diamines in comparison to aromatic amines which was suggested to be a consequence of the poor miscibility of the latter with polyethylene. The gel content and dynamic viscoelastic data suggested that the maximum crosslinking (32% gel content) occurred at NH_2/MA molar ratio 2.0.

The current article is a continuation of our recent work using low viscosity funtionalized polyolefins and polyamines [1-3]. Although the formation of thermally activated reactive prepolymers and formation of thermoset materials was presented in the earlier articles, the physical properties of the thermoset materials so obtained were not fully appreciated. In the current article the thermal, mechanical and thermomechanical characteristics of the thermoset materials obtained by reacting functionalized polyolefins and polyamines are presented.

5.3 Experimental

5.3.1 Materials

Low molecular weight maleic anhydride grafted polyethylene was a commercial grade Licocene® PEMA4351 supplied by Clariant Canada Inc. Maleic anhydride was grafted randomly using free radical chemistry in a batch process [9]. Polyetherdiamine, ED600, was supplied by Huntsman Chemicals, TX, USA and used as received. The backbone of

ED600 is predominantly the polyethylene oxide unit. The important characteristics of the materials are presented in Table 5.1.

Table 5.1 Characteristics of materials

	M_w	M_n	M_w/M_n	Viscosity	MAH content[3]
PEMA4351	3000	1200	2.5	300 mPa.s [1]	5.20 wt. %
ED600	-	600	-	77.6 mPas	-

[1] measuresd at 140 °C; [2] measuresd at 20 °C
[3] assessed by colorimetric titrations

5.3.2 Procedures

Reactive prepolymers were obtained by melt mixing PEMA4351 and ED600 at several NH_2/MA molar ratios using either a melt blender or a resin kettle. Details of formation of these prepolymers are given elsewhere [3]. Thermoset materials were obtained by melt pressing these prepolymers at 180 °C for 60 minutes using aluminum molds in a hot press. Specimens were produced as circular discs (25 mm diameter × 2 mm thick), dumbbells (2 mm thick; ASTM D638; type V) and thin rectangular bars (25 mm × 5 mm × 0.5 mm) for different tests.

To assess the gel content, approximately 0.2-0.3 g of thermoset material were cut into small pieces and enclosed in pouches made of 120×120 mesh type 304 stainless steel wire cloth. These pouches were left in refluxing xylene for more than 12 hours (ASTM D2765) for extraction of the non-crosslinked “sol” fraction. After extraction, samples were removed from the solvent, washed with acetone, and allowed to dry. The loss in weight was used to calculate the fraction of insoluble material or “gel content”.

Thermal properties of the thermosets and the neat PEMA4351 were measured using a Q2000 Differential Scanning Calorimeter, TA Instruments, USA. Approximately 5 mg of sample was encapsulated in aluminum pan for testing. The first heating cycle from room temperature to 140°C at 10 °C/min was used eliminate the thermal history of the material. It was followed by a controlled cooling and a second heating cycle at similar rates. Peak melting temperatures and heat of fusion data presented are from the second heating cycle.

The tensile tests were performed on an Instron 3366, USA, tensile testing machine at room temperature. The specimen gauge length was 7.62 mm and a crosshead speed of 5 mm/s was used. All reported mechanical properties are based on an average of a minimum of 4-5 specimens.

Thermomechanical properties were measured on Dynamic Mechanical Analyzer 2980, TA Instruments, USA. Specimens were cooled down to -110 °C using liquid nitrogen and then heated at 5 °C/min to 200 °C. All measurements were conducted using film tension clamps at a frequency of 10 Hz and amplitude strain of 10 μm.

Morphology of the blends was captured by means of a Scanning Electron Microscopy (SEM) instrument (JSM 7000F). Samples were fractured in liquid nitrogen and coated with gold before testing.

5.4 Results and Discussion

As reported in an earlier study [3], all the prepolymers obtained from the melt mixing operation in a resin kettle or a melt blender were thermoplastic and showed negligible gel content. Results for gel content of the prepolymers melt pressed for 60 minutes at 180 °C as a function of NH_2/MA molar ratio of the reactive mixture are presented in Figure 5.1. Gel content increases with decreasing NH_2/MA molar ratio, reaches a maximum at NH_2/MA molar ratio 1.5 and then starts to decline with further decrease in NH_2/MA molar ratio. As the gel content corresponds to the extent of crosslinking, theoretically the maximum degree of gel content was expected at equimolar stoichiometry [4,10]. Lu and Macosko [4] while studying the reaction between hexamethylenediamine (HMDA) and maleic anhydride grafted polypropylene at various NH_2/MA molar ratios observed maximum viscosity at equimolar stoichiometry. On the other hand, Colbeaux et al. [5] while studying melt reactions between maleic anhydride grafted polyethylene and several diamines reported a maximum viscosity and gel content at NH_2/MA molar ratio 2.0. Although, ideally a maximum extent of reaction and thus crosslinking is expected at equimolar stoichiomtery, it is dependent on the degree of mixing that could be practically achieved in the reaction mixtures, especially in polymeric systems where the viscosities are significantly high. Interestingly, the gel content obtained for the thermoset materials produced using the prepolymer technique are comparable to that of crosslinked polyolefins produced using conventional methods [11-15] .

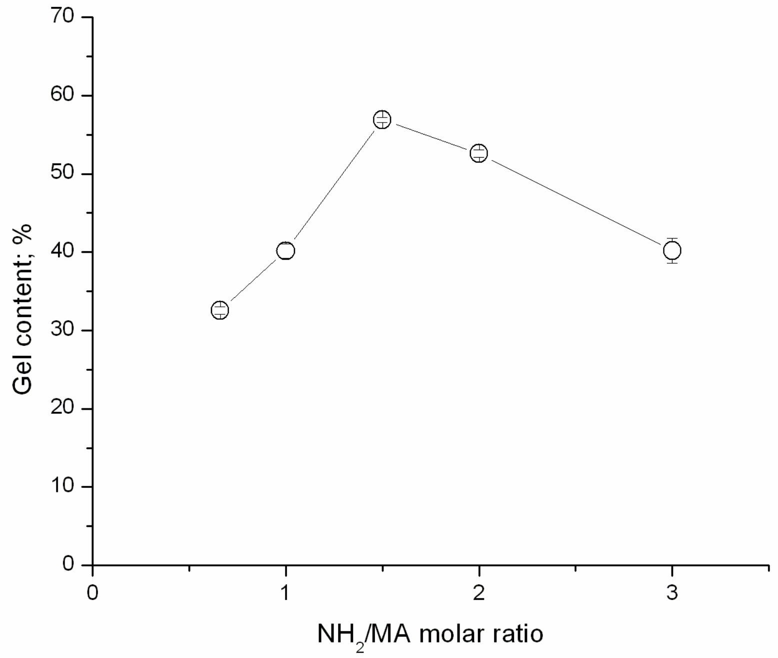

Figure 5.1 Gel content as a function of NH$_2$/MA molar ratio

The thermal characteristics of the themoset materials were studied using Differential Scanning Calorimetry (DSC). The second heating curves for PEMA4351 and all the thermoset materials prepared using several NH2/MA molar ratios are presented in Figure 5.2. The melting behavior of thermoset products is different from the neat PEMA4351 starting material. Whereas, PEMA4351 shows a very sharp and a single melting peak around 118 °C, the thermoset materials showed two distinct relatively broad peaks. The higher temperature melting peak in the thermoset materials closely correspond with the melting peak in PEMA4351 and are suggested to represent the melting of an unmodified/non-crosslinked PEMA4351 crystal population in the thermosets. This crystal population most probably represents the fraction of non-grafted PEMA4351 that did not become part of the network polymer. The relatively low intensity of this peak in thermoset scans compared to that of PEMA4351 suggest that most of the functionalized polyolefin did become part of the network. On the other hand, the new low temperature melting transition observed around 110 °C in thermoset materials is attributed to a crystal population of modified/crosslinked PEMA4351 chains that did become part of the network polymer. The decreased melting point of this crystal population is believed to be a consequence of crystal defects introduced in chain folding because of the presence of crosslinks and branches. To confirm the hypothesis, DSC scans were performed on the gel (crosslinked) fraction obtained after solvent extraction of the thermoset materials. The overlaid second heating scans for these tests are presented in Figure 5.3. Unlike the scans for thermoset materials, only a single melting peak is observed in these endotherms. The temperatures for these peaks closely correspond to the lower temperature melting transition observed in Figure 5.2, confirming that these transitions were in fact due to the modified/crosslinked PEMA4351 crystallites that became part of the crosslinked network.

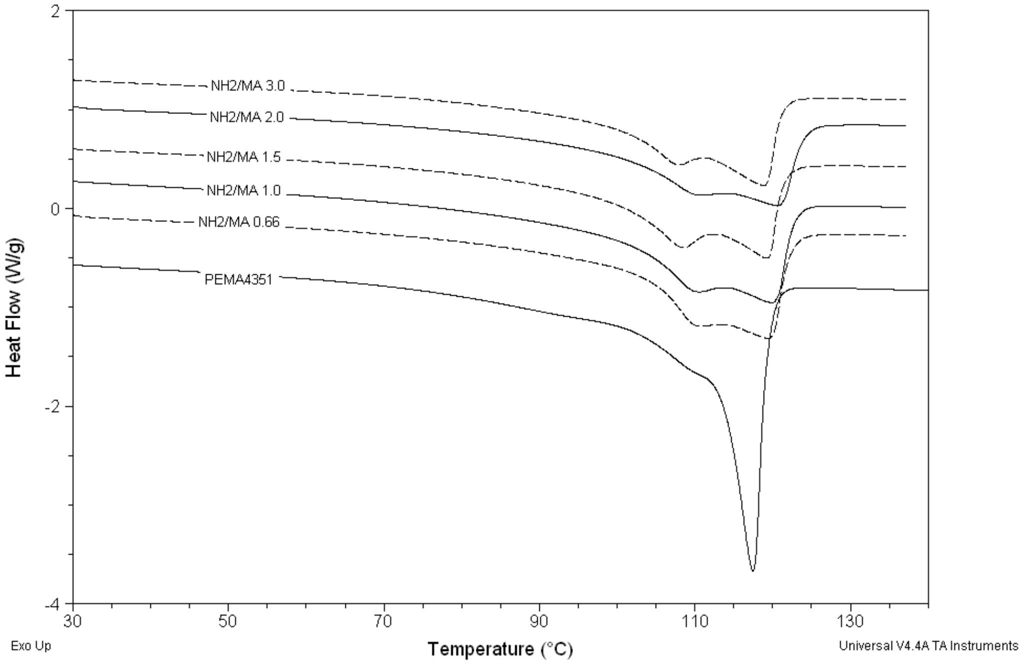

Figure 5.2 DSC second heat curves for all thermosets

The heat of fusion assessed by integration of the two melting transitions observed for the thermoset materials are plotted in Figure 5.4 as a function of NH_2/MA molar ratio. The theoretical heat of fusion based on the weight fraction of PEMA4351, the semi crystalline component of the thermoset, in the thermoset materials are also plotted as a reference. The experimentally assessed heat of fusion is always less than the theoretically estimated value, suggesting the branching and crosslinking suppressed the crystallization of the PEMA4351 in the thermoset materials.

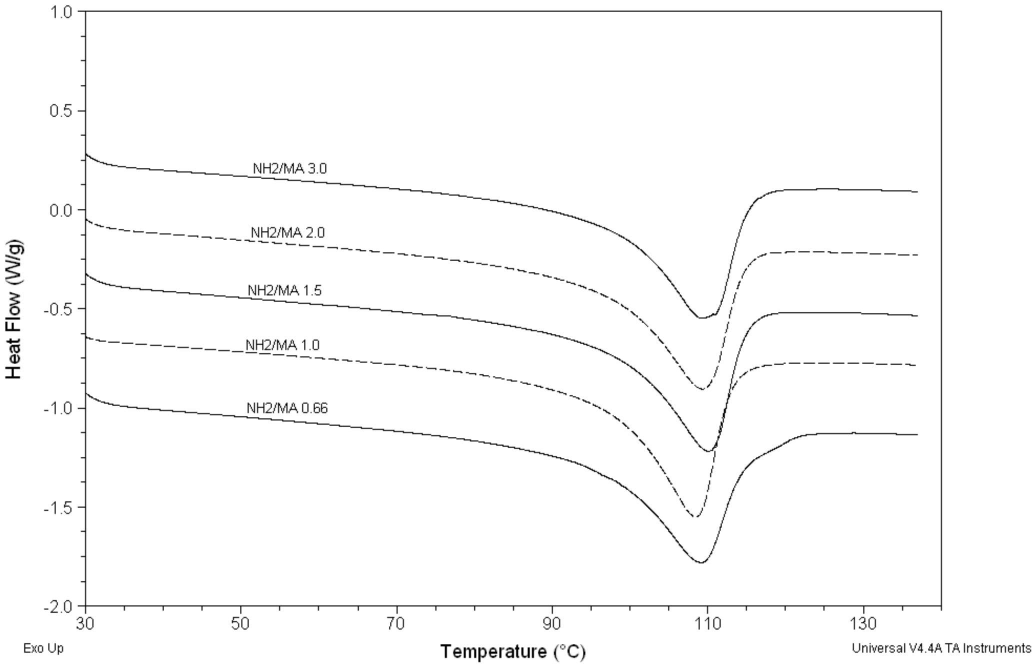

Figure 5.3 DSC second heat curves for gel fraction of thermosets

Dynamic mechanical analysis is a technique widely used to characterize the morphology of polymeric materials [14,16-19]. Phase separated polymeric blends and elastomers [20] show distinct glass transition temperatures (T_g) corresponding to the each component in the multi phase system whereas a single T_g that is intermediate in temperature between the glass transition temperatures of the components, is taken as evidence of miscibility or partial miscibility of such polymeric systems. Temperature sweep data for the three thermoset materials representing NH_2/MA molar ratios of 1.5, 2.0 and 3.0 are presented in Figure 5.5. Thermosets materials formed using compositions NH_2/MA molar ratios 0.66 and 1.0 were too brittle and weak to be tested for the dynamic mechanical properties.

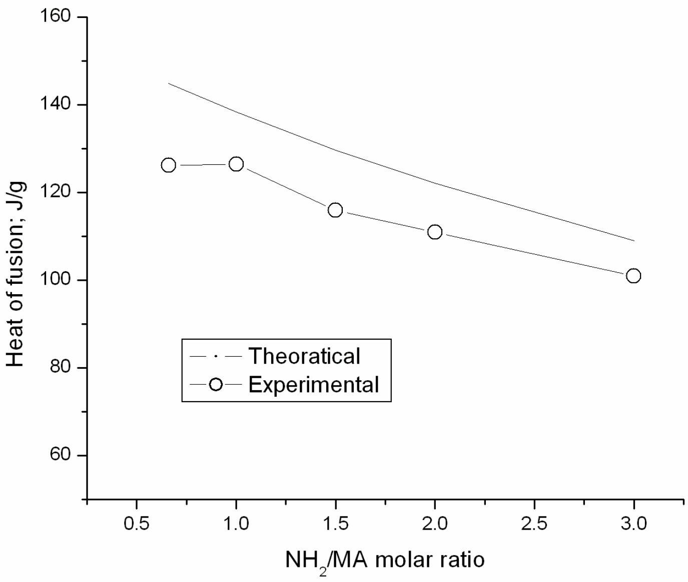

Figure 5.4 Heat of fusion as a function of NH_2/MA molar ratio of the thermosets

All thermosets materials tested showed comparable moduli below the T_g. A unique T_g was observed for each of the three thermosets that shifted towards a higher temperature with decreasing NH_2/MA molar ratio. For polymer blends and segmented polyurethanes, the presence of an intermediate glass transition temperature between those of the individual components is indicative of good phase mixing between blend components [20]. On the other hand, when new chemical bonds between chains of a polymer or polymer blend are formed, the linkages/bonds restrict the mobility of the polymeric chain segments which results in an increase in the observed glass transition temperature.

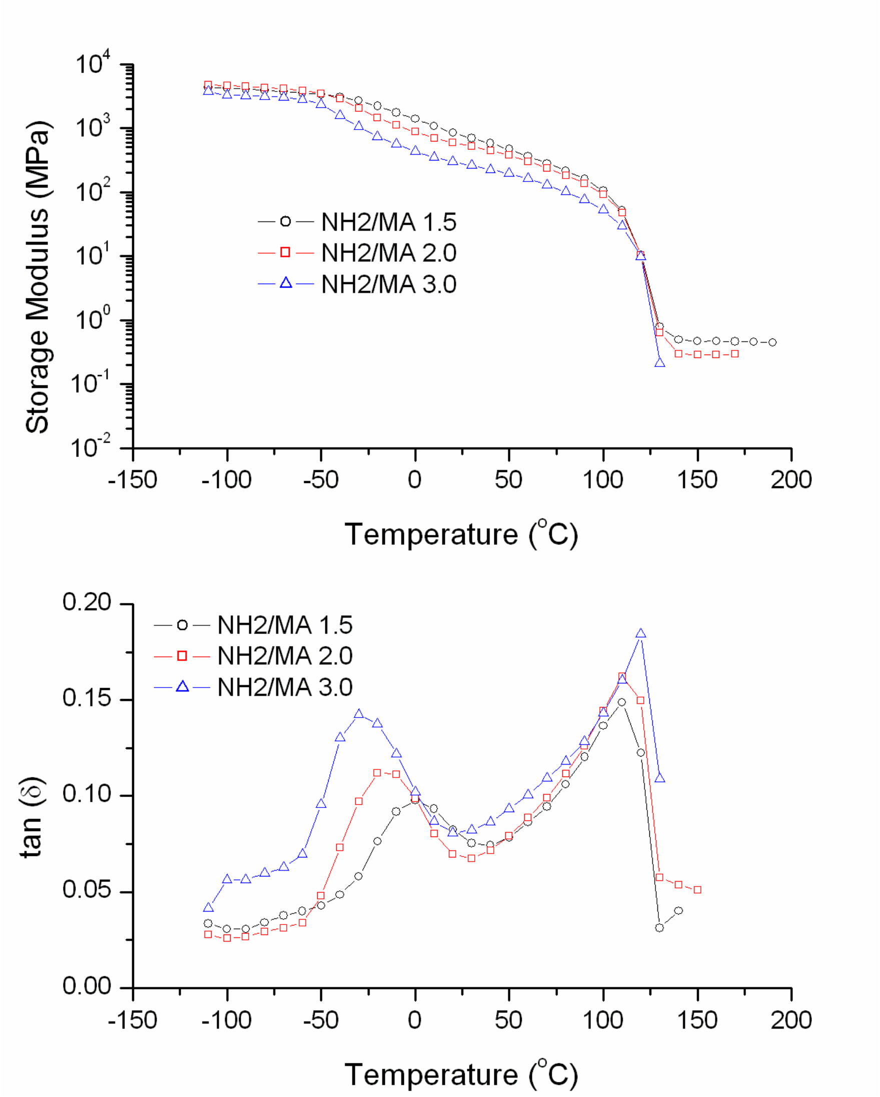

Figure 5.5 Storage moduli and tanδ vs. temperature curves for the thermosets

Thermosets characterized in the current study are composed of polyethylene and polyethylene oxide chains linked by cyclic imide linkages [1-3]. The polyether chains of varying lengths have been reported to possess T_g values around -40°C in phase segregated polyurethane systems [20]. A DSC scan performed on ED600 confirmed a T_g of -40 °C. The T_g observed for the system containing the highest weight fraction of polyether (NH_2/MA molar ratio 3.0) and least crosslinks (Figure 5.1) is very close to this value and seems to correspond to the T_g of the polyether component in the thermoset. T_g values for polyethylene have been reported to be around -110 °C [14,21]. The DMA equipment used in the current study did not allow us to attain low enough temperatures to measure transitions in that range. The observed shift in the glass transition temperature in the current investigation is towards a higher temperature with decreasing NH_2/MA molar ratio and is most probably due to the increase in crosslinking of polyether component. If it were a response from a miscible or partially miscible polyethylene and polyether phase, the shift in the glass transition temperature would be in the opposite direction.

The observed trend is very much consistent with the degree of crosslinking in Figure 5.1. The degree of crosslinking increases with decreasing NH_2/MA molar ratio restricting the mobility of chain segments and raising the observed glass transition temperature. This analysis suggests that the polyether and polyethylene parts of the thermoset exist in discreet or partially discreet phases and that the change in the observed glass transition temperature is a consequence of the impact of crosslinking on the mobility of polyether chain segments.

The rubbery plateau region in the temperature sweeps of the three thermosets is obscured by the semi crystalline morphology of the polyethylene phase until melting occurs. Beyond the melting transition, distinctive rubbery crosslink plateaus are observed for the two most highly crosslinked samples. Crosslink plateaus were observed for thermoset products NH_2/MA 1.5 and 2.0 which sustained the mechanical strain up to 200°C without further transition to liquid-like behavior. No such plateau was observed for the material in which the NH_2/MA molar ratio is equal to 3.0. In this case the modulus decays rapidly and consistent with a transition to liquid-like behavior upon complete melting of the PEMA4351. However, it is interesting to note that although the thermoset with NH_2/MA molar ratio 3.0 did not show a crosslink plateau no significant deformation (necking) in the specimen shape was observed at the end of the test similar to the other two thermoset materials. The absence of a crosslink plateau in the DMA spectrum of NH_2/MA molar ratio 3.0 material indicates that the material is behaving like a thermoplastic and that the extensive gel content measured for this material (>35%) is present in localized gels.

Figure 5.6 shows typical SEM micrographs for the product NH_2/MA molar ratio 2.0. The micrographs for other products were similar and hence not shown. It is hard to contrast between polyethylene and polyether. A plausible explanation is the very low molecular weight and high degree of functionality of the two components results in good mixing and interlocking of the chains retarding significant phase change. In the absence of good phase contrast it is hard to infer miscibility of the two phases.

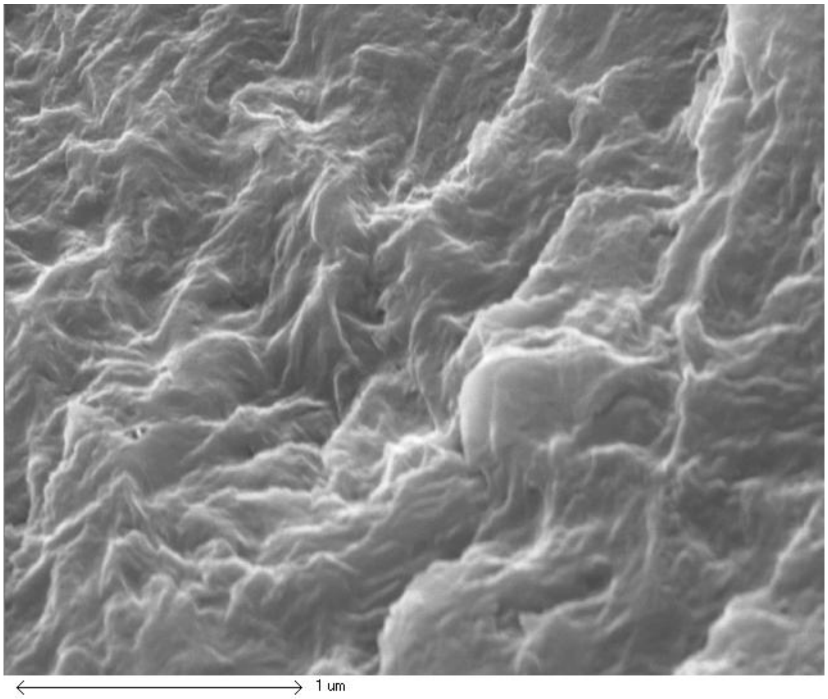

Figure 5.6 SEM micrograph of product NH_2/MA molar ratio 2.0

Representative stress vs. strain curves from the tensile property measurements of the thermoset materials are presented in Figure 5.7. The thermoset material NH_2/MA molar ratio 3.0 showed a rubber-like behavior with no yield point and failed at relatively low elongation at break. On the other hand, the two thermosets NH_2/MA 1.5 and 2.0 were much stiffer, stronger and tougher as evident from the modulus (initial slope), strength at break and area under the curve for these materials. They also showed yield behavior typical of semi crystalline polymers. A decrease in strength in the post yield region before failure is typical of crosslinked polymers unlike thermoplastic materials which usually show strain hardening before failure. Finally, the curve for the thermoset NH_2/MA molar ratio 1.0, depicts the highest modulus but the strength and ductility observed was less than that shown by thermoset materials with NH_2/MA molar ratio 1.5 and 2.0. Tensile properties of the thermoset NH_2/MA 0.66 could not be measured since specimens could not be produced due to the brittleness of the material.

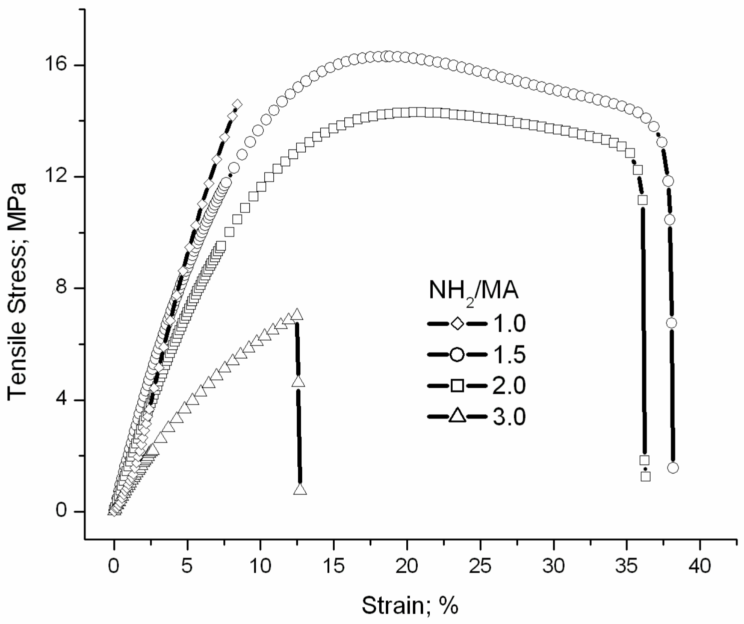

Figure 5.7 Representative stress vs. strain curves for the thermosets

The mechanical properties Young's modulus, maximum strength, elongation at break and energy to break are plotted as a function of NH_2/MA molar ratio in Figure 5.8. Young's modulus increases with decreasing NH_2/MA molar ratio. In fact, a linear relationship with R^2= 0.99 was observed. This was expected since the weight fraction of semi-crystalline material increases at lower NH_2/MA molar ratios making the material stiffer. On the other hand, the maximum strength vs. NH_2/MA trend was different. The highest maximum strength was observed for NH_2/MA molar ratios 1.0, 1.5 and 2.0 showing comparable values. The maximum strength shown by thermoset NH_2/MA molar ratio 3.0 was relatively low. The trend observed in strength at break is probably a consequence of combined effect of molecular weight build up due to extensive crosslinking in these thermosets as well as the crystallinity. This relationship between the mechanical properties and the abovementioned factors is also manifest in the elongation at break trends. Elongation at break values are highest and similar for thermosets with NH_2/MA molar ratios 1.5 and 2.0. Whereas, the elongation at break values of thermosets with NH_2/MA molar ratio 1.0 and 3.0 is quite low. Comparison of strength at break and elongation at break curves highlight the combined role of crosslinking and crystallinity on the tensile properties of the thermosets. Although thermosets NH_2/MA 1.0, 1.5 and 2.0 show similar strength at break, thermoset NH_2/MA 1.0 shows relatively low ductility although it has a higher crystallinity than the other two materials. On the other hand the product with the highest concentration of ED600 (NH_2/MA 3.0) was expected to show the highest ductility, however, the observed elongation at break is much lower. This is likely a consequence of the relatively low extent of crosslinking in this thermoset. Finally, the energy expended before failure follows similar trends as observed for elongation at break values. These observations suggest that optimum tensile properties for these thermosets could be obtained around the NH_2/MA ratios 1.5 and 2.0. It is interesting to mention that the mechanical properties depicted by these thermosets are comparable to crosslinked polyolefins prepared using conventional techniques [22].

5.5 Conclusion

Thermosets produced by reacting highly functionalized maleic anhydride grafted polyethylene and a polyether diamine at several NH_2/MA molar ratios were characterized for their gel content, thermal, mechanical and thermo-mechanical behavior. Maximum gel content was observed when NH_2/MA molar ratio of the reactive mixture was 1.5. Two melting transitions were observed for thermosets, representing the semi-crystalline polyethylene fraction in the gel and sol part of the material in contrast to a single transition for the starting semi-crystalline polyethylene. Crosslinking overall suppressed the crystallinity of the polyethylene in the thermoset. The glass transition temperature of the polyether component was observed to shift to a higher temperature with increasing crosslinking. Tensile properties of the thermosets were observed to be a strong function of composition and degree of crosslinking and the best mechanical performance was observed for the NH_2/MA molar ratio 1.5 and 2.0.

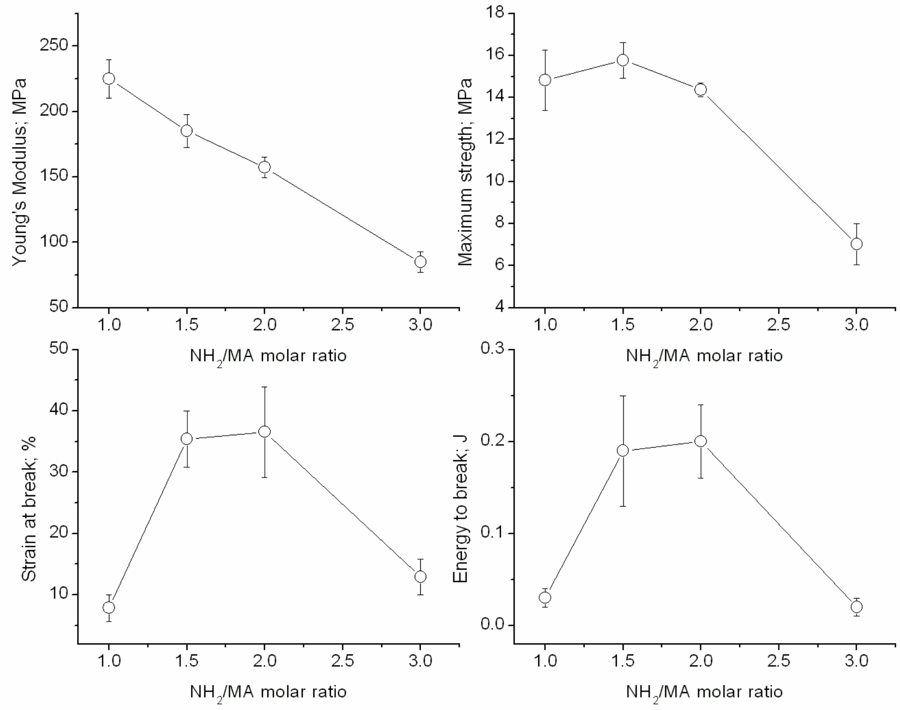

Figure 5.8 Tensile properties as a function of NH$_2$/MA molar ratio

5.6 References

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Chapter 6. Conclusions and Recommendations

The aim of this thesis work was to investigate the preparation and characterization of thermoset material produced by reactions between a highly functionalized low viscosity maleic anhydride grafted polyethylene and diamines. Reactions were performed both in solution and in the melt state to generate the target thermoset materials. Products from these reactions were extensively explored using different techniques to understand the reaction kinetics and mechanism. Thermosets generated were also characterized for the degree of crosslinking, thermal, mechanical and thermo-mechanical properties.

Reactions in solution showed that the degree of reaction could be easily controlled by manipulating the concentration of reactants in the reaction mixture. The products recovered from solution were found to be reactive prepolymers that turned into thermosets on application of high temperature as evidenced by sintering and rheological techniques.

Mixing torque data generated from a melt blender during reactions in the melt phase suggested that reaction between anhydride and amine moieties in this these low molecular weight systems, happen at a much slower rate than widely reported for conventional high molecular weight polymeric systems. Unlike the single, or two closely merged, peaks in mixing torque associated with melting of polymer and chain extension and crosslinking widely reported, two separate peaks were observed in this study. A combination of FTIR and gel content data suggested that the first peak observed in mixing torque is due to a combination of melting and partial reaction between anhydride and amine functionality. The second peak in the mixing torque is due to the initiation of crosslinking. The reaction mixture remains mainly thermoplastic before the appearance of the second peak in mixing torque, signifying delayed crosslinking. The delay between mixing and initiation of crosslinking made it possible to prepare useful one component reactive prepolymers that could be cured into a thermoset product by application of heat at high temperatures.

The slower kinetics observed in the current investigation does not appear to be a consequence of immiscibility of polyether diamine and polyethylene or the relatively higher molecular weight of diamines utilized in some reactions since using a low molecular weight aliphatic diamine, hexamethylenediamine, produced similar trends. The observed kinetics are suggested to be most likely a consequence of the low molecular weight nature of the functionalized polyethylene used in these reactions.

Extensive FTIR and gel content (insoluble fraction) data generated on the prepolymers by processing them at different temperatures and for different periods of time produced intriguing results. The observance of anhydride peak in the FTIR spectra was dependent on amine to maleic anhydride (NH_2/MA) molar ratio. No anhydride peak was observed in the prepolymer spectra when NH_2/MA molar ratio was greater than 1.0. When NH_2/MA was lower than 1.0, a broad peak was observed that could be deconvoluted into an anhydride and cyclic imide peak. All products showed a peak for amide intermediate. Interestingly, for systems in which NH_2/MA >1.0, where no anhydride peak was observed, gel fractions were observed to grow steadily, together with an increase in cyclic imide response when the preopolymers were melt processed at high temperature for different time periods. The increase in cyclic imide was accompanied by a decrease in the amide response. However, the increase in cyclic imide could not be explained by a mere conversion of amide intermediate into cyclic imide as the gel fraction also increased. The only explanation for this could be a reaction between residual anhydride and amine functionality resulting in increased cyclic imide linkages leading to a crosslinked product. This observation renders the popular monitoring of anhydride peak in such systems, to assess the degree of reaction, highly questionable. In other words FTIR alone failed to identify the presence of anhydride functionality which existed in the reaction mixture and was confirmed by colorimetric titrations. FTIR analysis suggested that the reaction in fact occurs via an amide linkage rather than amic acid salt, as claimed in some of the published literature.

Cured thermosets from the prepolymers produced using functionalized polyethylene and a polyether diamine showed gel fractions of the same magnitude as in traditional commercial crosslinked products. DSC heat scans on the thermosets showed two peaks in the endotherm suggesting two different crystal populations compared to a single sharp peak in the starting material (grafted polyethylene). It was demonstrated that the two peaks could be associated with the polyethylene crystals in the gel (crossslinked) and sol (non crosslinked) fractions. A decrease in the heat of fusion suggesting a suppression of crystallinity due to crosslinking was also observed. Dynamic mechanical analysis showed the glass transition temperature to increase with an increase in crosslinking. Thermosets withstood temperature up to 200 °C without exhibiting flow behavior and a crosslink plateau could be observed in the modulus data following the melting temperature. Tensile properties of the thermosets were observed to be composition dependent. All materials showed a yield point but no strain hardening. The ultimate tensile strength was observed to be composition dependent and a maximum was observed when NH_2/MA molar ratio was 1.5 coinciding with the maximum in gel content. Unlike tensile strength, the Young's modulus followed a linear trend and changing with the weight ratio of semi-crystalline grafted polyethylene in the thermoset system.

The properties of investigated thermosets are related to the original materials (functionalized polyolefin and polyamine) used to produce them. It is recommended that reaction be carried out using other functionalized polyolefins and polyamines with different backbone e.g. polypropylene based polyolefins and polymaines with ethyleneoxide, propyleneoxide and PTMEG backbones. The reactivity between amines and anhydride in these systems is expected to vary with the degree of functionality (degree of grafting on polyolefin and functionality of polyamines) and composition of the backbone. Physical properties of thermosets obtained using different materials are expected to vary based on the choice of starting materials.

It is also recommended that the reactive prepolymer obtained by partial reaction of functionalized polyolefins and polyamines should be investigated as a possible heat activated adhesive system. The properties of such adhesives systems could be improved by addition of appropriate tackifiers, rubber additives and other fillers.

Another interesting direction of investigation might be thermosetting molding compounds. The low viscosity and reactivity of these prepolymers would be an advantage over the conventional injection molding of high viscosity polymeric products. It would allow molding of intricate and much bigger articles than could be achieved by conventional methods.

The high degree of functionality and low viscosity of these polymers can also be exploited to produce composites with inorganic fillers. The low viscosity and functionality is expected to help in providing improved wetting and bonding of the inorganic resulting in better dispersion and improved interfacial strength.