



## Reactively dispersed olefins in polyurethanes: A new class of polymer/polymer composite



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### ABSTRACT

Maleic anhydride grafted polyethylenes (MAH-g-PE) can be reacted with polyols to create fine phase dispersions in polyurethanes. Desirable blends can only be realized when the anhydrides are in the dehydrated state prior to reaction. The reaction of anhydride with hydroxyls can occur with the polyol prior to addition of isocyanate and chain extender to make the polyurethane, or with an already formed polyurethane heated up above its reversion temperature when hydroxyl functionality becomes available. Phase dispersion kinetics are a function of MAH-g-PE molecular weight and percentage grafted maleic anhydride along the chain, but also on viscosity matching of the forming polyurethane and the MAH-g-PE during the blending operation which maximizes shear stress between the phases. The final result is not strongly dependent on the preparation path. Thermoplastic polyurethane elastomers (TPUs) based on polypropylene oxide and polyethylenoxide/polypropylene oxide triblock copolymer soft segments are compared to industry standard TPUs prepared from polytetramethylene ether glycol (PTMEG) and polycaprolactone (PCL) soft segments. The control TPUs prepared from polypropylene oxide and the polyether triblock are inferior to those of PTMEG and PCL. However; when the polypropylene oxide and the triblock soft segments are prepared with 20% substitution of MAH-g-PE, the creep, thermal and solvent resistance of these elastomers exceeds those of the industry standards, and the tensile properties are comparable. Additionally, TPUs from PTMEG and PCL with added MAH-g-PE can also have their properties improved. The property improvements are a function of improved hard segment phase separation from the soft segment, and the creation of polyester crosslinks between the MAH-g-PE and the polyurethane.

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### 1. Introduction

Blending polymers to improve or modify performance is well known and widely practiced [1–3]. Since most polymers are incompatible and readily phase separate [4], the challenge has always been to develop techniques to overcome free energy barriers to mixing. The goal has rarely been to achieve polymer miscibility, but rather to sufficiently reduce differences in surface tension such that one polymer, acting largely as a bulk material, can significantly improve the properties of another [5–7]. One way to achieve this goal is to develop inter-phase adhesion either via polar forces, or by direct covalent bond formation between the phases [8–10]. In

polyurethanes, a covalent interfacial adhesion mechanism is present in copolymer polyols. These products are stable blends of styrene-acrylonitrile (SAN) in a polyether polyol. The phase adhesion to the soft segment is generated by chain transfer to the host polyol during the SAN radical polymerization.

Olefin blends with urethanes have been particularly challenging since polyolefin interfacial surfaces offer no polar or reactive handles with which to reduce interfacial tension and so promote phase dispersion [11–13]. Blend studies of polyethylene or polypropylene with thermoplastic polyurethane have confirmed their immiscibility, but shown that if polymer viscosity is matched, the dispersion of the phases can be maximized. The use of anhydride-modified polyethylene has also been shown to provide improved dispersion by reducing interfacial tension between the phases. However; in these studies there was no obvious attempt to assure that the added maleic anhydride grafted polyolefin was indeed in the anhydride state rather than the hydrated di-acid form [14]. Improvements in blend properties were noted.

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**Table 1**  
Properties of the maleic anhydride grafted olefin resins used in this work.

Amplify olefin	MAH wt%	M.I.	Density (g/cm <sup>3</sup> )
GR202	1.2	8	0.93
GR209	0.8	2	0.89
GR216	0.8	1.2	0.87
EG8407	1	10,000 cps@ 190° C	0.88

In this study we assure grafting of maleic anhydride grafted polyethylenes (MAH-g-PE) to the polyurethane backbone by employing a rigorous drying procedure followed by infra-red analysis. The MAH-g-PE is then reacted with polyol resulting in a polyol grafted copolymer via an ester linkage along the polyolefin backbone. The polyethylene ester alcohol may then react with adventitious isocyanate. Alternatively, the MAH-g-PE may react directly into a molten polyurethane resin as alcohol and isocyanate functionalities are available through well known urethane thermal reversion chemistry [15–17].

## 2. Experimental

Maleic anhydride (MAH) grafted polyethylenes were obtained from Dow Chemical. These MAH-g-PE samples are referred to herein individually by their commercial identification numbers (i.e. GR XXX). MAH-g-PE characteristics are described in Table 1 as reported from product data sheets. The polyethylene base materials are copolymers of ethylene and 1-octene. The amount of octane is added in quantity sufficient to reduce crystallinity and create elastomeric performance. The percentage incorporation of 1-octene co-monomer is reflected in the stated polymer density with lower density reflecting increased co-monomer. Polyols were obtained from Sigma–Aldrich (PTMEG and polycaprolactone), Chemtura Corp. (Fomrez 44–56) polybutylene adipate (PBA), or Dow Chemical and were dried prior to use. Polyol characteristics are provided in Table 2. Pellethane<sup>2</sup> TPU with a Shore A value of 70 was obtained from Dow Chemical. It is a block copolymer of 2000 g/mol PTMEG and 4,4'-methylene bis(phenyl isocyanate) with 1,4 butane diol in weight ratio of ca. 3:1 PTMEG:MDI-BDO. 4,4'-Methylene bis(phenyl isocyanate) (MDI) was obtained from Dow Chemical (Isonate M125). 1,4-butanediol (BDO), tin(II) 2-ethylhexanoate (T9), anhydrous *para*-toluenesulfonic acid, and all reagents for hydroxyl number determination were obtained from Sigma–Aldrich.

The hydroxyl number was determined using a standard titration method provided in detail within [supplemental on-line information](#).

### 2.1. Confirmation of maleic anhydride content in MAH-g-PE

Received MAH-g-PE resins were uniformly in a hydrated state (ca. 1.2 wt% water). Maleic anhydride grafted olefins were dried under vacuum at 160 °C for at least 12 h prior to use. The reversion of the diacid to the anhydride was confirmed by IR spectroscopy (PerkinElmer Spectrum One<sup>3</sup>), which is evidenced by the disappearance of the hydrogen bond OH stretch centered at ca. 3350 cm<sup>-1</sup>, the carboxylic acid related resonance centered at 1710 cm<sup>-1</sup>, and the growth of the cyclic anhydride resonance at 1784 cm<sup>-1</sup>. A weaker band at 1830 cm<sup>-1</sup> may also appear at high enough MAH grafting and high conversion of the diacid to the anhydride [18]. Virtually all the diacid can be converted to MAH by thorough drying of the MAH-g-PE resins. Obtaining dried maleic

**Table 2**  
Properties of the polyols used in this work.

Polyol	M <sub>N</sub> (g/mol)	mol% 1° hydroxyl	mol% PO	wt% PO
PTMEG	1000,2000 <sup>a</sup>	100	–	–
PCL	2000 <sup>a</sup>	100	–	–
PBA	2000 <sup>a</sup>	99 <sup>b</sup>	–	–
P2000	2000	0	100	100
EO/PO triblock Polyether polyol	1725/1766 <sup>c</sup>	82.9	64.8	70.8

<sup>a</sup> Manufacturer specification.

<sup>b</sup> Based on measured acid number.

<sup>c</sup> Based on OH number.

grafted resin is a key requirement of the technology described herein and a critical difference with all prior work mixing MAH-g-PE with urethanes. Furthermore, we have observed that processing hydrated MAH-g-PE through a vented twin-screw extruder does not sufficiently dehydrate the diacid to develop blend properties shown herein. Representative spectra of hydrated and anhydride forms are provided in [supplemental on-line information](#).

### 2.2. Thermoplastic polyurethane (TPU) preparation and physical property evaluation

Shore A hardness was determined using ASTM D2240. Melt-flow rate (a measure of processability) was determined according to ASTM D1238. Measurement temperature was 224 °C with an 1100 g weight (unless otherwise noted) using a Tinius Olsen Extrusion Plastometer. Reported values are the average of three replicate measurements.

Dispersions of MAH-g-PE and the resulting polyurethane elastomers in diol polyols were made in a Haake dispersive mixer [19–23]. MAH grafting was nominally present at the published weight percentage in the MAH-g-PE as shown in Table 1. Our work had shown that titration of a maleimide functionalized secondary amine olefin by isocyanate would normally result in MAH incorporations stoichiometrically inconsistent with the stated amount. Thus, we found that a nominally 0.4 wt% MAH-g-PE titrated to approximately a 3000–4000 g/mol equivalent weight secondary amine per mole of polymer. GPC determined MAH-g-PE were between M<sub>n</sub> = 35,000 Da and 70,000 Da suggesting between 10 and 20 MAH grafts per polyethylene chain. In the current study, the functionality of the MAH-g-PE was ignored in calculating the urethane stoichiometry for polymerization. Although this would normally result in a polymer that was over-indexed in isocyanate, it will be shown that the resulting polymer elongation at break was sufficiently high to neglect the contribution of MAH-g-PE. The MAH-g-PE, polyol, and a small amount (~0.1%) of anhydrous *para*-toluene sulfonic acid as a catalyst was added to the Haake mixer at 150 °C and allowed to react. During this time the dispersion would become milky and progressively more viscous as the polyol grafted to the MAH-g-PE. Reaction during this time was not complete but did usually go to completion in the next step. The addition of MDI and BDO to the mixture increased shear mixing to complete the dispersion. The reacting mixture was heated for 5 min 200 °C and promptly removed from the mixer. These materials were subsequently molded into plaques for materials testing.

Alternatively, the MAH-g-PE could be added directly to prior synthesized polyurethane in the Haake mixer. The mixture was allowed to mix until the reaction appeared uniform to the eye and the measured mixer torque was stable for a period of minutes. <sup>13</sup>C NMR analyses of polyol directly grafted to the MAH-g-PE showed that up to ca. 80% of the available MAH could react with polyol to produce the ester-acid groups pendant to the polyolefin main-

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