Reactions of Low Molecular Weight Highly Functionalized Maleic Anhydride Grafted Polyethylene with Polyetherdiamines

Tayyab Hameed,[1] David K. Potter,[1,2] Elizabeth Takacs[1]

[1]Department of Chemical Engineering, McMaster University, Hamilton L8S 4L7, Ontario, Canada
[2]Xerox Centre for Engineering Entrepreneurship & Innovation, School of Engineering Practice, McMaster University, Hamilton L8S 4K1, Ontario, Canada

ABSTRACT: Reaction 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. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 2285–2297, 2010

Key words: maleic anhydride grafted polyolefin; polyolefin wax; polyether diamines; crosslinked products

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 engineering for the desired end use application is possible. Materials with a wide range of molecular weights (MW) (polyolefin waxes to ultra high MW 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 undesired free radical side reactions (crosslinking with polyethylene and degradation with polypropylene), which are 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 comaptibilizer 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 MAH 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 s 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 MAH functionalized polyolefin reactions with polyamines have utilized traditional polyolefins with high molecular weight 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 and that the associated processing costs might be lower than the cost of processing conventional thermoplastic polyolefin. Although it is expected that the material cost of these thermosets would be higher than conventional thermoplastic polyolefins, it is also anticipated that these materials might have utility in markets and applications that can support the higher costs. In the current investigation reactions between highly functionalized, MAH grafted low MW polyethylene and polyether diamines 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.

EXPERIMENTAL

Materials

The MAH 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 I. The molecular weight data (M_w, M_n, and MWD) was obtained by high

TABLE I
Characteristics of Polyolefin Waxes

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

temperature GPC at 135°C (using PE standards for calibration) and was kindly provided by the manufacturer. The 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. 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.

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 min 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.

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.

FTIR

FTIR spectra were collected using a Thermo Nicolet IR300 spectrometer fitted with a Pike Technologies Diffuse IR^{TM}, 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.

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 disks 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.

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.

TABLE II
Maleic Anhydride 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

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 video-recorder 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.

RESULTS AND DISCUSSION

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[5,9,16–20,24–27] and colorimetric titrations[9,24–26,28] have been reported in the literature to assess the MAH content in functionalized polyolefins. Titration and FTIR techniques are most popular as 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[6,9,24–26,28]

Titration results for the four MAH grafted polyolefins are presented in Table II. These include both polyethylene and polypropylene products functionalized to varying degrees. Some studies[25] 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 3–5 times higher than the 1–1.5% that is typically observed with functionalized commodity polymers.

The reported assessment of MAH grafting using the titration method assumes that all of the grafted MAH exists in the anhydride form. As 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 MAH functionality of grafted products. The FTIR absorbance spectra of nongrafted PE4201 and MAH grafted PEMA4351 (vacuum dried at 100°C for 24 h) used in this study are shown in Figure 1. Three distinct absorbance peaks at ∼ 1715, 1780, and 1860 cm^{-1} are present in the PEMA4351 spectrum while they are absent in the nongrafted PE4201. The 1780 and 1860 cm^{-1} absorptions are responses from symmetric and asymmetric stretching of the MAH carbonyl.[5] The absorption at 1715 cm^{-1} arises from the carbonyl stretching of a carboxylic acid group.

The carboxylic acid absorbance at 1715 cm^{-1} in the PEMA4351 spectra is very strong indicating that a significant portion of the MAH 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[5,20,24,27] For example, Schmidt et al. [2003] 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 h, 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 h. Our experience here is consistent with the observations of Battinni and Agnelli.[25]

More intense processing of the MAH 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 shown in Figure 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
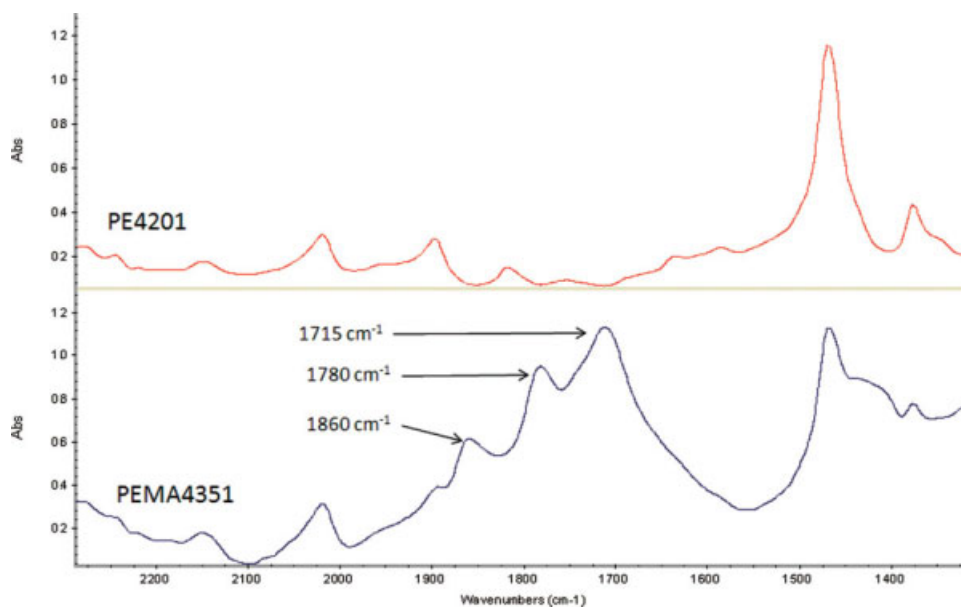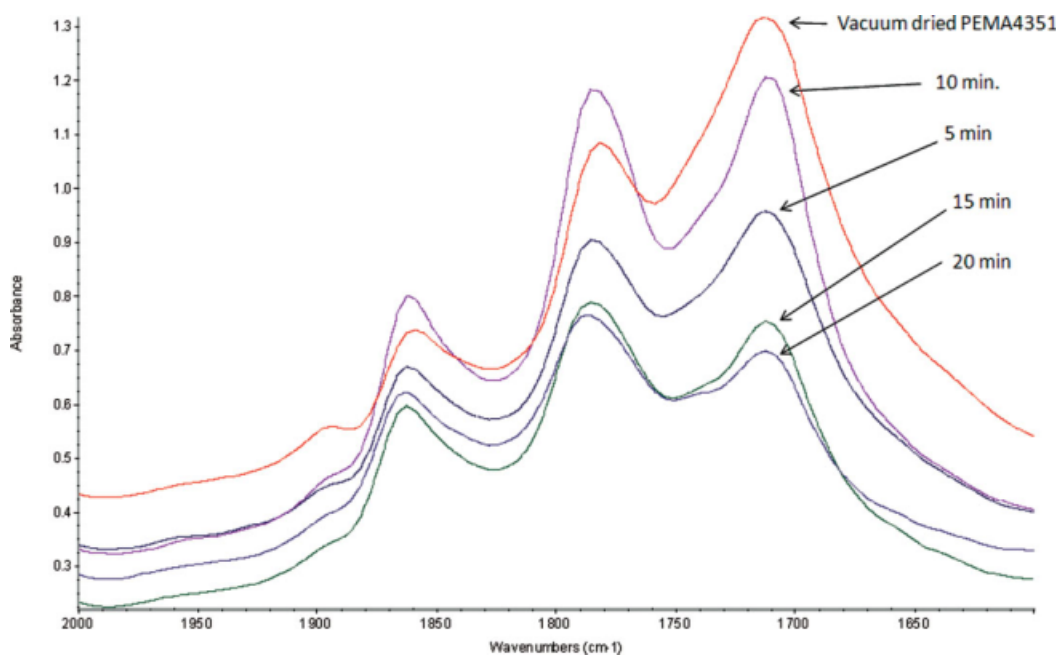
Figure 1 FTIR spectra of PEMA4351 and PE4201. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

absorbance intensities for these functionalities are plotted as a function of melt processing time in Figure 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,[5,24] blends were prepared by melt mixing 2-dodecen-1-yl succinic anhy-dride with ungrafted PE4201 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 4 show strong anhydride absorbance at 1780 cm^{-1} and significant absorbance due to anhydride (1860 cm^{-1}) and carboxylic acid (1715 cm^{-1}). The anhydride absorbances (relative to methylene at 1460 cm^{-1}) are plotted in Figure 5

Figure 2 Overlaid FTIR spectra for PEMA4351 melt processed for different time intervals at 150°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
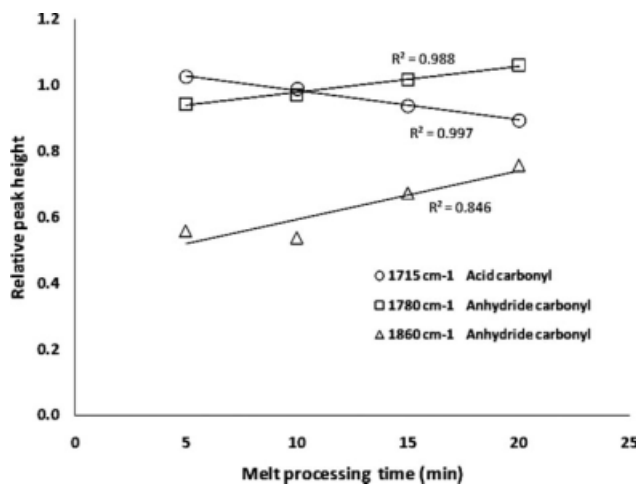
Figure 3 Relative peak height vs. melt processing times for PEMA4351.

against the known stoichiometry and a linear trend is observed. The 1780 cm^{-1} absorbance is more sensitive (higher slope) than the 1860 cm^{-1} absorbance in agreement with earlier reports.[16]

The calibration plots in Figure 5 provide estimates of MAH content in PEMA4351 that are lower than the MAH content measured by titration ($\sim$ 70%). This is likely a consequence of the relatively large amount of anhydride in acid form in the PEMA4351 as compared to that in the calibration blend with comparable anhydride content (4.9%) (Fig. 6). As we were unable to convert the acid groups into anhy-

dride by vacuum drying or melt treatment, the assessment of anhydride using FTIR to assess the degree of reaction will not be workable. Earlier reports[5,24] where such calibration plots were successfully generated did not present any FTIR spectra for the standard blends.

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 III. 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 as 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
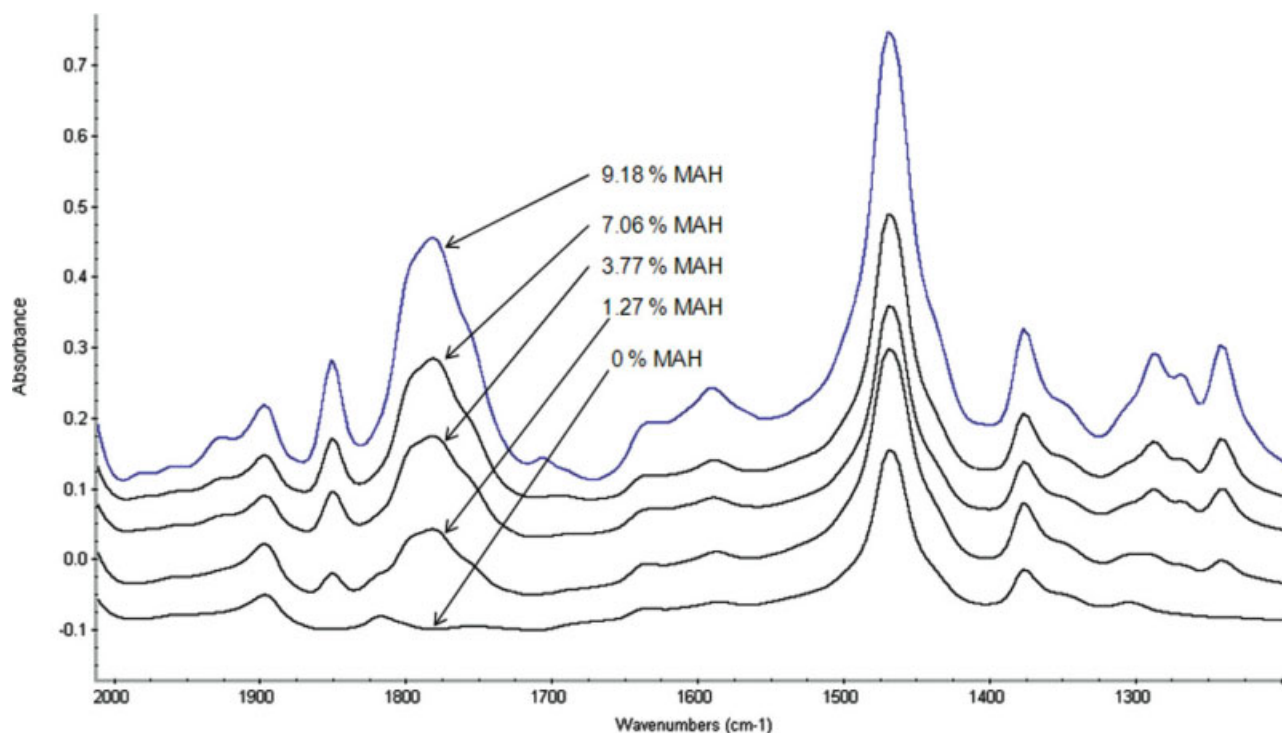
Figure 4 FTIR spectra of standard blends of dodecenyl succinic anhydride and PE4201 at various compositions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
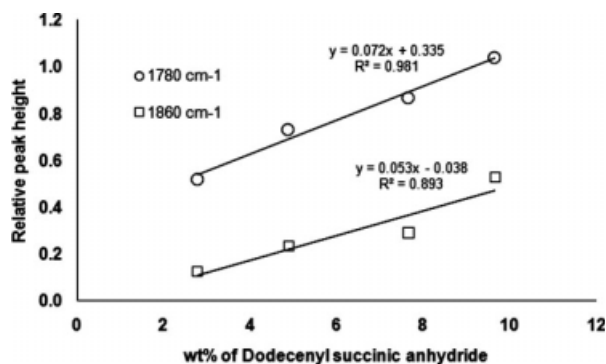
Figure 5 Relative peak heights of 1780 and 1860 cm^{-1} peaks vs. wt % of dodecenyl succinic anhydride in the blend.

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 was observed, the recovered reaction product could not be processed into films or disks for further characterization.

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 III 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 disks 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 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 (Fig. 8) which suggests it is more likely to be an amine absorption.

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.
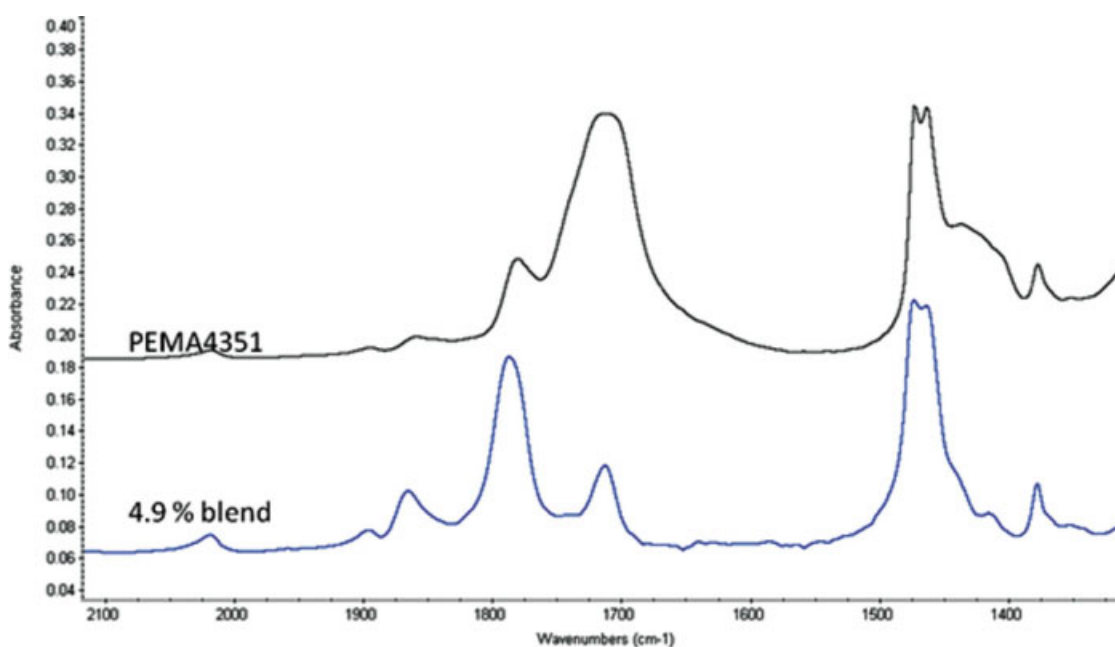
Figure 6 FTIR spectra for PE4201 blend containing 4.9% dodecenyl succinic anhydride and PEMA4351. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
Summary of Composition and Critical Observations During the Reactions PEMA4351 and Diamines of Varying Molecular Weights

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

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 (1715 cm^{-1}) and MAH (1780 cm^{-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 1780 cm^{-1} to 1770 cm^{-1}, and from 1715 cm^{-1} to 1700 cm^{-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 1700 cm^{-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
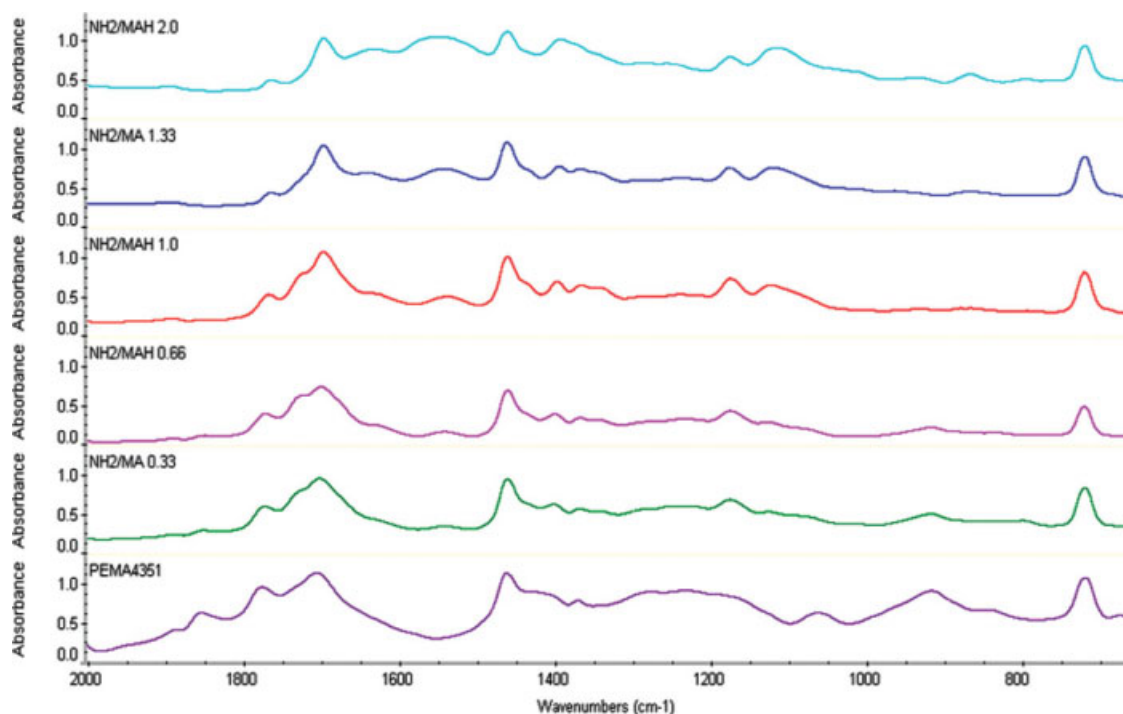
Figure 7 Overlaid FTIR spectra for PEMA4351 and its reaction products with EDR176. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
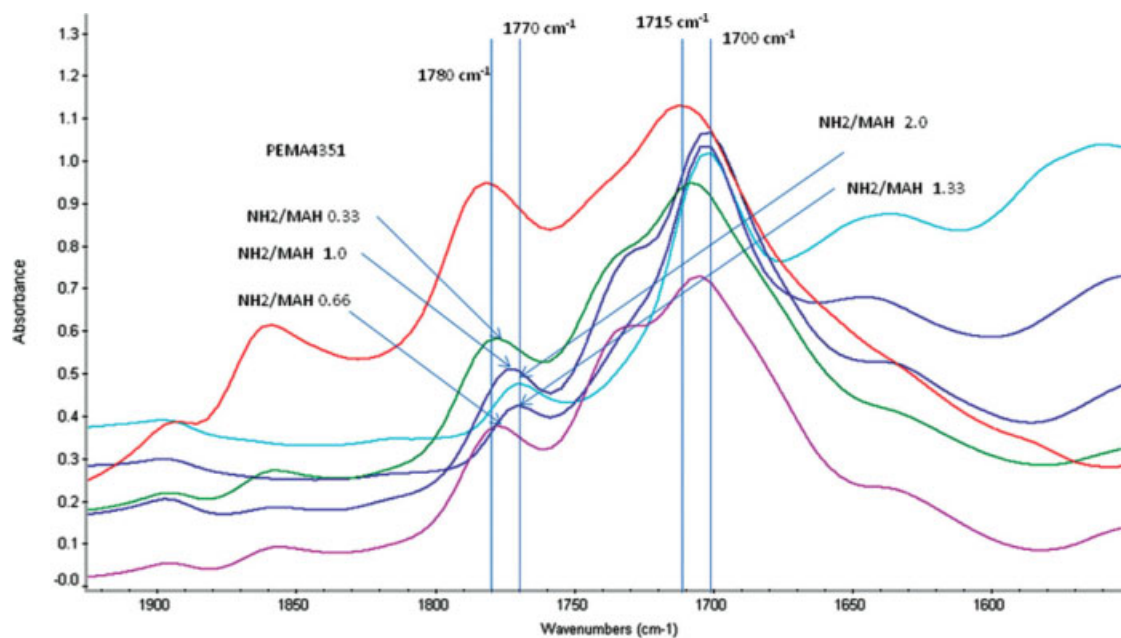
Figure 8 Development of imide peak (1700 and 1770 cm^{-1}) with NH$_2$/MAH molar ratio. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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 9 for the PEMA4351-EDR176 reaction products. The decreasing level of residual MAH with increasing amine mole ratio that is observed in Figure 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 as no anhydride or acid absorption could be 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.

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 reaction that leads 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 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
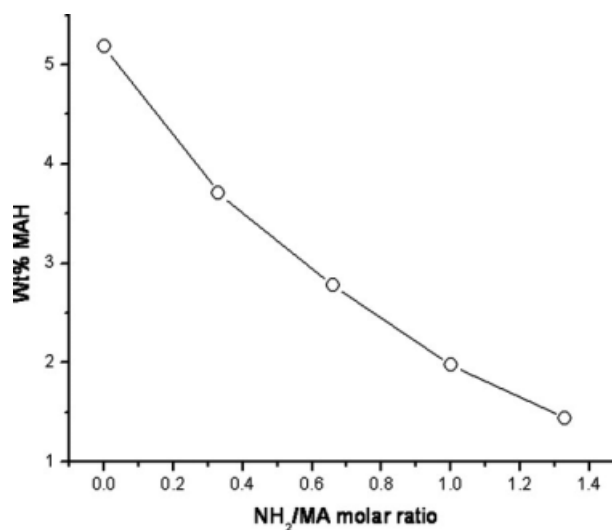
Figure 9 MAH content in PEMA4351 and its reaction products with EDR176 assessed by colorimetric titrations as a function of NH$_2$/MA molar ratio.
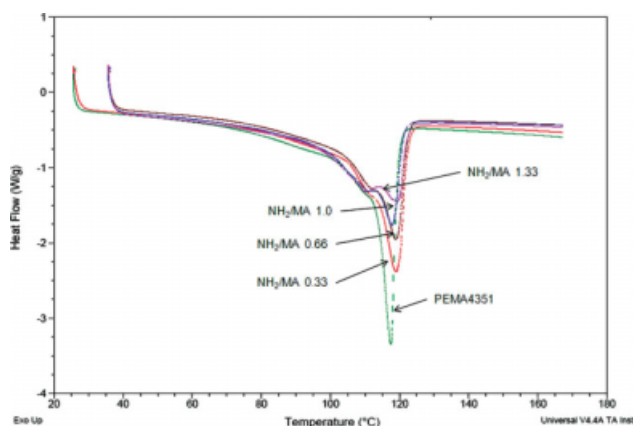
Figure 10 Second DSC heating scan for PEMA4351 and its reaction products with EDR176. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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 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 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.

Dynamic frequency sweeps followed the time sweep measurements. Data from these frequency sweeps for processed PEMA4351-EDR176 reaction products are shown in Figure 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 dependence has been reported to decrease with introduction of long
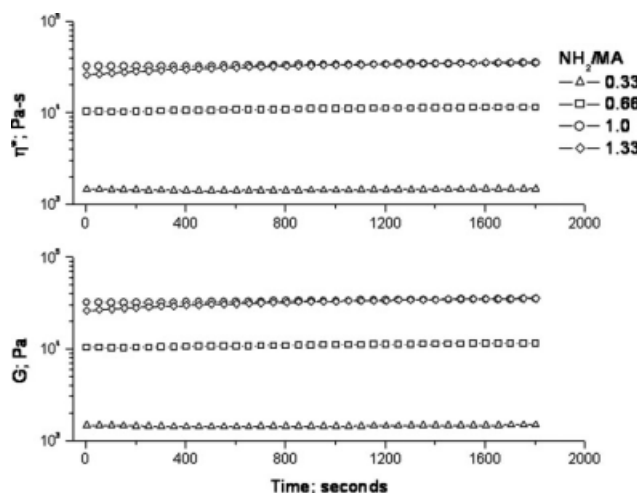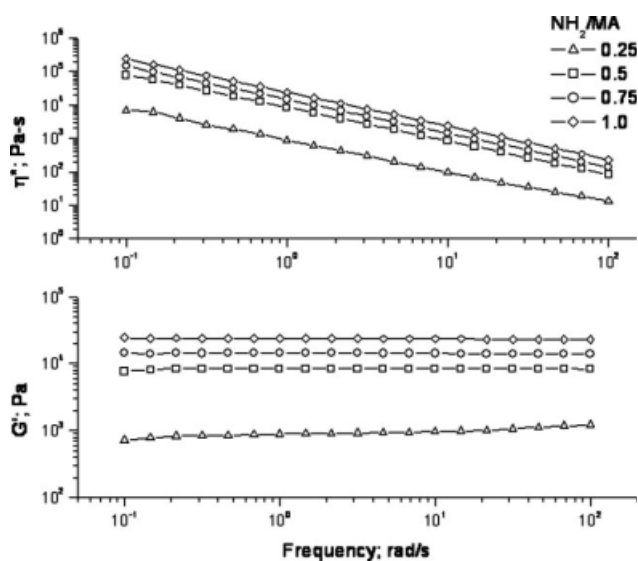
Figure 11 G′ and η* data from dynamic time sweep for PEMA4351-EDR176 reaction products at different NH_2/MA molar ratios. (T_{test} = 140°C; $\gamma°$ = 0.05; ω = 1 rad/sec).

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. The viscosity shows typical power law behavior with no zero-shear plateau at low frequencies. This is different than the zero-shear plateau shown by most thermoplastic materials at low frequencies and suggests the crosslinking of the
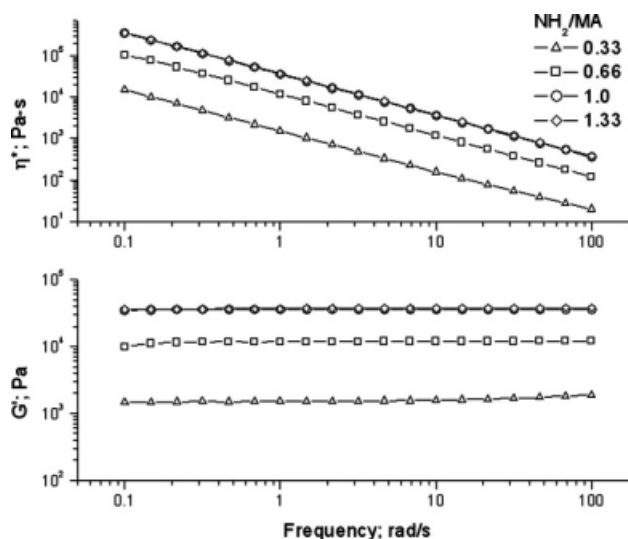
Figure 12 G′ and η* data from dynamic frequency sweep for PEMA4351-EDR176 reaction products at different NH_2/MA molar ratios. (T_{test} = 140°C; $\gamma°$ = 0.05).

Figure 13 G' and η^* data from dynamic frequency sweep for PEMA4351-ED600 reaction products at different NH_2/MA molar ratios. ($T_{test} = 140°C$; $\gamma° = 0.05$).

reaction products. Dynamic frequency sweeps for the PEMA4351-ED600 are shown in Figure 13 and show very similar results, with the exception of the reactor product having the lowest amine to MAH mole ratio. The low frequency data for this sample appears to be trend toward a zero-shear viscosity limit, which would suggest that this sample is not networked to the same extent.

The nature of the observed plateau zone was further explored with stress relaxation experiments. At elevated temperatures, samples capable of significant flow 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 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.

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 pro-

pensity of the material to sinter was used as a gauge of thermoplasticity.

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 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.

Similar behavior is observed in Figure 15(a) for PEMA4351-EDR176 reaction product NH_2/MAH of 1.33 that has been exposed to elevated temperature for a period of 1 min before the sintering experiment. In fact, this same behavior is repeated for material that has been maintained at elevated temperatures for 2 min and for 3 min (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 min, different behavior is observed [Fig. 16(b)]. 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 min 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
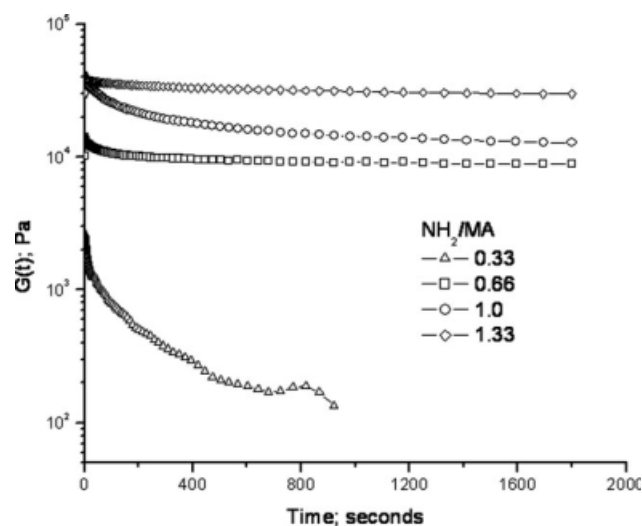
Figure 14 Relaxation modulus as a function of time for PEMA4351-EDR176 reaction products at different NH_2/MA molar ratios. ($T_{test} = 140°C$; $\gamma° = 0.05$).
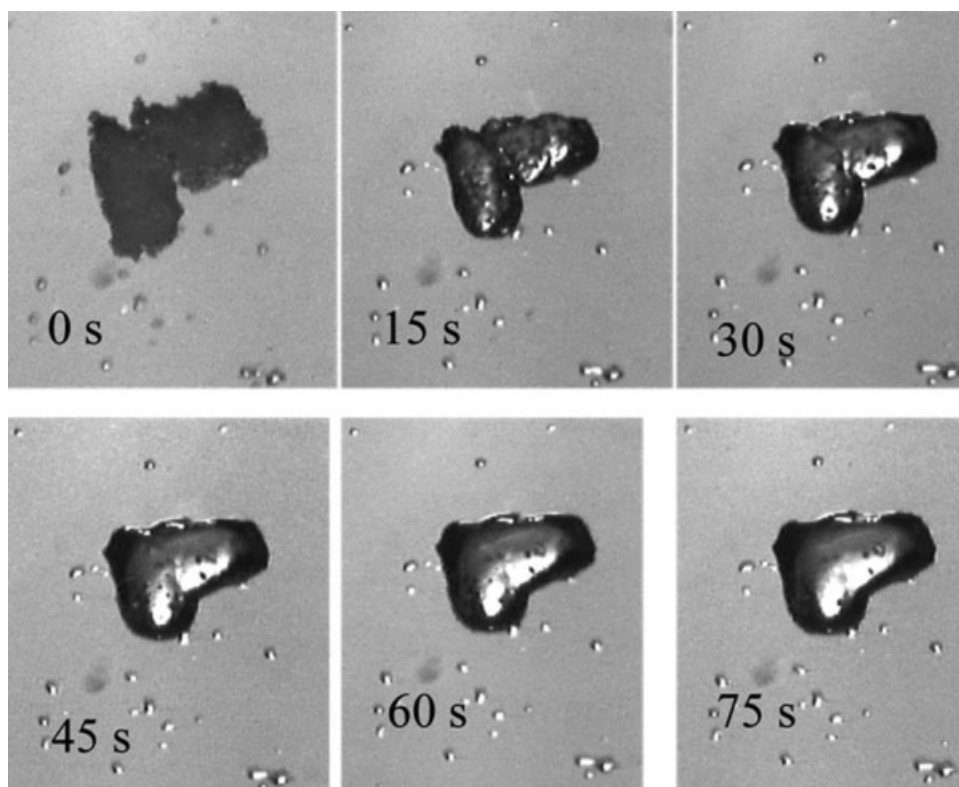
Figure 15   Sintering of PEMA4351-EDR176; NH2/MA 1.0 reaction product with time.
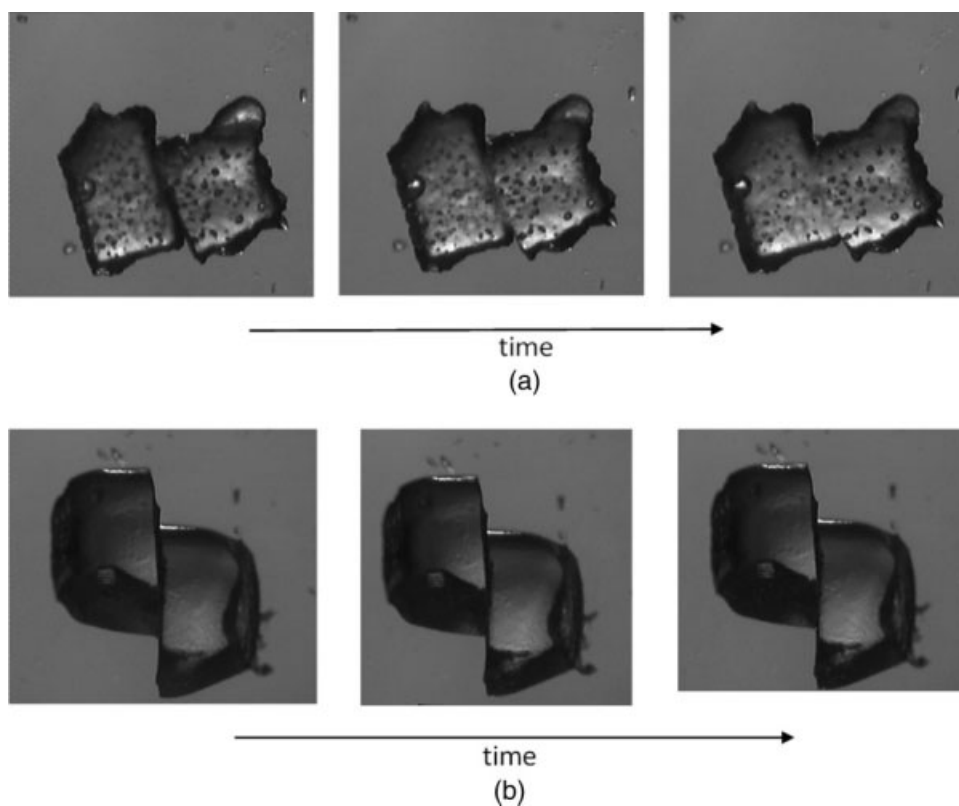
Figure 16   (a) Sintering of PEMA4351-EDR176 raction products NH_2/MA 1.33; left in the melt state at 150°C for 1 min, (b) PEMA4351-EDR176 reaction products NH_2/MA 1.33; left in the melt state at 150°C for 6 mins.

characteristic of the material after such a time and temperature history.

This evidence of a delayed reaction to yield thermosetting material is interesting as 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.

CONCLUSIONS

Thermosetting materials were produced by reacting a highly functionalized MAH 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 MAH, 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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