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Nylon grafted ethylene propylene diene monomer thermoplastic elastomers

David Paul Ching
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NYLON GRAFTED
ETHYLENE PROPYLENE DIENE MONOMER
THERMOPLASTIC ELASTOMERS

A Thesis

Presented to

The Faculty of the Department of Materials Engineering

San Jose State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

David Paul Ching

May 1997

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ABSTRACT

NYLON GRAFTED ETHYLENE PROPYLENE DIENE MONOMER THERMOPLASTIC ELASTOMERS

by David Paul Ching

Thermoplastic elastomers (TPEs) were successfully prepared. To accomplish this, two synthesis routes were used: (1) graft copolymerization of commercial nylon 12 with maleic anhydride functionalized EPDM rubbers during Brabender melt mixing and (2) polymerization of 11-aminoundecanoic acid to nylon 11 in the presence of the same set of EPDM rubbers. Transmission FTIR on thin films revealed the cyclic imide group even at 0.4 wt.%, showing evidence of a graft. The physical and mechanical evidence for grafting was more convincing for TPEs made by route 2. Dynamic mechanical test cycling between 30 °C - 210 °C using parallel plates revealed different elastic modulus, G' , behaviors between reactive TPEs and non-reactive blend controls. SEM micrographs revealed that small nylon domains ($< 1\ \mu\text{m}$) yielded TPEs with high tensile strength (up to 1,270 psi) and toughness (up to 7,150 psi). The shore A hardness ranged from 57 to 90 for all the compositions evaluated.

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Section 1

Introduction

Thermoplastic elastomers (TPEs) are copolymers which contain both hard and soft chains. Examples of hard chains include polyethylene, polypropylene, and polystyrene while soft chains include polyisoprene rubber and polybutadiene rubber. The TPEs can be processed by conventional thermoplastic fabrication techniques such as extrusion, injection molding, or blow molding to yield a material that has performance properties similar to those of thermoset (vulcanized) rubber. One of the trends is to replace thermoset rubbers with TPEs and still maintain rubber-like performance, especially in the area of durometer hardness and low compression set. Other properties such as chemical resistance, weatherability, selective permeation in films, resin compatibility, and processability can be improved with TPEs.¹

Some major markets for TPEs include automotive, medical and consumer products.²⁻⁴ Between 1993 and 1994, the sale of thermoplastic elastomers in the United States increased by 10% from 786 million pounds to 867 million pounds.⁵ This increase was slightly higher than the 8.5% average which included the sales of eighteen other resins totaling 76 billion pounds. Polyethylene, polypropylene, and polyvinyl chloride resins accounted for 61% of the sales, TPEs accounted for 1.1% of the sales, and fourteen other resins accounted for less than 5% of sales each.

Thermoplastic elastomers can be divided into six major classes. In the approximate chronological order of appearance in the scientific literature and commercial use, they are: thermoplastic polyurethanes⁶, styrene block copolymers⁷, thermoplastic olefins⁸, copolyester elastomers⁹, thermoplastic vulcanizates¹⁰, and copolyamide elastomers¹¹. Thermoplastic vulcanizates contain a minor amount of vulcanized elastomer in a plastic matrix that is usually polypropylene. During the late 1950s, B.F. Goodrich and Mobay Chemical introduced thermoplastic polyurethane elastomers. During the middle and late 1960s, the styrene butadiene and styrene isoprene block copolymers were produced by the Shell Chemical Company. In the early 1970s, the Du Pont Company commercialized copolyester block copolymers and the Uniroyal Chemical Company produced thermo-plastic olefin blends, which were primarily polypropylene and EPDM rubber. In the 1980s, the Monsanto Chemical Company introduced thermoplastic vulcanizates and the Upjohn Company introduced high performance thermoplastic polyamide elastomers.¹² Within each class of TPEs, there are many synthetic routes which yield different grades to provide a wide range of properties.

The architecture of thermoplastic elastomers falls into three categories. They are either elastomeric diblock copolymers (A-B), linear or radial triblock copolymers (A-B-A), or multiblock copolymers (A-B)_n. The A represents the minor fraction of hard polymeric segment in the copolymer while the B represents the major fraction of soft polymeric segment. The hard segment has a glass transition temperature (T_g) and/or melting temperature (T_m) above room temperature while the soft segment has a T_g (and

possibly a T_m) below room temperature. An example of a triblock copolymer is polystyrene-polybutadiene-polystyrene (PS-PB-PS), which is commercially available. A schematic morphology of the PS-PB-PS triblock copolymer is shown in Figure 1.

Figure 1. Schematic morphology of polystyrene-polybutadiene-polystyrene triblock copolymer. (Adapted from reference 13. Used with permission of Prentice-Hall, Copyright 1987)

This polymer is synthesized by anionic block copolymerization.¹⁴ This was the only process that produced well-defined PS-PB-PS triblocks. The Shell Chemical Company conducted the original research and developed the domain theory to explain thermoplastic elastomer behavior.¹⁵ In short, the polystyrene and polybutadiene form two immiscible phases, each of which retains many properties of the homopolymer. At room temperature, the polystyrene-terminated elastomer associates to form physical domains which act as multifunctional junction points. This gives the elastomer network similar

properties to that of a vulcanized rubber. However, when it is heated near the T_g (100 °C) of polystyrene, the domains soften and allow the block copolymer to flow. When the block copolymer is cooled down, the domains become hard again and the original properties are regained.

The success of the domain theory has helped the development and growth of new TPEs with improved temperature resistance and flexibility in tailoring mechanical properties. These new TPEs include polyurethane, copolyester, and copolyamide elastomers. Their formation involves some form of condensation reaction to produce multiblock architectures. The synthesis details and applications are many and varied for these elastomers.¹⁶

The polymer network of a TPE is thermo-reversible and this feature allows the TPE to be easily reprocessed and recycled. For example, a molded article made from a TPE can be heated and reshaped in the mold if there was a defect in the article. Reprocessing the TPE molded article saves materials cost and reduces scrap. At the end of the service life, a TPE article is potentially easier to recycle than a thermoset article. The ability to reprocess and recycle TPEs easily are some reasons for its continuing demand and strong growth. Advances in thermoplastic processing technology can improve product quality and reduced manufacturing costs relative to thermoset processing.¹⁷ Another area of TPE development involves novel manufacturing processes such as reactor modification, grafting, and alloying.¹⁸ These techniques allow the formation of well controlled architectures through chemically reactive processing.

Motivation for the Research

Despite the advancements made in TPE technology over the past 40 years, today's commercial TPEs still have a limited range of physical and mechanical properties. Those properties are determined by what the polymerization processes (anionic and condensation) can produce. The physical and mechanical properties of TPEs can be varied by changing: (1) the chemical structure of the hard and soft polymeric blocks, (2) the ratio of the hard and soft blocks, and (3) the molecular weight (chain length) of the blocks. However, the chemical adjustments necessary to produce a particular set of properties are made during polymerization and can not be changed after the thermoplastic elastomer is synthesized. The request for a custom synthesized thermoplastic elastomer from the manufacturer is sometimes not feasible or economical.

In mechanical sealing for an automotive application, for example, one may need a soft but tough thermoplastic elastomer which could function between room temperature and 170 °C. Such a TPE might initially have a shore A hardness of 60, a tensile strength of 2000 psi, and an elongation of 1000 % at room temperature. High toughness is characterized by a material with high tensile strength and high elongation. Table 1 shows the upper use temperature, defined as a high temperature limit for continuous use, of four commercial thermoplastic elastomers and their range of room temperature mechanical properties. The shore D scale indicates a higher hardness than the shore A scale. The hardness, tensile strength, and 300% modulus of the TPEs increased with upper use temperature. The elongation decreased with upper use temperature. Table 1

demonstrates that a soft and tough thermoplastic elastomer that could be used between room temperature and 170 °C is not commercially available.

Table 1. Properties of commercial block copolymer thermoplastic elastomers^{19,20}

Material Property*	Styrenics	Polyurethanes	Copolyesters	Polyamides
High-temperature limit (continuous), °C	100	120	125	170
Hardness, shore	52A - 75A	77A - 45D	40D - 72D	25D - 63D
Tensile strength, psi	2900 - 5000	3700 - 9000	4000 - 6600	4200 - 7400
Modulus, 300%, psi	203 - 800	1300 - 3200	2800 - 4500	1300 - 5500
Elongation, %	1200 - 500	550 - 460	550 - 350	715 - 380

*All properties, except row 1, are at room temperature.

The ability to tailor properties of the thermoplastic elastomers through preparation and characterization is the motivation for this research. The approach taken was to use commercially available polymers or resins with co-reactive groups and conduct graft copolymerization in the melt. Grafting provides a convenient method to covalently bond hard and soft block polymers together in various proportions and arrangements. The molecular architecture that is formed from grafting is different from the triblock and multiblock structures of the commercial thermoplastic elastomers. This is discussed in more detail in the next section on chemical grafting. Since grafting provides structural variation there may be some interesting effects on the mechanical properties.

A literature survey found little activity on the development of thermoplastic elastomers using graft copolymerization of nylon 11 or nylon 12 and maleic anhydride grafted

EPDM rubber. Chemical structures so described are indicated in Section II of the report. There is much discussion in the literature about using maleic anhydride grafted EPDM rubber to modify the impact strength of nylon 6. In these compositions, the maleic anhydride grafted EPDM rubber is the minor component (less than 50 weight percent) and the nylon 6 is the major component (greater than 50 weight percent).

This thesis research seeks to explore the other end of the composition range in order to make soft thermoplastic elastomers. This is accomplished by using maleic anhydride grafted EPDM rubber as the major component and nylon 11 or nylon 12 as the minor component. A summary of two relevant patents^{29,30} considering this approach is presented in Section III.

Section II

Background

A. Chemical Crosslinking and Chemical Grafting

Chemical grafting is a method which allows some control over molecular architecture and hence mechanical properties. Crosslinking that occurs along the interface of an immiscible polymer blend is known as **reactive polymer blending**. In this case, two or more immiscible polymeric segments are functionalized with chemical groups that are co-reactive. The chemical groups are distributed along the polymer backbone. During polymer melt processing, the chemical groups react to form crosslinked polymers at the interface between the phases. These crosslinked polymers provide mechanical locking between the phases. Figure 2a shows a schematic of the interface that contains crosslinked polymers between two immiscible phases. The reactive polymer blend retains the chemical and mechanical properties of the individual polymeric phases.

Figure 2. Polymer structures due to (a) chemical crosslinking at the interface of two immiscible phases, and (b) chemical grafting in the bulk phase.

Grafting that takes place in the bulk phase and along the backbone of a polymer is known

as **graft copolymerization**. The graft copolymer is formed during polymer melt processing when a second rigid polymer (A) covalently bonds to the reactive sites on the main flexible polymer (B) and forms side chains, as shown in Figure 2b. These “comb” structures form a phase morphology that is schematically shown in Figure 3. The hard and soft polymers again form separate phases. This time the disperse hard block phases (A) occur randomly along the polymer backbone (B) instead of at both ends of a soft block segment, as illustrated in Figure 1. The size and shape of the disperse phase depends on several factors including the relative proportions of the two constituents and the method of preparation of the specimens. The chemical and mechanical properties of this grafted copolymer are expected to be different from the properties of the individual polymers. The grafting technique was used during the thesis research.

Figure 3. Thermoplastic elastomer morphology obtained by graft copolymerization. The hard disperse phase is represented by A and the soft rubbery continuous phase by B.

B. Maleic Anhydride Grafted EPDM Rubber and Nylon 11 or Nylon 12

The thermoplastic elastomers were synthesized by two routes to determine which produced a tougher TPE. One route was to graft a commercial nylon polymer to the maleic anhydride functionalized EPDM rubber during Brabender melt mixing (see section E). The other route was to polymerize the nylon monomer in the presence of the EPDM rubber during melt mixing. Since the nylon 12 monomer (12-aminododecanoic acid) was expensive, the decision was made to use the lower cost nylon 11 monomer (11-aminoundecanoic acid).

The chemical structures of nylon 12 and maleic anhydride grafted EPDM rubber are shown in Figure 4. The diene in this particular EPDM rubber illustration is 5-ethylidene norbornadiene (END). The relative amounts of the monomers in the EPDM rubber varies. One of the commercial EPDM rubbers used for this thesis work had 51 wt.% ethylene, 42 wt.% propylene, and 7 wt.% END. The amount of grafted maleic anhydride was between 0.5 - 2.0 wt.%. The EPDM polymer has good resistance to thermal oxidation even though the unsaturation is located in the pendant position of the main chain. The polymerization of 11-aminoundecanoic acid to nylon 11 is shown in Figure 5. This reaction proceeds by anionic polymerization in the melt and produces a linear polymer.

Nylon 11 and nylon 12 were chosen because they were two of the lower melting commercial nylons ($T_m = 185\text{ }^{\circ}\text{C}$ and $175\text{ }^{\circ}\text{C}$, respectively). A lower processing temperature can then be used to conduct the graft copolymerization and minimize the thermal degradation of the EPDM rubber. The combination of nylon and EPDM rubber

was chosen because the grafting reaction between these functionalized polymers is well characterized, as discussed in the next section.

Figure 4. Chemical structures of (a) maleic anhydride grafted ethylene propylene diene monomer (EPDM) and (b) nylon 12.

Figure 5. Anionic polymerization of 11-aminoundecanoic acid to nylon 11.²¹

C. Grafting Reactions

Polyimides are formed from either stepwise condensation reactions²² or stepwise addition reactions.²³ The grafting reaction between nylon and maleic anhydride grafted EPDM rubber forms a cyclic imide by stepwise condensation reaction. Figure 6 shows a

schematic of a polyimide that is formed by stepwise condensation reaction. The maleic anhydride reacts with a primary amine to form the amic acid, Figure 6a. The imide ring is then closed through a condensation reaction, Figure 6b. Reaction 6a proceeds rapidly at room temperature while reaction 6b requires heating. The imide linkage is stable and has high heat-resistance.

Figure 6. Reaction of a primary amine and maleic anhydride to form a cyclic imide.²⁴

The amount of polyimide grafts in a polymer blend or graft copolymer can be analyzed by Fourier transform infrared (FTIR) spectroscopy.²⁵ Each of the carbonyl groups in Figure 6 has a characteristic absorption wavenumber. The peak locations and peak heights give quantitative information when they are calibrated with concentration standards. The commercial EPDM rubbers usually contain 0.5 wt.% to 2.0 wt.% of grafted maleic anhydride. This low concentration of maleic anhydride will make quantitative measurements difficult. However, the presence or absence of certain chemical species can still be qualitatively measured.

Another method to determine the amount of grafted copolymer is to use Soxhlet extraction. The TPE is extracted with xylene, a solvent for EPDM rubber but a non-solvent for nylon, and the undissolved material is weighed. This undissolved material should be the nylon grafted EPDM.

D. Morphology

Morphology refers to a spatial arrangement of phases when two or more immiscible polymers are melt blended. The morphology generated during mixing depends on the miscibility, the volume fraction, and the melt viscosity ratios of the polymeric components at some mix temperature, as well as the thermal and rheological history. The size of the dispersed phase is determined by relative rates of drop breakup and drop coalescence as it is deformed in a Brabender internal mixer, extruder or Banbury mixer. The component with the lower viscosity tends to encapsulate the more viscous or more

elastic component during mixing because this reduces the rate of energy dissipation. This effect of the viscosities may be offset by changing the proportion of the components to control which one becomes the continuous phase. A co-continuous morphology is formed when the viscosity ratios and volume ratios are balanced, as shown in Figure 7.

Figure 7. Phase morphology as a function of viscosity ratio and volume ratio.²⁶

E. Melt mixing

The Brabender Plasticorder™ system is a common melt mixing apparatus that is used to prepare small samples for laboratory research evaluations. One was used for this thesis research. Figure 8 illustrates a melt mixing experiment that was conducted in a Brabender mixing bowl by Macosko²⁷. The mixing torque is compared between a reactive blend and a non-reactive blend of 30 wt.% ethylene propylene rubber in 70 wt.% aromatic amorphous nylon (Zytel 330). This nylon was reported to be functionalized

with amine groups on the chain ends by the Du Pont Company. The upper curve shows a higher mixing torque due to an interfacial chemical reaction in the reactive blend. The chemical reaction builds molecular weight and increases the viscosity of the mixture. This results in an increased torque needed to drive the rotors at a fixed speed. The lower curve shows the mixing torque of a non-reactive blend. The mixing torque due to graft copolymerization is also expected to be higher than a non-reactive blend because molecular weight is increased during the grafting reaction. In this example, the mixing torque for the reactive blend is still varying while the mixing torque for the non-reactive blend reached a plateau after 6 to 7 minutes of melt mixing.

Figure 8. Brabender mixing torque curves for a reactive and non-reactive blend of 30 wt. % ethylene propylene rubber in an aromatic amorphous nylon. (Adapted from references 27 and 28. Used with permission of Society of Plastics Engineers, Copyright 1995, and Carl Hanser GmbH & Co., Copyright 1995)

Section III

Thermoplastic Graft Copolymers - Patent Reviews

Two patents were found that are somewhat related to the thesis topic. These patents contain nylon and EPDM compositions that are closer in composition to a thermoplastic elastomer than to a rubber toughened, engineered plastic. One patent was granted to Clarence F. Hammer and Harold K. Sinclair in 1977 for "Novel Elastomeric Graft Copolymers."²⁹ The other was granted to Errol J. Olivier in 1991 for "Polyamide Thermoplastic Elastomer Obtained By Blending."³⁰

The Hammer and Sinclair patent claimed various combinations of trunk structures and side chains that formed a thermoplastic graft copolymer. Examples of the reported trunk structures are indicated in Figure 9. The side chain polymers were either low molecular weight amine terminated nylon 6 or nylon 12. The degree of polymerization of the nylons varied between 5 - 60. The stepwise grafting reactions that occurred between the primary amine terminated nylons and the maleic anhydride containing trunk polymers are illustrated in Figure 6. The patent claimed that the amount of nylon grafting was between 15 - 55 weight percent. One of the examples was the grafting reaction between amine-terminated nylon 12 and maleic anhydride grafted (2.23 wt.%) ethylene/propylene/1,4-hexadiene. The composition was 60 wt.% maleic anhydride grafted EPDM, 22.4 wt.% nylon 12, 17 wt.% mineral oil, and 0.6 wt.% antioxidant. The grafting was accomplished by combining the two polymers, mineral oil, and antioxidant at 250 °C in a Brabender mixer. Mixing was for 12 minutes and under a nitrogen blanket. The result was an

elastomeric graft copolymer that had thermoplastic behavior. The tensile strength was 900 psi, elongation was 600%, modulus at 100% was 480 psi, and shore A hardness was 84. The patent did not comment on the efficiency of the chemical graft (that is, how much nylon 6 or nylon 12 was actually grafted to the EPDM rubber). This patent is relevant to the thesis work because it demonstrated that a thermoplastic elastomer was made by grafting an amine terminated nylon 12 onto a maleic anhydride grafted EPDM rubber.

Figure 9. Polymer trunk structures described in the Hammer and Sinclair patent.

The other patent, by Errol Olivier, describes a polyamide thermoplastic elastomer formed by reactive blending. The compositions consisted of a maleic anhydride grafted ethylene propylene rubber (EPM) and a non-functionalized EPDM rubber in a nylon 6 or

nylon 11 matrix. The maleic anhydride grafted EPM rubber reacted with the amine end groups of the nylon in a stepwise manner to form an imide graft, as illustrated in Figure 6. A non-functionalized EPDM was added to provide more unsaturated sites for further crosslinking. This non-functionalized EPDM was miscible with the maleic anhydride grafted EPM and together they formed a separate phase from the nylon phase. Crosslinking this rubber phase with peroxides, metal stearates, metal oxides, phenolic resins or sulfur yielded a thermoplastic elastomer with improved tensile strength, elongation, and oil resistance. A similar thermoplastic elastomer whose rubber phase was not crosslinked had poor tensile strength, elongation, and oil resistance. The compositional range claims were 40 - 90 percent by weight of the anhydride functionalized EPM rubber dispersed in 10 - 60 percent by weight of the polyamide resin. The nylons used in this patent have a degree of polymerization of 100 - 400. The thermoplastic elastomer blend was formed by reaction of the components between 195 °C - 240 °C. Processing was done using a Brabender mixer. The results for one of the thermoplastic compositions are shown in Table 2 and illustrate the benefits of curing the rubber phase. The materials and preparation methods just reviewed are not the same as those that were used in the thesis research. However, this patent illustrates an alternate approach to preparing thermoplastic elastomers with high tensile strength and elongation.

The two patents made claims on material compositions for producing a thermoplastic elastomer. Neither one showed evidence to support claims of thermoplastic behavior. Dynamic mechanical analyses were not provided to verify the existence of a thermo-

reversible polymer network. Analyses of the microphase structure by SEM were not presented to examine the relation between morphology and mechanical properties. Thermal analyses to demonstrate the temperature transitions of the thermoplastic elastomers were not included.

Table 2. Comparison of properties for an uncured and peroxide cured thermoplastic elastomer (30 wt.% nylon, 35 wt.% grafted EPM, 35 wt.% EPDM)

Property	Uncured	Peroxide cured
Tensile strength, psi	320	1118
Elongation, %	125	120
Shore D hardness	22	32
Volume swell, %	256	90

Section IV

Hypothesis

The thesis seeks to determine how well a thermoplastic elastomer can be prepared from graft copolymerization of nylon 11 or nylon 12 with a maleic anhydride grafted EPDM rubber. The grafted copolymer will have both a plastic and elastic behavior that is thermo-reversible. The physical and mechanical properties of the grafted copolymers are hypothesized to be different from the starting materials. To verify the hypothesis, the thesis research will focus on determining the parameters that are necessary to design the synthesis of a thermoplastic elastomer made by graft copolymerization of nylon 11 or nylon 12 and EPDM rubber. The rheology, morphology, mechanical, and thermal properties of the new TPEs will be characterized.

Research Approach

The research approach focused on two main areas: (1) to prepare and characterize TPEs made by graft copolymerization of commercial nylon 12 polymer and maleic anhydride grafted EPDMs and (2) to prepare and characterize TPEs made by graft copolymerization of nylon 11 monomer (11-aminoundecanoic acid) to nylon 11 polymer in the presence of the same set of EPDMs. The goal is to determine the parameters (materials, composition, synthesis route) that will yield a soft but tough thermoplastic elastomer.

Several blends were prepared by melt mixing in a Brabender bowl. FTIR measurements were conducted on a model compound to obtain a verification of the

absorbance peaks for the cyclic imide. A semi-quantitative analysis was also performed to establish the detection limit of the FTIR instrument. FTIR measurements were conducted in transmission mode on compression molded thin films. The purpose was to highlight the cyclic imide absorption peaks as evidence of grafting. Soxhlet extraction was performed to give indication of the extent of grafting. Dynamic mechanical measurements were conducted on specimens between parallel plates. The materials were heated and cooled twice between 30 °C and 210 °C to observe the thermo-reversible behavior of the elastic modulus (G'). SEM microscopy was conducted to observe the size and distribution of the discrete phase and to show how the microphase morphology influenced tensile properties. Tensile testing was conducted at room temperature to determine the tensile strength, elongation, and toughness of the TPEs. Shore A hardness measurements were also conducted. All of the research work was conducted at Raychem Corporation in Menlo Park, California.

Section V

Experimental

A. Sample Preparation Of Raw Materials and Nylon/EPDM Compositions

Molecular Weight Determination of Raw Materials

Table 3 shows the materials that were used during the thesis research. There were four EPDM rubbers, two nylon 12s, and one nylon 11 monomer (11-aminoundecanoic acid). The levels of maleic anhydride grafted to the EPDM rubbers are: 2.0 wt.%, 1.0 wt.%, 0.4 wt.%, and 0 wt.%. The extrusion grade of nylon 12 has a higher melt viscosity, hence a higher molecular weight, than the molding grade of nylon 12.³¹ Additional molecular properties of the EPDM rubbers and the nylon 12 polymers are shown in Table 4. The number-average (M_n) and weight-average (M_w) molecular weights of the EPDM rubbers were determined by size exclusion chromatography (GPC) at 140 °C in ortho-dichloro-benzene. The M_n and M_w values for the EPDM rubbers were referenced to equivalent polystyrene molecular weights. The M_n values for nylon 12 AESNO and nylon 12 AMNO were obtained by intrinsic viscosity measurements at 25 °C in sulfuric acid (96%). Five solutions ranging from 1 wt.% to 0.125 wt.% were prepared and measured in an Ostwald-Fenske capillary viscometer. The limiting viscosity numbers, obtained by using the Huggins extrapolation method³² to zero concentration, were used in the Mark-Houwink-Staudinger-Sakurada equation with appropriate coefficients³³ to determine the relationship between intrinsic viscosity and M_n . The number of maleic anhydride groups per chain of EPDM rubber was derived from the M_n values. The last column in Table 4

shows two different diene monomers in the EPDM rubbers: 1,4 hexadiene (7 wt.%) in Fusabond MF-280D and Fusabond MF-274D and 5-ethylidene norbornadiene (7 wt.%) in Royaltuf 465. Information on the type and the amount of diene monomer in Royalene 306 was not available from the manufacturer.

Table 3. Materials for thesis research

Vendor	Material*	Grade	Properties*
Du Pont Chemical	MA-g-EPDM	Fusabond MF-280 D	2 wt.% MA, 75/25 E/P
Du Pont Chemical	MA-g-EPDM	Fusabond MF-274 D	0.4 wt.% MA, 75/25 E/P
Uniroyal Chemical	MA-g-EPDM	Royaltuf 465	1 wt.% MA, 55/45 E/P
Uniroyal Chemical	EPDM	Royalene 306	0 wt.% MA 53/47 E/P
Atochem North America	Nylon 12	AESNO- extrusion	Higher melt viscosity
Atochem North America	Nylon 12	AMNO - molding	Lower melt viscosity
Aldrich Chemical	11-aminoundecanoic acid		Nylon 11 monomer

* MA = maleic anhydride, E/P = wt.% ethylene/ wt.% propylene

Table 4. Molecular properties of EPDM rubbers and nylon 12

Material	M_n^*	M_w^*	Number of MA groups per chain	Diene monomer**
Fusabond MF-280 D	51,100	109,700	10	1,4 hexadiene (7 wt.%)
Fusabond MF-274 D	43,000	98,700	1.7	1,4 hexadiene (7 wt.%)
Royaltuf 465	55,200	154,100	6	5-ethylidene norbornadiene (7 wt.%)
Royalene 306	67,600	216,000	0	not available
Nylon 12 AESNO	50,700	not available	N/A	N/A
Nylon 12 AMNO	40,300	not available	N/A	N/A

* The M_n and M_w values for the EPDM rubbers were obtained by GPC and were referenced to polystyrene equivalent molecular weights. The M_n values for nylon 12 were obtained by intrinsic viscosity measurements at 25 °C in sulfuric acid (96%).

** According to the manufacturer's literature.

Nylon/EPDM Compositions

The different amounts of maleic anhydride graft on the four EPDM rubbers and the different molecular weights of the three nylons provides variables for adjusting the physical and mechanical properties of the graft copolymerized TPEs. The experimental matrix for preparing TPEs with nylon 12 is shown in Table 5, and with nylon 11 monomer in Table 6. Table 7 shows three 'control' formulations for preparing non-reactive blends.

Table 5. Compositions for graft copolymerized TPEs containing nylon 12 (wt. % MA-g-EPDM/ wt. % nylon 12)

Nylon 12	Fusabond MF-280D	Royaltuf 465	Fusabond MF-274D
AESNO	60/40	60/40	60/40
	75/25	75/25	75/25
	90/10	90/10	90/10
AMNO	60/40	60/40	60/40
	75/25	75/25	75/25
	90/10	90/10	90/10

Table 6. Compositions for graft copolymerized TPEs containing nylon 11 monomer (wt. % MA-g-EPDM/ wt. % 11-aminoundecanoic acid)

Fusabond MF-280D/ 11-aminoundecanoic acid	Royaltuf 465/ 11-aminoundecanoic acid	Fusabond MF-274D/ 11-aminoundecanoic acid
75/25	75/25	75/25

Table 7. Compositions for non-reactive blends (wt. % EPDM/ wt. % nylon)

Royalene 306/ Nylon 12 AESNO	Royalene 306/ Nylon 12 AMNO	Royalene 306/ 11-aminoundecanoic acid
75/25	75/25	75/25

Brabender Melt Mixing

Melt mixing was performed in a 54 cc Brabender bowl at 200 °C using roller blades rotating at 50 rpm. A mixing temperature of 25 °C above the melting point of nylon 12 (175 °C) was chosen to ensure its melting while minimizing the possibility for thermal oxidation of the EPDM rubber. A 1 wt.% hindered phenol antioxidant (Irganox 1010, Ciba Geigy) was added to every composition to minimize thermal oxidation during high temperature melt mixing. A typical batch size was 42 grams. The individual raw materials, except 11-aminoundecanoic acid, were melt mixed first to establish physical, mechanical, and thermal baseline properties so that any change in property due to grafting or non-reactive blending could be quantified. The mixing time was 7 minutes for raw materials and for compositions containing nylon 12. The mixing time was increased to 25 minutes for compositions containing nylon 11 because the nylon 11 monomer required more time to polymerize into nylon 11 polymer. The mixing temperature and torque were continuously monitored by computer software.

Compression Molding

After melt mixing, the materials were immediately compression molded into 6" x 6" x 0.030" slabs for various tests. The molding conditions were: 5 minutes at 200 °C and 0 psi ram pressure, 3 minutes at 200 °C and 2000 psi ram pressure, and 5 minutes cooling in a water cooled press at 2000 psi ram pressure.

B. Characterization of Raw Materials and Nylon/EPDM Compositions

FTIR Analysis of Cyclic Imide Absorbance

FTIR analyses were conducted in the transmission mode for free standing polymer films. The raw materials and nylon/EPDM compositions were compression molded into 2-3 mil films using approximately 40 mg of material and following the procedure described in part A, above. The FTIR instrument used was model FTS-60A, made by Bio-Rad Digilab Division. The set-up parameters for obtaining IR spectrum on the thin films are shown in Table 8.

Table 8. FTIR set-up parameters for obtaining IR spectrum on thin films

Spectral Parameters	Setting	Spectrometer Parameters	Setting
Number of scans	16	Aperture, cm^{-1}	2
Resolution, cm^{-1}	8	Mirror velocity, kHz	5
Wavenumber, cm^{-1}	4000 - 700	Signal filter, kHz	1.12

The following procedure describes how an absorbance spectrum was obtained for each sample. A background interferogram (continuous electrical signal) was collected from 4000 cm^{-1} to 700 cm^{-1} without any sample in the sample holder. This interferogram was Fourier transformed into a background single-beam spectrum. A sample was inserted into the beam and a sample interferogram was collected. This interferogram was Fourier transformed into a sample single-beam spectrum. To produce an absorbance spectrum, the background single-beam spectrum was divided by the sample single-beam spectrum, and the logarithm (base 10) was taken of the ratio. The data collection, Fourier transformation, and absorbance spectrum display were facilitated by the instrument's

software, Bio-Rad Win-IR™ version 3.04.

Soxhlet Extraction

Soxhlet extraction was performed on two EPDM rubber specimens, one nylon 12 specimen, several graft copolymerized TPEs and several non-reactive blends. The materials were extracted with refluxing xylene for 10 days. The solid fraction remaining in the Soxhlet thimble was dried in an 80 °C oven for 3 to 4 days until the weight loss from the xylene was no longer significant. The sol fraction was difficult to recover and was not included in the results. The degree of grafting is better indicated by the solid fraction because there is less solvent to be removed, which can be misinterpreted as extra weight due to grafting. Caution is advised when using this technique to determine the degree of grafting because it is difficult to account for some grafted species having low molecular weights that may be soluble in xylene.

Dynamic Mechanical Measurements

A controlled strain rheometer was used to measure the temperature dependence of the viscoelastic properties of the raw materials, the graft copolymerized TPEs, and the non-reactive blends. The rheometer was Advanced Rheometric Expansion System (ARES) made by Rheometric Scientific, Inc. A dynamic shear strain at a fixed angular frequency was applied by the motor and the resulting torque on the specimens was measured by the transducer. The viscoelasticity of the specimens was represented by the elastic storage modulus (G') and viscous loss modulus (G''). The G' is proportional to the component of

the torque that is in phase with the sinusoidal strain. The G'' is proportional to the component of the torque that is 90° out of phase with the sinusoidal strain.

The measurements were conducted on compression molded disk specimens (30 mils) between parallel plates. A set of 25.4 mm diameter plates was used for most of the sample measurements except for virgin nylon 12. The room temperature stiffness of the nylon 12 required using 8 mm diameter plates to keep the torque signal within the range of the torque transducer. The specimens were loaded at 30°C and a normal compression force of about 20 grams was applied to prevent specimen slippage between the parallel plates. Table 9 shows the set-up parameters for the dynamic mechanical test. The advanced expansion system allows the specimens to expand and contract, while keeping track of the gap distance, during temperature cycling. Since the applied strain on the sample decreases with increasing gap, the instrument's motor senses the gap change and adjusts the angular deflection of the parallel plates to maintain a constant strain. Two heating and two cooling cycles were conducted to show retraceability of the G' and G'' curves as a function of temperature.

Table 9. Dynamic mechanical test parameters for the ARES rheometer

Parameter	Setting	Parameter	Setting
Angular frequency, rad/s	1.0	Heating cycle, $^\circ\text{C}$	30 - 210
Strain, %	2.0	Cooling cycle, $^\circ\text{C}$	210 - 30
Parallel plates	25 mm	Ramp rate, $^\circ\text{C}/\text{min}$	2
Automatic compression adjustment	enabled	Environment	nitrogen

Scanning Electron Microscopy

The microphase morphology of the graft copolymerized TPEs and the non-reactive blends were imaged by using a scanning electron microscope, Amray 1810. The microscope contains a tungsten hairpin element as the electron source and the images were formed by collecting the low energy secondary electrons. The specimens were fractured in liquid nitrogen and vacuum sputtered with gold to make them conductive. The gold deposition was done under 1 mbar vacuum and 25 mA plasma current for 60 seconds using a Pelco Model 3 Sputter Coater 91000. Table 10 shows the conditions under which the electron micrographs were obtained. The normal operating range for the spot size of the condenser lens is a knob setting from 4 to 7 (from manual for the Amray 1810) with higher numbers representing a smaller beam diameter.

Table 10. Parameters for the Amray 1810 scanning electron microscope

Parameter	Setting	Parameter	Setting
Accelerating voltage, kV	10	Working distance, mm	10 - 13
Spot size (condenser lens) knob setting	5.5 - 6.0	Magnification range	500X - 10,000X

Room Temperature Tensile Properties

The room temperature tensile properties of the raw materials, graft copolymerized TPEs, and non-reactive blends were evaluated. Six dog bone specimens (ASTM Die C) were cut from the 30 mil compression molded slabs. A tensile tester, Instron Model 5567, was used to apply a strain rate of 5"/min. Series IX software, version 7.27, was used to collect the data and to calculate tensile strength, elongation, and toughness of the specimens.

Shore A Hardness

A hand-held durometer was used to measure shore A hardness according to ASTM D2240-95. Six measurements were taken across different areas of the 30 mil compression molded slabs and the average value was reported.

C. Semi-quantitative Calibration of Cyclic Imide Absorbance by FTIR

N-(3-hydroxyphenyl)phthalimide Powder

The N-(3-hydroxyphenyl)phthalimide was synthesized in-house. It was used as a compound standard to identify the cyclic imide peak absorbances. The chemical structure is shown in Figure 10. A miniature diamond anvil cell (Type IIa diamonds) was used to examine the powder directly in transmission mode. The powder was placed between the diamond anvils and the cell was checked for parallelism by using a white light fringe technique. The set-up parameters for obtaining an IR spectrum on the N-(3-hydroxyphenyl)phthalimide powder is shown in Table 11. A background spectrum of the diamond cell was obtained and then the sample spectrum. The absorbance was plotted as a function of wavenumber.

Figure 10. Chemical structure of N-(3-hydroxyphenyl)phthalimide.

Table 11. FTIR set-up parameters for analysis of N-(3-hydroxyphenyl)phthalimide powder

Spectral Parameters	Setting	Spectrometer Parameters	Setting
Number of scans	256	Aperture	open
Resolution, cm^{-1}	8	Mirror velocity, kHz	20
Wavenumber, cm^{-1}	4000 - 600	Signal filter, kHz	4.5

N-(3-hydroxyphenyl)phthalimide in Tetrahydrofuran

Three solutions were prepared in tetrahydrofuran (THF): 2.0 wt.%, 0.4 wt.%, and 0.1 wt.% to bracket the concentrations of interest. The 2.0 wt.% solution was prepared by dissolving 0.89 grams of N-(3-hydroxyphenyl)phthalimide into 50.0 grams of THF ($\rho = 0.889 \text{ g/cc}$). The other two solutions were obtained by diluting a portion of the 2.0 wt.% solution by 1/5 and 1/20 with fresh THF.

The FTIR set-up parameters were similar to those in Table 11 except the number of scans was increased to 512 to improve the signal-to-noise ratio of the interferograms. A background spectrum was taken of THF smeared between NaCl plates. The sample spectrums were measured in a liquid cell with NaCl window plates. The cell thickness was 0.018 mm (7 mils).

4-Phenoxyaniline in Maleic Anhydride Grafted EPDM Rubbers

The 4-phenoxyaniline was purchased from Aldrich Chemicals. It has a reactive amine group on one end of the molecule as shown in Figure 11. This compound is expected to react with the maleic anhydride on the EPDM rubber during Brabender melt mixing to form the cyclic imide group, as shown in Figure 6. Table 12 shows three compositions of

4-phenoxyaniline and maleic anhydride grafted EPDM rubber. The molar ratio of each composition was calculated to be 1.0 equivalent of amine to maleic anhydride, assuming the full amount of maleic anhydride in each EPDM rubber and that all of it was converted to cyclic imide. Melt mixing was done as described in part A of sample preparation (see page 25) except the mixing time was 20 minutes instead of 7 minutes. Thin film preparation and FTIR measurements were completed as described in part B of sample preparation (see page 26).

Figure 11. Chemical structure of 4-phenoxyaniline. Melting point is 185 °C.

Table 12. Compositions of 4-Phenoxyaniline and Maleic Anhydride Grafted EPDM Rubber* (Mole ratio was calculated to be 1.0 amine to maleic anhydride)

Sample No.	EPDM Type**	EPDM weight, gram	4-Phenoxyaniline weight, gram
1	Fusabond MF-280 D (2 wt.% MA)	42	1.6
2	Royaltuf 465 (1 wt.% MA)	42	0.8
3	Fusabond MF-274 D (0.4 wt.% MA)	42	0.32

* Each of the formulations contained 1 wt.% anti-oxidant (Irganox 1010). ** MA = maleic anhydride.

Section VI

Results and Discussion

A. Semi-quantitative Calibration of Cyclic Imide Absorbance by FTIR

Carbonyl Absorption in N-(3-hydroxyphenyl)phthalimide Powder

An important element of this thesis research is to show that a TPE was synthesized by grafting nylon 11 or 12 to maleic anhydride grafted EPDM rubbers. The graft site is a cyclic imide that is formed according to the reaction shown in Figure 6. The following experiment was conducted on N-(3-hydroxyphenyl)phthalimide powder, which contains the cyclic imide group, to obtain strong absorbance peaks. This allows positive verification of the peak's wavenumber obtained on the FTIR instrument used for this thesis research.

The absorbance spectrum for N-(3-hydroxyphenyl)phthalimide is shown in Figure 12. The absorption energy increases to the left with increasing wavenumbers. The magnitude of the absorbance is expressed in dimensionless units. The absorbance of the two carbonyls in the N-(3-hydroxyphenyl)phthalimide powder can be clearly seen at 1706 cm^{-1} and 1766 cm^{-1} . These absorbances and their band separation are consistent with those reported by Bellamy.³⁴ The lower frequency absorbance (1706 cm^{-1}) is strong (0.88 units) and is due to asymmetric stretching between the carbonyls. The higher frequency absorbance is much weaker (0.14 units) and is due to symmetric stretching. The height of these absorbance peaks was determined by using the FTIR software to draw a baseline under each peak and to calculate its height.

Carbonyl Absorption of N-(3-hydroxyphenyl)phthalimide in THF Solutions

Since the EPDM rubbers have low concentrations of grafted maleic anhydride (see Table 3), it was important to be able to detect by FTIR the cyclic imide after chemical grafting. The cyclic imide absorbance peaks of the N-(3-hydroxyphenyl)phthalimide powder are identified in Figure 12 and were used to establish a semi-quantitative calibration of the peak height with the concentration of N-(3-hydroxyphenyl)phthalimide in THF and establish the lower detection limit of the FTIR instrument. THF does not have carbonyl groups which can interfere with absorption from the cyclic imide.

The FTIR absorbance spectrum for one of the lower concentrations, 0.4 wt.%, of N-(3-hydroxyphenyl)phthalimide is shown in Figure 13. Note that the asymmetric absorbance at 1706 cm^{-1} (see Figure 12) can be seen even at this low concentration, but shifted to a higher absorbance at 1717 cm^{-1} (see Figure 13). This shift is not surprising because the THF solution provides more mobility for the N-(3-hydroxyphenyl)phthalimide molecules to stretch and bend with higher energy. The absorbance at 1717 cm^{-1} was also observed in THF with the 2 wt.%, but not the 0.1 wt.% of N-(3-hydroxyphenyl)phthalimide as shown in Figures 1 and 2 of Appendix A, respectively. The symmetric absorbance at 1766 cm^{-1} (see Figure 12) or its shift to some reasonable higher absorbance is not observed in Figure 13. The 1766 cm^{-1} peak was weak in the powder sample and must be a solid state effect.

The semi-quantitative calibration of cyclic imide absorbance by FTIR is shown in Table 13. The peak height and peak area for three different concentrations of the N-(3-hydroxyphenyl)phthalimide in THF are compared and are normalized relative to the

Figure 12. Absorbance spectrum for N-(3-hydroxyphenyl)phthalimide powder. Number of scans: 256, resolution: 8 cm⁻¹.

Figure 13. Absorbance spectrum for 0.4 wt.% N-(3-hydroxyphenyl)phthalimide. The THF absorbance was subtracted out. Number of scans: 512, resolution: 8 cm⁻¹.

2.0 wt.% N-(3-hydroxyphenyl)phthalimide solution. The normalized height and area ratios agree with a 7% deviation from linearity compared with the concentration of N-(3-hydroxyphenyl)phthalimide in THF. Inspection of the 1717 cm^{-1} peak in Figure 13 suggests that a peak with half the height of the 0.4 wt.% sample should be visible. This places the lower detection limit of cyclic imide by FTIR at 0.2 wt.% and a peak height that is greater than 0.015 units.

Table 13. FTIR absorbance height and area at 1717 cm^{-1} for different concentrations of N-(3-hydroxyphenyl)phthalimide in THF

N-(3-hydroxyphenyl) phthalimide, wt. %	Peak height, units	Peak area, cm^{-1}	Normalized height ratio*	Normalized area ratio*
2.0	0.14	2.22	2.0	2.0
0.4	0.03	0.48	0.43	0.43
0.1	not found	not found	0	0

*The height and area ratios were normalized to the 2.0 wt.% N-(3-hydroxyphenyl)phthalimide solution.

Carbonyl Absorption of Cyclic Imide Grafts in EPDM Rubbers

The amount of maleic anhydride in the EPDM rubbers was not certified by the manufacturers. This presented a need to verify the amount by comparison of maleic anhydride specifications with the amount of cyclic imide grafts. A comparison is shown in Table 14 between the estimated weight percent of cyclic imide grafts in three EPDM rubbers and their absorbance peak height and peak area ratios. Two assumptions were made for this comparison: (1) the EPDM rubbers contained the correct amount of maleic anhydride as specified by the manufacturers and (2) the stoichiometric reaction proceeded to completion between the amine in 4-phenoxyaniline and the maleic anhydride grafted

EPDM rubber according to the reaction scheme shown in Figure 6. The peak height ratios at 1717 cm^{-1} scale linearly with the cyclic imide grafted Fusabond MF-280D with a 7% deviation. The peak height for each of the cyclic imide grafted EPDM rubbers was divided by the peak height of the cyclic imide grafted Fusabond MF-280D and the result was multiplied by two. The same procedure was used to calculate the peak area ratios.

Table 14. Estimated concentration of cyclic imide grafted EPDM rubbers versus peak height and peak area ratios at 1717 cm^{-1}

EPDM rubber before grafting*	Estimated cyclic imide graft, wt. %	Peak height ratio**	Peak area ratio**
Fusabond MF-280D (2.0 wt.% MA)	2.0	2.0	2.0
Royaltuf 465 (1.0 wt.% MA)	1.0	1.2	1.7
Fusabond MF-274D (0.4 wt.% MA)	0.4	0.4	0.2

* MA = maleic anhydride.

** The peak height and peak area ratios are relative to the cyclic imide grafted Fusabond MF-280D.

Table 14 shows good agreement between the concentration of cyclic imides in the EPDM rubbers and their peak height ratios. This establishes some confidence that cyclic imides can be detected by looking for the absorbance peak at 1717 cm^{-1} . The peak heights can be used to estimate the cyclic imide concentration in TPE samples prepared by grafting nylon to maleic anhydride grafted EPDM rubbers.

The correlation between cyclic imide graft concentration and peak area ratio was not good. The absorbance peak area should be proportional to sample concentration and path length, according to Beer's law.³⁵ However, the sample thicknesses varied between 2 to 3 mils and was not accounted for when the peak areas and its ratios were calculated.

B. Characterization of Nylon 12 and Maleic Anhydride Grafted EPDM Rubbers

Evidence of Slight Grafting by FTIR Analysis

FTIR analyses of the eighteen reactive blends of nylon 12 and maleic anhydride grafted EPDM rubbers (see Table 5) did not provide evidence for grafting. The evidence for grafting was not strong because the absorbance peaks for the cyclic imide group, $\sim 1701\text{ cm}^{-1}$ and $\sim 1771\text{ cm}^{-1}$, were not clearly present in the FTIR spectra. There was a peak at 1717 cm^{-1} which is consistent with the presence of 4-phenoxyaniline (see previous section). It is also possible that by unfortunate coincidence, the peak at 1717 cm^{-1} is due to the presence of maleic acid.³⁶ The maleic anhydride group can hydrolyze in the presence of moisture at room temperature and form maleic acid as shown in Figure 14. During high temperature melt mixing, the maleic acid is known to revert back to maleic anhydride.

Figure 14. Hydrolysis of maleic anhydride to maleic acid at room temperature.

Figure 15 shows an absorbance spectrum for Fusabond MF-280D that was prepared by compression molding a single pellet of the EPDM rubber. The maleic anhydride and maleic acid peaks are clearly present in Fusabond MF-280D. Figure 16 shows a melt

mixed composition containing 75 wt.% Fusabond MF-280D and 25 wt.% nylon 12 AESNO. The maleic anhydride and maleic acid absorbance peaks have decreased in height and a new smaller peak at 1702 cm^{-1} appeared indicating the cyclic imide group. The stronger cyclic imide absorbance at 1771 cm^{-1} was masked by the maleic anhydride peak at 1789 cm^{-1} . These results indicate that some grafting occurred but not all of the maleic anhydride converted to the cyclic imide. The other 17 reactive blends of nylon 12 and maleic anhydride EPDM rubbers all showed similar FTIR spectrums. This suggests that partial grafting took place in all of them.

Evidence of Slight Grafting by Soxhlet Extraction

Soxhlet extraction can be used to determine the amount of insolubles in a blend containing insolubles and sol fraction. In a reactive blend, for instance, the amount of insolubles formed by grafting can be determined by comparing the amount of insolubles remaining in the Soxhlet tube with the amount in the original specimen. Soxhlet extraction in xylene was performed on two EPDM rubber specimens and one nylon 12 specimen to verify that the rubber was soluble in xylene and the nylon was not. The verification was necessary in order to interpret the Soxhlet extraction results for the nylon 12 grafted EPDM blends, of which four are shown in Table 15.

As seen in the results for the seven samples in Table 15, nylon 12 AESNO was not soluble in xylene while Fusabond MF-280D was completely soluble, and Royaltuf 465 was partially soluble. The partial solubility of Royaltuf 465 in xylene was unexpected and is probably due to differences in the diene monomer. Duplicate samples were extracted for each blend and the difference between the results was less than 10%.

Figure 15. Absorbance spectrum for a Fusabond MF-280D pellet (2 wt.% maleic anhydride grafted EPDM). Number of scans: 16, resolution: 8 cm^{-1} .

Figure 16. Absorbance spectrum for a reactive blend of 75 wt.% Fusabond MF-280D and 25 wt.% nylon 12 AESNO. Number of scans: 16, resolution: 8 cm^{-1} .

The 60/40 compositions show increases in solid fraction relative to nylon 12 (0.34 and 0.31) and suggests some grafting (23% and 20% of the rubber is grafted) to insolubles. The 75/25 blends suggest no reaction or, within experimental error, the product is soluble (0.3% and 0% of the rubber is grafted). These results are consistent with the FTIR results which showed that the maleic anhydride peak heights at 1789 cm^{-1} and 1866 cm^{-1} decreased more for the 60/40 blends than for the 75/25 blends.

Table 15. Solids fraction for raw materials and EPDM blends after extraction with xylene for 10 days (wt. % EPDM rubber/ wt. % nylon 12 AESNO)

Material	Unextracted solids, wt. %	Ungrafted rubber, %	Grafted rubber, %	Ratio of grafted rubber/ nylon 12*
100% Nylon 12 AESNO	98.4	0	N/A	N/A
100% Fusabond MF-280D	0	100	N/A	N/A
100% Royaltuf 465	43	57	N/A	N/A
60/40 Royaltuf 465/ nylon 12	79.5	77	23	0.34
60/40 Fusabond MF-280D/ nylon 12	52.3	80	20	0.31
75/25 Fusabond MF-280D/ nylon 12	25.2	99.7	0.3	0.01
75/25 Royalene 306/ nylon 12	21.6	100	0	0

* The weight percentage of nylon 12 in each EPDM composition was used as the basis for the ratio.

Effect of Reactive Melt Mixing on Brabender Torque

During melt mixing of the nylon 12 and EPDM blends, the Brabender mixing torque was recorded to differentiate the melt behavior of the blends. It was anticipated that a significant torque increase would be observed for mixing the reactive blends, as shown in Macosko's work (see Figure 8). The mixing torque curve for one of the reactive blends, 60 wt. % Fusabond MF-280D with 40 wt. % nylon 12 AESNO, is shown in Figure 17.

The early sharp peak is due to material loading, followed by a plateau region of nearly constant mixing torque. There was no significant increase in mixing torque to indicate grafting, contrary to the FTIR and Soxhlet extraction results for this reactive blend. FTIR evidence indicated partial grafting, and Soxhlet extraction results (see Table 15) showed a 31% increase in the amount of insolubles. The level of grafting was probably not enough to increase the melt viscosity and raise the mixing torque. Similar mixing torque curves were observed for the other 17 reactive blends and the 2 non-reactive blends.

Figure 17. Brabender temperature and torque trace for a reactive blend of 60 wt.% Fusabond MF-280D and 40 wt.% nylon 12 AESNO. Mixing was done with roller blades rotating at 50 rpm and the batch size was 43.4 grams

There are two important differences between the reactive blends prepared in this thesis and the reactive blend prepared by Macosko (see Figure 8) that could account for the different mixing torque behaviours. The first is the compositional range of the EPDM rubber and the nylon. The reactive blends prepared in this thesis contained greater than

60 wt.% EPDM rubber and less than 40 wt.% nylon, whereas the reactive blend prepared by Macosko contained 30 wt.% EPDM rubber and 70 wt.% nylon. (The EPDM rubber contained 0.7 wt.% of grafted maleic anhydride.) To verify this supposition, a reactive blend containing 30 wt.% Royaltuf 465 EPDM rubber and 70 wt.% nylon 12 AESNO was prepared. The mixing torque curve had the same profile as Figure 17. Clearly composition was not a factor.

The second and more likely difference is the type of nylon that was used. Macosko reported that the aromatic amorphous nylon was specifically modified with amine groups on the chain ends by the Du Pont Company. The concentration of the amine end groups was not specified. In contrast, the nylon 12s used in this thesis were not modified with amine groups. They were produced inherently by the anionic polymerization of 12 amino acids. It appears that the concentration of amine end groups determines whether there is sufficient grafting to increase the melt viscosity and the mixing torque of the reactive blends. The results from the other synthesis route using 11-aminoundecanoic acid, described in part C, will show that the mixing torque increases significantly if a stoichiometric amount of amine end groups reacts with the maleic anhydride on the EPDM rubber. A better technique for measuring the melt behavior of these nylon 12 blends is to use a dynamic mechanical analyzer.

Dynamic Mechanical Analysis of Thermoplastic Elastomer Behavior

The neat EPDM rubbers, the nylon 12, and several blends of nylon 12 grafted EPDM were evaluated for their dynamic mechanical behavior between 30 °C and 210 °C. The

goal was to understand the rheological behavior of the raw materials and compare them with the graft copolymerized TPEs. Both the elastic modulus (G') and the viscous modulus (G'') varied in a parallel manner during the temperature sweep test. Therefore, only the elastic modulus behavior is described to simplify the discussion. The comparison was made with the elastic modulus curves from the second heating and cooling cycles. Sample adhesion to the parallel plates was insufficient in the first heating.

The elastic modulus curves for the heating and cooling of Fusabond MF-280D (see Figure 18) and nylon 12 AESNO (see Figure 19) almost overlap, except near the melting transition temperatures. This behavior is consistent with the case where the high molecular weight polymer chains take longer to order and recrystallize than to disorder and melt. The ethylene propylene crystalline domains melt at about 115 °C in Fusabond MF-280D. The nylon 12 shows a glass transition temperature at 45 °C and a melting transition at 175 °C, which agrees with the values reported in the literature.³⁷

When 60 wt.% Fusabond MF-280D and 40 wt.% nylon 12 AESNO were melt mixed, the nylon 12 displayed a different elastic modulus behavior upon cooling (see Figure 20). The recrystallization of nylon 12 during cooling was greatly suppressed in the reactive blend. A third heating and cooling cycle on the same sample showed that this recrystallization behavior was repeatable. This cooling behavior is contrasted with a non-reactive EPDM rubber (Royalene 306) where the recrystallization of nylon 12 was not significantly suppressed, as shown in Figure 21.

Figure 18. Elastic modulus behavior of Fusabond MF-280D during heating and cooling at 2 $^{\circ}\text{C}/\text{min}$.

Figure 19. Elastic modulus behavior of Nylon 12 AESNO during heating and cooling at 2 $^{\circ}\text{C}/\text{min}$.

Figure 20. Elastic modulus behavior of a reactive blend (60 wt.% Fusabond MF-280D/ 40 wt.% nylon 12 AESNO) during heating and cooling at 2 $^{\circ}\text{C}/\text{min}$.

Figure 21. Elastic modulus behavior of a non-reactive blend (75 wt.% Royalene 306/ 25 wt.% nylon 12 AESNO) during heating and cooling at 2 $^{\circ}\text{C}/\text{min}$.

One possible explanation for the suppressed nylon recrystallization may be the phenomena of molecular order and disorder transition.³⁸ This phenomena involves the kinetics of the thermodynamic transition which is controlled by balancing two physical factors: the enthalpy and the entropy of the rate process. This has been observed in block copolymer systems where there are two immiscible phases not unlike the thermoplastic elastomers synthesized in this thesis research.

Figure 22 illustrates schematically the phase morphology for the order-disorder transition in a symmetric ($f = 0.5$) A-B diblock copolymer where a lamellar structure is observed. In the “ordered state” the block copolymers form “microdomains” of segment A (hard polymeric segment in the copolymer, see page 2) and segment B (soft polymeric segment in the copolymer) with a long-range order of the size of the polymer coil. The size of the microdomain is characterized by the radius of gyration of the block polymer R_g . The block copolymers can also form a homogeneous structure in the melt in which the A and B segments are molecular mixed in the “disordered state.” The transition from the disordered state to the ordered state is known as “microphase separation.” The result of this phase separation is the formation of microdomain structures. The transition from the ordered state to the disordered state is known as “microphase dissolution.”

In the case of the non-reactive blends of nylon and EPDM rubber, the nylon and the rubber are incompatible and form two separate phases. When they are in the melt, these two phases are molecularly mixed in the disordered state, but not attached. When the blend is cooled, the nylon and rubber microphase separate, going from the disordered state to the ordered state. Since the two phases are not chemically attached, the nylon has

more mobility and is able to phase separate readily and recrystallize near its melting temperature.

Figure 22. Schematic of ordered and disordered phase morphology of a symmetric ($f = 0.5$) A-B diblock copolymer. (Modified from reference 36. Used with permission of Prentice Hall, Copyright 1987.)

In the case of the reactive blends of nylon and EPDM rubber, the nylon and the rubber are still incompatible and still form two separate phases. The two phases in the melt are molecularly mixed with some attachment between the rubber and the nylon occurring, due to grafting. When the reactive blend is cooled, microphase separation occurs, but the nylon is not able to completely phase separate from the rubber during time of scan. Hence, the recrystallization of the nylon is suppressed until it crystallizes with the ethylene propylene in the EPDM rubber near its melting temperature of about 135 °C.

This observation of the suppressed recrystallization of nylon in reactive blends (and not in non-reactive blends) strongly suggests the presence of grafting and is consistent with Soxhlet extraction results in Table 15 and FTIR results described on pp. 38-39.

As seen in Figure 19, the neat nylon 12 has no difficulty recrystallizing at about 160 °C (which is near its melting temperature of 175 °C) when it is not grafted to the EPDM rubber or in the presence of the non-reactive Royalene 306 rubber (see Figure 21). Thermal analyses by differential scanning calorimetry were not reported because new information was not gained that could not be found by looking at the temperature transitions of the blends during dynamic mechanical testing.

Morphology of Reactive and Non-Reactive Blends

The selection of different EPDM rubbers, nylon 12, and the experimental matrix to prepare various compositions was an attempt to understand the factors that allow the synthesis of a TPE. Physical characterization by melt rheology provided evidence for the presence of a chemical graft. The evaluation of the blend's morphology will help understand the relationship between the chemical graft of the TPE and its mechanical performance in tensile testing. The morphology is not only a result of the raw materials and how they were melt mixed together, but is also an important link to understanding how the resulting microphase structure affects the mechanical performance of the TPE.

The dramatic difference in morphology between a reactive blend and a non-reactive blend of 75 wt.% EPDM and 25 wt.% nylon 12 is seen in SEM micrographs in Figure 23. The dark areas are EPDM rubber while the light areas are nylon 12. In the reactive blend, Figure 23a, the nylon 12 regions are so small that they are difficult to find. The white arrows point to two small regions of nylon 12 that are less than 2 microns in diameter. This morphology is fairly characteristic of the entire sample. In the non-reactive blend, Figure 23b, the nylon 12 is clearly visible among the EPDM rubber. The shape and size

of nylon 12 particles vary up to 20 microns. Note that some of the nylon 12 regions are cylindrical and extend out from the rubber phase at the fracture surface. The morphology of these two blends is consistent with the literature reports that a reactive blend yields smaller phase domains than a non-reactive blend.²⁷ Domain size will have an effect on the mechanical properties of the blends. In general, the finer morphology will yield higher tensile strength and greater elongation at room temperature.

Figure 23. SEM micrographs of (a) a reactive blend of 75 wt.% Fusabond MF-280D/ 25 wt.% nylon 12 AESNO and (b) a non-reactive blend of 75 wt.% Royalene 306/ 25 wt.% nylon 12 AESNO.

Room Temperature Tensile Properties

Tensile properties were tested at room temperature for convenience. The room temperature tensile strength, elongation, and toughness were compared for the raw materials, reactive blends and non-reactive blends of nylon 12 and EPDM rubber. The results presented in Figures 24 through 26 are for blends with nylon 12 AESNO. Blends with nylon 12 AMNO showed similar trends for property change with composition, so

they will not be described. The tensile strength, elongation, and toughness of the nylon 12 AMNO blends are shown in Figures 1 through 3 of Appendix B, respectively.

The tensile strength of the EPDM/nylon 12 AESNO reactive and non-reactive blends is shown in Figure 24. Adding nylon 12 to the EPDM rubbers did not significantly increase tensile strength, except at 40 wt.% for Royaltuf 465. The increase in tensile strength for Royaltuf 465 is consistent with the Soxhlet results (see Table 15) that showed the amount of unextracted solids to increase by 34 % as a result of grafting. The higher tensile strength of the two virgin Fusabond EPDM rubbers over Royaltuf 465 and Royalene 306 is attributed to their greater percentage of ethylene groups, leading to higher crystallinity (see Table 3).

Figure 25 shows that the elongation of all four EPDM rubbers decreased as more nylon 12 AESNO was added. The decrease was steeper for Royaltuf 465 and Royalene 306 than for the two Fusabond EPDM rubbers. The Royaltuf 465 blends contained grafted nylon 12 that reduced its elasticity. The Royalene 306 blend was not made compatible with the nylon through grafting like the other EPDM rubbers. This incompatible blend did not have good load transfer between the nylon and rubber phases during tensile testing and failed at low elongations.

Figure 26 shows that the toughness of the blends generally decreased when more nylon 12 AESNO was included. Only the Royaltuf 465 EPDM rubber showed an increase in toughness between 25 wt.% and 40 wt.% of added nylon 12. The toughness increased from 1030 in-lb/in³ to 2950 in-lb/in³ respectively.

Shore A Hardness

One of the goals of this research was to prepare soft thermoplastic elastomers. Shore A hardness results in Figure 27 show that many of the reactive blends were still soft (less than 90 shore A) with up to 40 wt.% grafted nylon 12. In general, the shore A hardness of the blends increased with more nylon 12.

Comparison of tensile properties and hardness with a patented TPE

It would be interesting to compare the tensile properties and shore hardness of a TPE prepared in this thesis with a TPE described in the Hammer and Sinclair patent. This would establish some mechanical property relationship between the claim for having synthesized a TPE in this thesis and the claims already stated in the patent. Table 16 shows a comparison of properties between two TPEs with similar compositions. The physical properties between the two TPEs are comparable taking into consideration that some details of the raw materials were not fully described in the patent. In the patent sample, the EPDM rubber had a higher amount of maleic anhydride and the nylon 12 was functionalized with an unknown amount of primary amino end groups. Both of these factors tend to produce a stronger grafted TPE compared to the ones synthesized in this thesis. The effect of maleic anhydride and amine end group concentrations was discussed on page 43. The mineral oil tends to decrease the tensile strength and increase the elongation and can be used to modify both properties as well as the shore A hardness.

Figure 24. Tensile strength of EPDM/Nylon 12 reactive and non-reactive blends. ASTM Die C. Strain rate: 5"/min at room temperature.

Figure 25. Elongation of EPDM/Nylon 12 reactive and non-reactive blends. ASTM Die C. Strain rate: 5"/min at room temperature.

Figure 26. Toughness of EPDM/Nylon 12 reactive and non-reactive blends. ASTM Die C. Strain rate: 5"/min at room temperature.

Figure 27. Shore A hardness of EPDM/Nylon 12 reactive and non-reactive blends.

Table 16. Comparison of TPE properties for a thesis sample and a patent sample

	Patent sample	Thesis sample
Maleic anhydride concentration, wt. %	2.23	2.0
Maleic anhydride grafted EPDM, wt. %	60	60
Nylon 12, wt. %	23	40
Mineral oil, wt. %	17	0
Tensile strength, psi	900	736
Elongation, %	600	407
Shore A hardness	84	79

C. Nylon 11 Monomer and Maleic Anhydride Grafted EPDM Rubbers

Evidence of Grafting by FTIR Analysis

There is good evidence by FTIR that grafting through the cyclic imide was achieved by reaction of nylon 11 monomer with maleic anhydride grafted EPDM rubbers. Figure 28 shows the absorbance spectrum for a melt mixed composition that initially contained 75 wt. % Fusabond MF-280D and 25 wt. % 11-aminoundecanoic acid. The cyclic imide absorbances at 1706 cm^{-1} and 1772 cm^{-1} are clearly seen. They agree well with the absorbance peaks in N-(3-hydroxyphenyl)phthalimide and with those cited in the literature.³⁴ The two strong absorbance peaks at 1553 cm^{-1} and 1642 cm^{-1} fall in the amide region and provide evidence that the 11-aminoundecanoic acid had polymerized into nylon 11 during melt mixing.

This absorbance spectrum is representative of the grafting that also occurred with Royaltuf 465 and Fusabond MF-274D EPDM rubbers at the same composition, except that their peak heights were smaller (see Figures 1 and 2 of Appendix C). The absorbance spectrum for the non-reactive EPDM rubber (Royalene 306) showed no cyclic

imide peaks, as expected, but showed strong peaks in the amide region providing evidence that non-grafted nylon 11 was formed (see Figure 3 of Appendix C).

Figure 28. FTIR absorbance spectrum showing evidence of cyclic imide grafting and polyamide formation. (75 wt.% Fusabond MF-280D and 25 wt.% 11-aminoundecanoic acid.)

Soxhlet extraction results in Table 17 show that some extra weight of material was insoluble in xylene over the amount of nylon 11 in the compositions. Two effects contribute to the percentage increase of solids by grafting and without further analysis of the insoluble fractions it is difficult to distinguish them. One contribution is from the polymerization of 11-aminoundecanoic acid to nylon 11 and the other is from the grafting of EPDM rubber to nylon 11. It is the net result of increased solids by grafting that is important.

A comparison of the 75 wt.% Fusabond MF-280D EPDM rubber with grafted nylon 11 in Table 17 and with grafted nylon 12 in Table 15 shows a significantly higher weight

percentage of unextracted solids (52.3 wt.% versus 25.2 wt.%) for the former composition. This is additional evidence that the 75 wt.% Fusabond MF-280D/ 25 wt.% nylon 11 composition is a graft copolymerized TPE. In Table 17, the amount of unextracted solids for the Royaltuf 465/nylon 11 composition was not adjusted to account for partial insolubility of the neat rubber in xylene, as shown in Table 15. Attempts to apply the correction may lead to a faulty result. For example, if one assumed the insoluble fraction (43.9 wt.% in Table 17) consisted of 25 wt.% nylon 11 and 43 wt.% Royaltuf 465, the adjusted amount of unextracted solids would result in a negative value. Clearly the amount of insoluble nylon 11 and Royaltuf 465 was less, but the proportion of both components remains undetermined without further analysis of the insoluble fraction. The weight percentage of unextracted solids for Royalene 306 was less than 25 wt.% and indicates that not all of the 11-aminoundecanoic acid polymerized to nylon 11. There is a consistent trend that a greater amount of maleic anhydride in the EPDM rubber leads to greater grafting, resulting in more unextracted solids.

Table 17. Solids fraction after extraction with xylene for nylon 11 grafted EPDM compositions (75 wt.% EPDM rubber/ 25 wt.% nylon 11)

Nylon grafted EPDM type	Unextracted solids, wt. %	Ungrafted rubber, %	Grafted rubber, %	Ratio of grafted rubber/ nylon 11*
Fusabond MF-280D (2 wt.% MA)	52.3	64	36	1.09
Royaltuf 465 (1 wt.% MA)	43.9	75	25	0.76
Fusabond MF-274D (0.4 wt.% MA)	28.8	95	5	0.15
Royalene 306 (0 wt.% MA)	10.5	100	0	0

* The basis for the ratio assumes that there is 100 % conversion of 25 wt.% 11-aminoundecanoic acid into 25 wt.% nylon 11.

Brabender Torque Increase During Grafting

The increase in Brabender mixing torque has often been used to indicate an increase in melt viscosity during reactive melt mixing. This was true for compositions with either Fusabond MF-280D or Royaltuf 465 EPDM rubbers and 11-aminoundecanoic acid. The Fusabond MF-274D and Royalene 306 EPDM rubbers, however, had no measurable torque during melt mixing which is expected since these EPDM rubbers contain little to no maleic anhydride.

Figure 29 shows the mixing torque profile at 200 °C for a reactive composition containing 75 wt.% Fusabond MF-280D EPDM rubber and 25 wt.% 11-aminoundecanoic acid. The initial torque peaks at 2300 meter-gram as the EPDM rubber and 11-aminoundecanoic acid mixture is heated to 200 °C. The torque then decreases to 0 meter-gram within five minutes when the 11-aminoundecanoic acid powder melts into a low viscosity fluid and envelopes the EPDM rubber. The melt viscosity of the mixture increases as 11-aminoundecanoic acid grafts to EPDM and polymerizes to nylon 11, and reaches a maximum of 2360 meter-gram. There was noticeable bubbling during the time the mixing torque was rising. This observation is consistent with the out-gassing of the water produced during the formation of nylon 11 (see Figure 5). The mixing was terminated after 25 minutes because the torque had reached a stable value and further mixing at 200 °C might cause the EPDM rubber to degrade. The compression molded slab was soft (79 shore A), had the amber color of nylon 11, and was transparent, indicating good compatibility.

Figure 30 shows the mixing torque profile at 200 °C for a second reactive composition containing 75 wt.% Royaltuf 465 EPDM rubber and 25 wt.% 11-aminoundecanoic acid that is different from the reactive blend shown in Figure 29. The increase in torque after 15 minutes of melt mixing was smaller and more gradual for Royaltuf 465 than for Fusabond MF-280D. Although the torque curve showed a continued increase up to 720 meter-gram, the mixing was terminated after 25 minutes because there was concern that the EPDM rubber might begin to degrade with further mixing at 200 °C. The compression molded slab was soft (64 shore A), had a light brown color, and was opaque.

The Fusabond MF-274D and Royalene 306 EPDM rubbers with 11-aminoundecanoic acid had significant torque during the first 2 minutes of melt mixing at 200 °C. When the 11-aminoundecanoic acid powder melted and enveloped the EPDM rubbers, the mixing torque dropped to 0 meter-gram and remained there for the 23 minutes of mixing. These EPDM rubbers were not well mixed because there was no shear on the material and no material transfer between the mixing chambers. The compression molded slabs were soft (78 and 47 shore A), light yellow with some amber spots of nylon 11, and were opaque.

The difference in melt mixing behavior may reflect a concentration effect where the EPDM rubbers with higher concentrations of maleic anhydride (2 wt.% and 1 wt.%) provide more sites for grafting of 11-aminoundecanoic acid. When the 11-aminoundecanoic acid then polymerizes to nylon 11, a significant melt viscosity increase is observed. The viscosity increase was higher for Fusabond MF-280D (2 wt.%) than for Royaltuf 465 (1 wt.%).

Figure 29. Brabender temperature and torque trace for a reactive blend of 75 wt.% Fusabond MF-280D and 25 wt.% 11-aminoundecanoic acid. Mixing was done with roller blades at 50 rpm and the batch size was 50.4 grams.

Figure 30. Brabender temperature and torque trace for a reactive blend of 75 wt.% Royaltuf 465 and 25 wt.% 11-aminoundecanoic acid. Mixing was done with roller blades at 50 rpm and the batch size was 50.4 grams.

In contrast, 0.4 wt.% maleic anhydride in the EPDM may not be sufficient to affect the viscosity. The low residual amount of unextractable solids listed for Fusabond MF-274D and Royalene 306 in Table 17 indicate that not much nylon 11 was formed. In the case of Fusabond MF-274D, FTIR results indicate cyclic imide grafting and amide formation even though the mixing torque was zero.

Dynamic Mechanical Analysis of Thermoplastic Elastomer Behavior

The objective of this analysis is to determine if the elastic modulus of the nylon 11 grafted EPDM rubbers show thermal reversible behavior similar to the nylon 12 grafted EPDM rubbers. The elastic modulus of the three nylon 11 grafted EPDM rubbers and the non-reactive blend were measured from 30 °C to 210 °C and two different cooling behaviors were observed, similar to the nylon 12 blends. The elastic modulus behavior for a reactive blend of 75 wt.% Fusabond MF-280D/ 25 wt.% nylon 11 shown in Figure 31 reveals a suppressed recrystallization temperature at 75 °C. This is consistent with evidence of grafting as described on pp. 47-48. The elastic modulus behavior was reversible, but the recrystallization around 75 °C was unusually low. The elastic modulus behavior for another reactive blend of 75 wt.% Royaltuf 465/ 25 wt.% nylon 11 shown in Figure 32 reveals only a slight suppression in the recrystallization temperature of nylon 11.

It was expected that the nylon 11 grafted Royaltuf 465 would show a suppressed recrystallization because FTIR analysis clearly indicated the presence of the cyclic imide graft, and Soxhlet extraction results (see Table 16) indicated an increased amount of

Figure 31. Elastic modulus behavior of a reactive blend (75 wt.% Fusabond MF-280D/ 25 wt.% nylon 11) during heating and cooling at 2 $^{\circ}\text{C}/\text{min}$.

Figure 32. Elastic modulus behavior of a reactive blend (75 wt.% Royaltuf 465/ 25 wt.% nylon 11) during heating and cooling at 2 $^{\circ}\text{C}/\text{min}$.

insolubles. The lower amount of maleic anhydride in Royaltuf 465 compared with Fusabond MF-280D indicates that there are fewer sites for grafting (to compatibilize the nylon 11 with the EPDM rubber). A longer mixing time may improve the compatibilization since the mixing torque was still increasing gradually when the melt mixing was terminated at 25 minutes. Similar compositions of nylon 11 with Fusabond MF-274D and Royalene 306 showed nylon 11 recrystallization transition near its melting temperature of 175 °C. The thermal behavior of the elastic modulus was also reversible.

SEM microscopy of nylon 11 grafted EPDMs

SEM micrographs of the nylon 11 grafted EPDMs were obtained to compare the effect of maleic anhydride concentration with the degree of compatibilization. The best and worst looking morphologies were compared to show how they affect mechanical properties, as described in the next section. Figure 33a shows an extremely fine phase morphology for a reactive blend containing 2.0 wt.% maleic anhydride EPDM. The specimen has 75 wt.% Fusabond MF-280D and 25 wt.% nylon 11. The white areas are nylon 11 and the dark areas are the EPDM rubber. The domain size of the nylon 11 is much smaller than 0.5 micron in diameter and is representative of the entire specimen. An image analysis of the white areas in Figure 33a revealed that the nylon 11 domains averaged $0.02\ \mu\text{m}^2$ and occupied 0.5% of the scanned area. Some white areas in the center portion and upper left corner of the SEM micrograph were not counted by the image analysis software, PrismView version 3.5, due to insufficient contrast. A higher magnification may yield better resolution of the nylon 11 regions among the EPDM rubber matrix. The tensile properties are expected to be good. Figure 33b show the

morphology for a reactive blend containing 1.0 wt.% maleic anhydride EPDM. The composition is 75 wt.% Royaltuf 465 and 25 wt.% nylon 11. These nylon 11 domains are much larger, varying from 1 micron to over 20 microns wide. The large variation in nylon 11 domains indicates poor mixing, as was described on page 59. The mechanical properties are not expected to be as good as the other reactive blend. Comparison of the two micrographs shows that higher levels of maleic anhydride form smaller domains of nylon 11, indicating better compatibility.

Figure 33. SEM micrographs of (a) a reactive blend of 75 wt.% Fusabond MF-280D and 25 wt.% nylon 11 and (b) a reactive blend of 75 wt.% Royaltuf 465 and 25 wt.% nylon 11.

Room temperature tensile properties of nylon 11 grafted EPDMs

A comparison was made between nylon 11/EPDM and nylon 12/EPDM with the same compositions to determine which synthesis route provides a stronger and tougher TPE. Table 18 shows room temperature properties of tensile strength, elongation, and toughness obtained at a strain rate of 5"/minute. The Fusabond MF-280D with the nylon 11

polymerized in-situ showed a significant improvement in tensile strength (1273 psi) and toughness (7160 in-lb/in³) compared with a similar composition obtained by melt mixing of nylon 12. This increased tensile strength and toughness is consistent with the phase morphology (see Figure 33a) which shows very small domains of nylon 11 dispersed in the EPDM rubber matrix. The tensile properties of the Fusabond MF-274D compositions are fairly good and are similar to those for the Fusabond MF-280D compositions. Their morphology (not shown) contains slightly larger nylon 11 domains (< 10 microns). The tensile properties of the Royaltuf 465 are very poor and are a result of the morphology which is shown in Figure 33b.

Table 18. Room temperature tensile properties of nylon 11 and nylon 12 grafted EPDM rubbers (75 wt.% EPDM/ 25 wt.% nylon). Stain rate: 5"/min.

	EPDM Type	Tensile strength, psi	Elongation, %	Toughness, in-lb/in ³
Nylon 11	Fusabond MF-280D	1273	440	7160
	Fusabond MF-274D	535	683	5043
	Royaltuf 465	172	217	550
Nylon 12	Fusabond MF-280D	598	540	4381
	Fusabond MF-274D	534	502	3469
	Royaltuf 465	281	227	1028

Shore A Hardness of nylon 11 grafted EPDM rubbers

Measurements were made to determine the effect of the synthesis route on the resulting hardness of the nylon 11 and nylon 12 grafted EPDM reactive blends. Table 19 shows that for the same composition of EPDM rubber to nylon, the shore A hardness is almost the same. The softer shore hardness for the Royaltuf 465/nylon 11 blend is a result of poor mixing and insufficient amount of grafting. Thus, soft TPEs can be

synthesized by grafting of an in-situ polymerized nylon monomer or by grafting of a nylon polymer to the maleic anhydride EPDM rubbers.

Table 19. Shore A hardness for reactive blends of 75 wt.% EPDM/ 25 wt.% nylon

EPDM Type	Nylon 11	Nylon 12
Fusabond MF-280D	79	80
Royaltuf 465	64	72
Fusabond MF-274D	78	78

Section VII

Conclusions

The synthesis and characterization of nylon grafted ethylene propylene diene monomer thermoplastic elastomers have been performed in accordance with the thesis proposal.

The following summarizes the findings of this research:

Nylon 12 reactive blends

The results for the eighteen reactive nylon 12 blends all indicate partial grafting of nylon 12 to maleic anhydride grafted EPDM rubbers. The following characterization techniques were used: FTIR, Soxhlet extraction, dynamic mechanical measurements, scanning electron microscopy, and room temperature tensile testing. The specific details of the results are summarized below:

- FTIR analyses of the eighteen reactive blends suggested only partial grafting of nylon 12 to maleic anhydride EPDM rubbers. This was based on the incomplete disappearance of the maleic anhydride absorbance peak at 1789 cm^{-1} and the presence of a weak cyclic imide absorbance peak at 1701 cm^{-1} .
- Soxhlet extraction in xylene showed that a larger percentage of grafted rubber was obtained for the 60 wt.%/40 wt.% reactive blends (23% and 20%) than for the 75 wt.%/25 wt.% reactive blends (0.3% and 0%). This is consistent with a greater decrease in the maleic anhydride peak heights at 1789 cm^{-1} and 1866 cm^{-1} for the 60/40 blends than for the 75/25 blends.

- Dynamic mechanical analyses suggested evidence of a chemical graft. The recrystallization of the nylon 12 was suppressed to re-crystallize with the ethylene propylene at about 135 °C.
- A scanning electron micrograph of the 60/40 Fusabond MF-280D/nylon 12 reactive blend showed small nylon domains (less than 2 microns), indicating good compatibility.
- The tensile strength (up to 600 psi) and toughness (up to 4380 in-lb/in³) were higher for reactive blends which had nylon 12 domains that were less than 2 microns.
- The tensile strength, elongation, and shore A hardness of some TPEs that were synthesized in this research showed reasonable mechanical properties compared with literature values.
- The Brabender mixing torque did not show a significant increase to indicate grafting, contrary to the FTIR and Soxhlet extraction results which indicated partial grafting.

Nylon 11 reactive blends

Results for the three reactive nylon 11 blends strongly indicate grafting of nylon 11 monomer (11-aminoundecanoic acid) to maleic anhydride EPDM and polymerization to nylon 11 polymer. The effects of grafting and polymerization from monomer to polymer were measured with similar techniques used to evaluate the nylon 12 reactive blends. The specific details of the results are summarized below:

- FTIR analyses showed evidence for the cyclic imide graft with absorbance peaks clearly identified at $\sim 1706\text{ cm}^{-1}$ and $\sim 1772\text{ cm}^{-1}$. This is an alternate method to synthesize thermoplastic elastomers.
- Soxhlet extraction in xylene showed greater amounts of unextracted solids for EPDM rubbers with higher concentrations of maleic anhydride grafting sites.
- The Brabender mixing torque provided strong evidence of a chemical graft. This was based on a significant increase in the mixing torque for nylon 11 compositions with Fusabond MF-280D and Royaltuf 465 EPDM rubbers. The mixing torque increased more sharply for Fusabond MF-280D, which has more maleic anhydride graft sites, than for Fusabond MF-274D.
- Dynamic mechanical analyses suggested evidence of a chemical graft. This was based on the elastic modulus behavior which showed a suppressed recrystallization of nylon 11 to re-crystallize with the ethylene propylene at about 75°C .
- The scanning electron micrographs for two reactive blends showed that smaller nylon domains (less than 0.5 micron) were obtained with EPDM rubbers that had higher amounts of grafted maleic anhydride (2 wt.% versus 1 wt.%).
- The 75 wt.% Fusabond MF-280D/ 25 wt.% nylon 11 composition had the highest tensile strength (1270 psi) and toughness (7160 in-lb/in³) of all the reactive blends. This is consistent with the small (less than 0.5 micron) nylon 11 domains observed in the SEM micrograph.

- One of the goals of this thesis research was to synthesize soft thermoplastic elastomers. Many of the reactive blends were still soft (with less than 90 shore A) with up to 25 wt.% grafted nylon 11.

Nylon 11 and nylon 12 non-reactive blends

The results for nylon 11 and nylon 12 non-reactive blends showed no grafting to form the cyclic imide. The analyses revealed similar physical and mechanical properties for both types of blends and so they are described together. The specific details of the results are summarized below:

- FTIR analyses showed no cyclic imide peak at 1701 cm^{-1} to indicate grafting.
- Soxhlet extraction in xylene after 10 days showed that 100% of Fusabond MF-280D was extracted into the sol fraction compared to only 57 % for Royaltuf 465. The difference in solubility is probably due to different diene polymers in the two rubbers.
- The Brabender mixing torque did not show an increase, which is consistent with melt mixing of a non-reactive blend.
- Dynamic mechanical analyses indicated no grafting in the non-reactive blends. This was based on comparing the elastic modulus behavior of nylon 12, both as virgin material and in the non-reactive blends. In both cases, it was observed that the recrystallization of nylon 12 was not suppressed. The recrystallization of nylon 11 was also not suppressed in the non-reactive blend.

- Scanning electron micrographs of non-reactive blends showed large nylon domains (up to 20 microns), which indicates poor compatibility.
- The tensile strength and toughness of the non-reactive blends were poor due to the large domains of ungrafted nylon 11 and nylon 12.

Section VIII

Presentations

This thesis work was presented at the following professional meetings in partial fulfillment of the requirements for the Masters degree:

“Nylon 12 EPDM Thermoplastic Elastomers,” presented at 32nd ACS Western Regional Meeting, San Francisco, California, November 1, 1996 and

“Synthesis and Characterization of Nylon Grafted Ethylene Propylene Diene Monomer Thermoplastic Elastomers,” presented at 213th ACS National Meeting, Division of Polymer Chemistry, San Francisco, California, April 13, 1997.

Section IX

Suggestions for Further Research

The synthesis and characterization of the nylon grafted EPDM thermoplastic elastomers yielded some inclusive results. It also revealed some new areas that merit further investigation. Here are some suggestions for future research in this area.

- To synthesize new thermoplastic elastomers, utilize other nylons which have been specifically modified with amino end groups to obtain improved grafting to maleic anhydride EPDM rubbers.
- Analyze the insoluble fractions by solid state NMR, both to determine the relative amounts of nylon and grafted EPDM rubber, and to obtain a more quantitative measure of the grafting efficiency.
- Investigate the phenomena of suppressed recrystallization in nylon grafted EPDM blends. Understand how cooling rates affect the recrystallization kinetics of the blend and what effect it has on mechanical properties.
- Evaluate tensile properties of graft copolymerized TPEs at an elevated temperature, such as 120 °C, to determine feasibility for use in new products.
- Explore other combinations of nylon monomers and maleic anhydride grafted EPDM rubbers to determine the parameters necessary to synthesize a viable thermoplastic elastomer using in-situ polymerization and grafting.

References

1. Toensmeier, P., "TPE formulations show new versatility," Modern Plastics, Vol. 72, May 1995, p. 70.
2. Ibid., pp. 70 - 75.
3. Chamberlain, G., "Elastomers: more design bounce to the ounce," Design News Vol. 50, February 20, 1995, pp. 550-55.
4. Toensmeier, P., "TPE elastomers: versatility and performance of materials drive growth," Modern Plastics, Vol 25, January 1995, pp. 53 - 61.
5. Ibid., p. 63.
6. Holden, G., and Legge, N. R., and Schroeder, H. E., Eds. Thermoplastic Elastomers: A Comprehensive Review, Hanser Publishers, New York, 1987, Chapter 2.
7. Ibid., Chapter 3
8. Ibid., Chapter 5
9. Ibid., Chapter 8
10. Ibid., Chapter 7
11. Ibid., Chapter 9A
12. Walker, B. M., Rader, C. P., Eds., Handbook of Thermoplastic Elastomers, Van Nostrand Reinhold Company, New York, 1988, pp. 4-5.
13. Holden, G., and Legge, N. R., and Schroeder, H. E., Eds., Thermoplastic Elastomers: A Comprehensive Review, Hanser Publishers, New York, 1987, p. 68.

References, continued

14. Noshay, A., and McGrath, J., Block Copolymers: Overview and Critical Survey, Academic Press, New York, 1977, pp. 186 - 194.
15. Holden, G., and Legge, N. R., and Schroeder, H. E., Eds., Thermoplastic Elastomers: A Comprehensive Review, Hanser Publishers, New York, 1987, pp. 48 - 51.
16. Noshay, A., McGrath, J., Block Copolymers: Overview and Critical Survey, Academic Press, New York, 1977, Chapter 7.
17. Walker, B. M., Rader, C. P., Eds., Handbook of Thermoplastic Elastomers, Van Nostrand Reinhold Company, New York, 1988, pp. 6-8.
18. Toensmeier, P., "TPE formulations show new versatility," Modern Plastics, Vol. 72, May 1995, p. 70.
19. Legge, N. R., "Thermoplastic Elastomer Categories: A Comparison of Physical Properties," Elastomerics, Vol. 123, 1991, pp. 14-20.
20. Walker, B. M., Rader, C. P., Eds., Handbook of Thermoplastic Elastomers, Van Nostrand Reinhold Company, New York, 1988
21. Roff, W. J., and Scott, J. R., Handbook of Common Polymers, Butterworth & Co. Ltd., London, 1971, p. 212.
22. Volksen, W., "Condensation Polyimides: Synthesis, Solution Behavior, and Imidization Characteristics," Advances in Polymer Science, 117 (High Performance Polymers), Springer-Verlag, New York, 1994, pp. 111-164.

References, continued

23. Stenzerberger, H. D., "Addition Polyimides," Advances in Polymer Science, 117 (High Performance Polymers), Springer-Verlag, New York, 1994, pp. 165-220.
24. Scott, C. E., Macosko, C. W., "Model Experiments for the Interfacial Reaction Between Polymers During Reactive Polymer Blending," Journal of Polymer Science: Part B: Polymer Physics, Vol. 32, 1994, p. 209.
25. Bellamy, L. J., The Infrared Spectra of Complex Molecules, Vol. 2, 2nd Ed., Chapman and Hall, New York, 1980.
26. Saltman, R. P., Raychem private communication, 1990.
27. Scott, C. E., Macosko, C. W., "Compounding and Morphology of Nylon/Ethylene-Propylene Rubber Reactive and Nonreactive Blends," International Polymer Processing, Vol. 10, 1995, pp. 36-45.
28. Sundararaj, U., and Macosko, C. W., and Nakayama, A., and Inoue, T., "Milligrams to Kilograms - An Evaluation of Mixers for Reactive Polymer Blending," Polymer Engineering and Science, Vol. 35, 1995, p. 101.
29. Hammer, C. F., Sinclair, H. K., "Novel Elastomeric Graft Copolymers," U.S. Patent No. 4,017,557 (1977).
30. Olivier, E. J., "Polyamide Thermoplastic Elastomer Obtained By Blending," U.S. Patent No. 5,003,003 (1991).
31. Pitz, T. J., AtoChem North America private communication, 1997.

References, continued

32. Billmeyer, F., Textbook of Polymer Science, 3rd Ed., John Wiley and Sons Inc., New York, 1984, p. 209.
33. Brandrup, J., and Immergut, E. H., Eds., Polymer Handbook, 3rd Ed., John Wiley and Sons Inc., New York, 1989, Chapter VII, p. 25.
34. Bellamy, L. J., The Infrared Spectra of Complex Molecules, Vol. 2, 2nd Ed., Chapman and Hall, New York, 1980, p. 135.
35. Streitwieser, Jr., A., and Heathcock, C., Introduction to Organic Chemistry, Macmillan Publishing Co., New York, 1976, p. 598.
36. Martuscelli, E., et al., "Acid and base functionalization of ethylene-propylene rubbers, 1," Makromol. Chem., Huthig & Wepf Verlag, Zug, No. 188, 1987, p. 959.
37. Charrier, J. M., Polymeric Materials and Processing, Plastics, Elastomers and Composites, Hanser Publishers, New York, 1991, p. 105.
38. Holden, G., and Legge, N. R., and Schroeder, H. E., Eds. Thermoplastic Elastomers: A Comprehensive Review, Hanser Publishers, New York, 1987, pp. 350-353.

Appendix A FTIR spectra of 2 wt.% and 0.1 wt.% N-(3-hydroxyphenyl)-phthalimide in tetrahydrofuran solutions.

Figure 1. Absorbance spectrum for 2.0 wt.% N-(3-hydroxyphenyl)phthalimide. The THF absorbance was subtracted out. Number of scans: 512, resolution: 8 cm⁻¹.

Figure 2. Absorbance spectrum for 0.1 wt.% N-(3-hydroxyphenyl)phthalimide. The THF absorbance was subtracted out. Number of scans: 512, resolution: 8 cm⁻¹.

Appendix B Room temperature tensile strength, elongation, and toughness of nylon 12 AMNO reactive and non-reactive blends.

Figure 1. Tensile strength of EPDM/Nylon 12 reactive and non-reactive blends. ASTM Die C. Strain rate: 5"/min at room temperature.

Figure 2. Elongation of EPDM/Nylon 12 reactive and non-reactive blends. ASTM Die C. Strain rate: 5"/min at room temperature.

Figure 3. Toughness of EPDM/Nylon 12 reactive and non-reactive blends. ASTM Die C. Strain rate: 5"/min at room temperature.

Appendix C FTIR spectra of nylon 11 reactive blends with Royaltuf 465 and Fusabond MF-274D EPDM rubbers and a non-reactive blend with Royalene 306 EPDM rubber.

Figure 1. FTIR absorbance spectrum showing evidence of cyclic imide grafting and polyamide formation. (75 wt.% Royaltuf 465 and 25 wt.% 11-aminoundecanoic acid.)

Figure 2. FTIR absorbance spectrum showing evidence of cyclic imide grafting and polyamide formation. (75 wt.% Fusabond MF-274D and 25 wt.% 11-aminoundecanoic acid.)

Figure 3. FTIR absorbance spectrum for a non-reactive blend showing no cyclic imide grafting but formation of polyamide. (75 wt.% Royaltuf 465 and 25 wt.% 11-aminoundecanoic acid.)

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