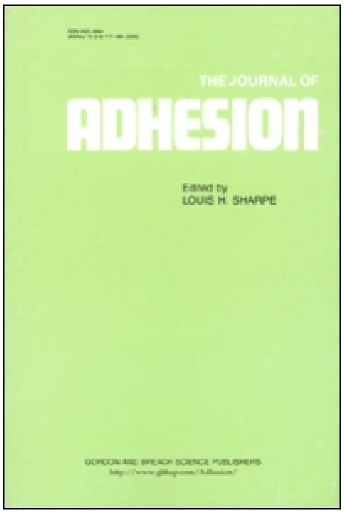

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Influence of polymer structure on melt miscibility of ternary polymer blends: A model for high performance polyurethane adhesives and coatings

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INFLUENCE OF POLYMER STRUCTURE ON MELT MISCIBILITY OF TERNARY POLYMER BLENDS: A MODEL FOR HIGH PERFORMANCE POLYURETHANE ADHESIVES AND COATINGS

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The miscibility behavior of reactive ternary blends, a model for reactive hot melt polyurethane adhesives, has been characterized. The model system is composed of polyether and polyester prepolymer blended with a high T_g polyacrylate. During prepolymer synthesis, the molecular weight and chemical composition of the polyether and polyester chains were altered. Phase diagrams of the prepolymer were found to differ significantly from those associated with the starting materials. Consistent with our earlier findings, polyether with or without chemical modification plays a crucial role in expanding the region of miscibility. Incorporation of reactive isocyanate groups onto these polymers significantly altered the miscibility behavior of the ternary blends. In contrast, modified polyesters did not improve blend miscibility. These changes in specific interchain interaction were offset by the increase in molecular weight of both components. The competitive influence of polyether and polyester miscibility behavior was analyzed in a quantitative manner. Balancing the polyether and polyester reaction chemistry is critical for controlling the melt miscibility of these ternary blend systems.

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Keywords: Hot melt adhesive; Polyurethane; Blends; Functionalization; Structure; Polyester; Polyether; Acrylics

INTRODUCTION

Polyurethane hot melt adhesives (PUHMAs) are increasingly important in a variety of applications. They combine many properties not found in other adhesives such as good bond durability, adhesion to a wide variety of substrates, high performance over a large temperature range, good chemical resistance, and fast set speed [1, 2]. There are additional environmental benefits since polyurethane-based hot melt adhesives do not involve solvents or volatile organic compounds (VOCs), and, in some cases, have replaced toxic phenol-formaldehyde–based adhesives.

PUHMAs are typically formulated as one-component systems consisting of a blend of isocyanate-functionalized prepolymer [3, 4]. Typically, the adhesive is melted and applied where it will cool rapidly to form a bond through a combination of curing with moisture in the environment [5, 6], crystallization [7], vitrification, and phase separation processes. Proper selection of the polymer components affords processing control and improves blend performance. In this particular case, a combination of polyethers and crystallizable polyesters are used. The polyether and polyester diols provide reactive functional groups for synthesis of urethane linkages. The polyester crystallites raise the overall viscosity considerably at elevated temperatures and, thus, the adhesive green strength. Upon cooling, polyester crystallites may also serve as reinforcement, enhancing the mechanical strength of the adhesive and raising the ultimate achievable properties, particularly at elevated temperatures [3, 8]. The elastic polyether toughens the overall mechanical joints. Acrylic copolymers are also added for two purposes. One is to improve compatibility between the polyether and polyester [9, 10]. The other reason is that owing to its high glass transition temperature and viscosity, it raises the green strength of the blend at elevated temperatures needed during application [11, 12].

We previously examined ternary blends of poly(propylene oxide) and poly(methyl methacrylate co n-butyl methacrylate) blended with either poly(hexamethylene adipate) or poly(hexamethylene sebacate) in order to model the phase behavior of the initial formulation prior to prepolymer synthesis [13]. A seemingly small change in polyester structure, the length of the methylene chain in the diacid portion of the repeat unit, from 4 to 8, was found to alter the miscibility behavior substantially. The binary interaction parameters for the three pairs of binary mixtures were measured. The resulting interaction parameters proved to have good predictive qualities when applied to ternary mixtures of the components. Morphological features developed for different compositions were also established. These simulation studies provided additional insight into the role of each component in the miscibility of the system.

The goal of the current study is to elucidate changes in miscibility behavior when polyurethane prepolymers are prepared from polyether, polyester, and acrylic ternary polymer blends. The basic reaction in PUHMA prepolymer synthesis is a polyaddition reaction between a diisocyanate and a polydiol. Alcohol groups are consumed and urethane groups are generated. The reaction is a step polymerization resulting in a distribution of products of different molecular weight. The incorporation of urethane functionality may change the balance of interchain interactions considerably and alter the miscibility of the system. From thermodynamic considerations, the increase in molecular weight decreases the entropic contribution to the free energy of mixing. In contrast, the increase in specific interactions lowers the free energy of mixing. It is speculated that the specific interactions from the urethane groups promote miscibility, while the increasing molecular weight tends to favor phase separation of the ternary blends. The net effect of these two contributions is often difficult to assess. In order to understand changes in the phase behavior that occur during reactive blending, model prepolymers were prepared. Characterization of the prepolymer involves defining both the functionalities introduced and the molecular weight distribution. We have separated the two effects by using prepolymers of well-defined molecular weight and type of functional groups present. The competitive effects of different pairs of polymers are reflected in the phase diagrams for the systems. The phase diagrams can be interpreted using simulation techniques developed previously [13]. Our results are reported here.

EXPERIMENTAL

The chemical structures of the polymers used in this study are shown in Figure 1. Poly(propylene glycol) (PPG; Bayer 2056, Bayer, Pittsburgh, PA, USA) with a hydroxyl value of 56 was dried in vacuum at 40°C for at least two days prior to use. Using ^{13}C-NMR, we have determined that Bayer PPG 2056 is terminated with secondary hydroxyl groups. Matrix-assisted laser desorption ionization time of flight (MALDI-TOF) mass spectroscopy was also used to characterize the

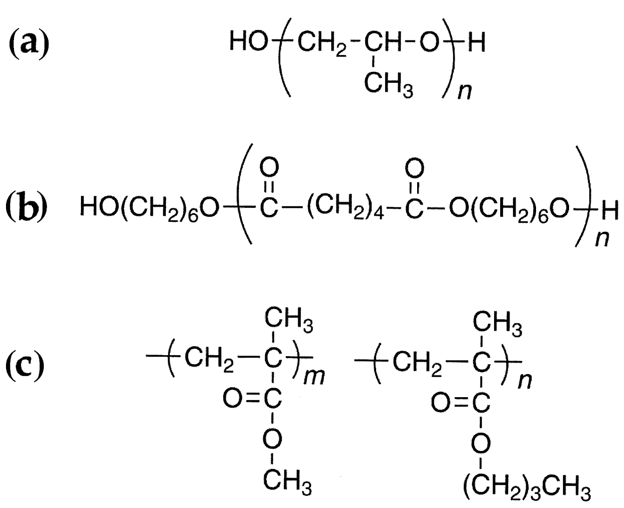

FIGURE 1 Structures of polymers used for blend studies: (a) poly(propylene glycol), (b) poly(hexamethylene adipate), and (c) acrylic copolymer of methyl methacrylate and n-butyl methacrylate.

starting PPG. This component has $M_n = 2000$ with a polydispersity index (PDI) of 1.02. Using Nuclear Magnetic Resonance (NMR), the amount of allyl and 2-propenoxy end groups is found to be 2.6 and 2.3 mole %, respectively [14]. These groups are not expected to affect the outcome of prepolymer formation. Poly(hexamethylene adipate) (PHMA) was obtained from Dow Chemical (Midland, MI, USA). The molecular weight of PHMA was determined to be 2505 using MALDI-TOF. All MALDI-TOF spectra were obtained using a Bruker Reflex-III spectrometer (Bruker Optics, Billerica, MA, USA). Matrix conditions have been reported previously [13, 14]. A random copolymer resin of methyl methacrylate and n-butyl methacrylate (P(MMAnBMA)) was obtained from INEOS Acrylics (Memplics, TN, USA). The acrylic copolymer composition was determined to be 0.75 and 0.25 mole fraction of MMA and nBMA, respectively, by ^{1}H-NMR [15]. The molecular weight of the acrylic copolymer was determined to be 30,900 by size exclusion chromatography (SEC) relative to poly(methyl methacrylate) (PMMA) standards. Methylene diphenyl diisocyanate (MDI) (Aldrich, 98%, Aldrich Chemicals, Milwaukee, WI, USA) was used as received; purity was determined prior to use by titration with butyl amine [14]. SEC was carried out with a Waters 510 High Pressure Liquid Chromatography (HPLC) pump (Waters Corp., Milford, MA, USA) equipped with 3 columns from Polymer

Labs, Inc. (Amherst, MA, USA) having 5 μm bead size (two with MIXED-D and one with 5 nm pore sizes). Tetrahydrofuran was used as eluent. A Waters R401 differential refractometer was used for detection. A SEC calibration curve of log(M_w) versus elution volume could be constructed for PPG prepolymers by combining the peak molecular weight (M_p) obtained from MALDI with curve fitting of the SEC traces [14].

The model polyether prepolymer, PPG*, was prepared as follows. A three-necked round bottom flask equipped with a stir bar, a nitrogen/vacuum adapter, and a rubber septum was charged with 20.0 g (19.99 mmol OH) of PPG. The system was evacuated to 100 mtorr and degassed by several successive cycles of nitrogen fill followed by evacuation for at least 2 h at 100°C. The water content at this point was found to be below the Karl Fisher limit ($<$0.02 wt%) [16]. In the final step, the system was evacuated to 100 mtorr, closed, and equilibrated at the reaction temperature of 122°C. MDI (4.18 g, 32.7 mmol NCO) was melted in a second round bottom flask, degassed, and added by syringe to the PPG. The reaction vessel was stirred under N_2 for 1.0 h to obtain the prepolymer. To simplify and understand the phase behavior of the full reactive system, model PPG and PHMA prepolymers were prepared separately. To mimic conditions used for synthesis of the full prepolymer system, PPG was reacted with a stoichiometric excess of MDI (ratio of OH/NCO groups is 0.62) under an inert atmosphere in the absence of water. At complete conversion of the OH groups, only NCO-end capped oligomers remain. A small amount of the prepolymer was either titrated with dibutyl amine (to measure the isocyanate content) or stirred with dry methanol for 24 h to cap any unreacted isocyanate groups at ends and avoid any further reaction with water [17]. The end-capped prepolymer was recovered via rotary evaporation of the methanol. This reaction scheme is shown in Figure 2. The polyester prepolymer of poly(hexamethylene adipate) (PHMA*) was prepared following the same procedure used for PPG* except for the methanol quenching step because of the crystallization of PHMA at room temperature. The NCO-terminated PHMA prepolymer (25 g) was dissolved in dry dichloromethane (200 ml) then mixed with dry methanol (200 ml) and stirred for 24 h under N_2. The PHMA* product was recovered by rotary evaporation of the solvents.

Binary and ternary polymer blends were prepared in glass vials, placed in a vacuum oven at the melt temperature and periodically mixed using a glass rod. Blends were allowed to equilibrate for a period of 12 to 24 h between mixings. Blend miscibility was evaluated in several ways. The physical appearance of many blends indicates

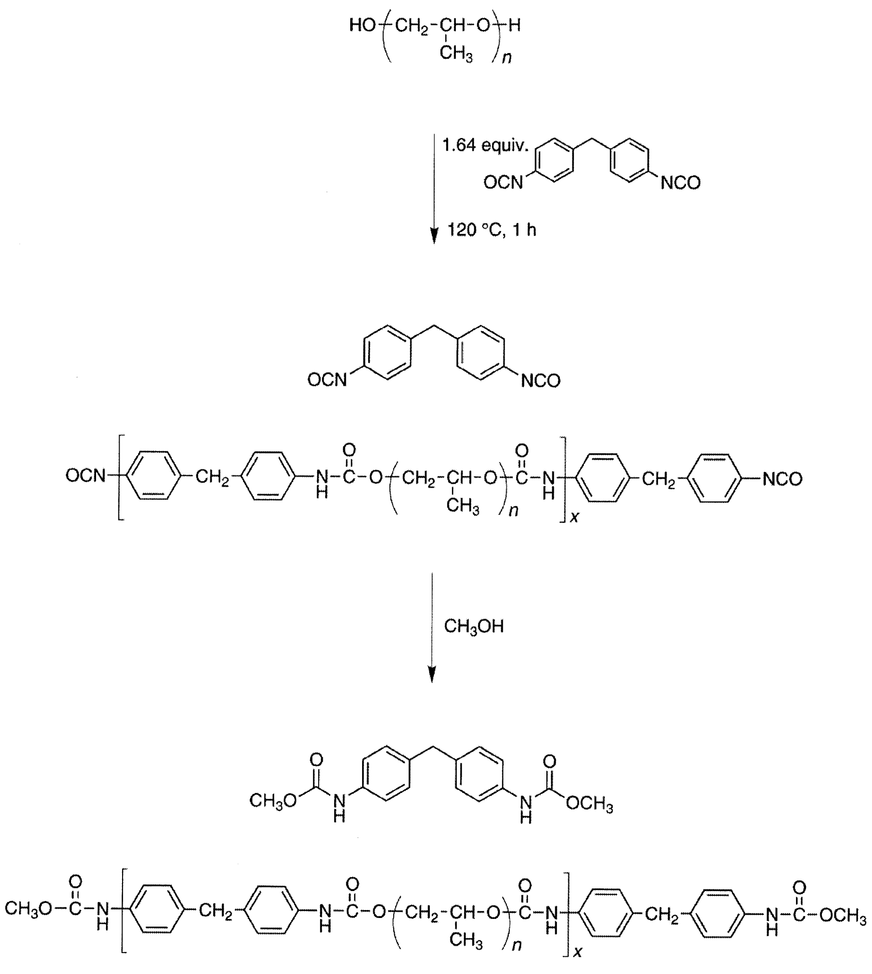

FIGURE 2 Prepolymer reaction scheme and structure of MeOH-quenched PPG* prepolymer. The prepolymer chain length will ultimately influence the molecular weight between crosslinks and, thus, the elasticity of the final product along with melt miscibility.

phase separation. For other samples a temperature-controlled light scattering cell of custom design coupled to a HeNe laser was used for determination of miscibility using the overall transmission of the sample. Micrographs of blends in the melt and at room temperature were recorded electronically using a VideoFlex 7300 digital camera (Ken-a-Vision, Kansas City, MO, USA) and an Olympus Vanox optical microscope [13] (Olympus America, Melville, NY, USA).

RESULTS AND DISCUSSION

Prepolymer Synthesis and Characterization

As mentioned above, the reaction forming the functionalized prepolymers involves formation of urethane groups. Prepolymer formation follows condensation polymerization kinetics. In order to reduce possible complexity due to reaction with water or urethane units of the prepolymers, the residual NCO groups were reacted with MeOH. This eliminates a degree of complexity that additional reactions introduce. The structure of the MeOH-quenched polyether prepolymer, PPG*, is shown in Figure 2. The polyester prepolymer prepared from PHMA by the same procedure is denoted as PHMA*, and the structure is schematically represented by Figure 2. Upon converting PPG to PPG*, the average molecular weight increased dramatically. After reaction to PPG*, the molecular weight, M_w, was 7960 measured with PDI of 2.0. In addition, after reaction each chain that contains initially two alcohol groups contained four or more urethane groups. Depending on the particular oligomer, the urethane groups were located both internally and at the ends of chains.

Chromatographic data obtained for the starting PPG and the prepolymer product, PPG*, are shown in Figure 3. After reaction, due to the narrow polydispersity of PPG, oligomer species with different numbers of PPG chains are clearly resolvable. Thus, after reaction the

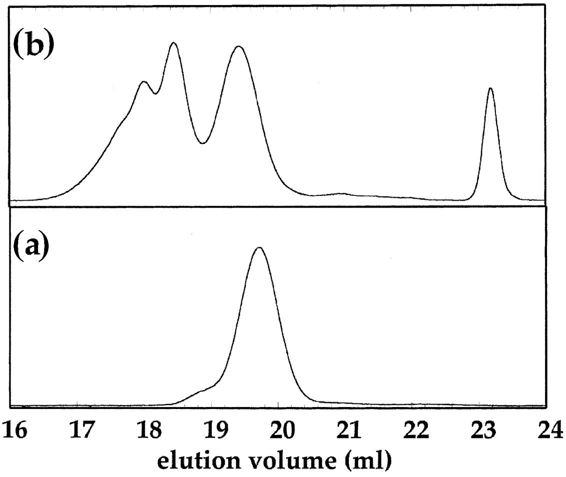

FIGURE 3 Chromatograms of PPG starting material and PPG* prepolymer reaction products.

discrete peaks at 23.20, 19.52, 18.50, and 18.12 ml correspond to species with 0, 1, 2, and 3 PPG units, respectively. Increasing the number of MDI units in an oligomer does not cause a discrete change but rather a shift in the peak elution volume (*i.e.*, molecular weight). For example, PPG is observed at 19.76 ml, while the "trimer" of PPG* (MDI-PPG-MDI) is observed at 19.52 ml. The resulting weight fraction distributions for PPG and PPG* are shown in Figure 4. The distributions were calculated from calibration curves based on MALDI-TOF data for the PPG-based prepolymers [14]. In the absence of side reactions, the number fraction and weight fraction of each oligomer can be determined as described by Flory [18]. Based on our previous studies, the experimental data compare favorably with those expected theoretically. In other words, PPG* exhibits the most probable distribution [14]. The importance of this finding is that the molecular weight distribution can be accurately predicted as a function of conversion during prepolymer synthesis. Figure 5 presents

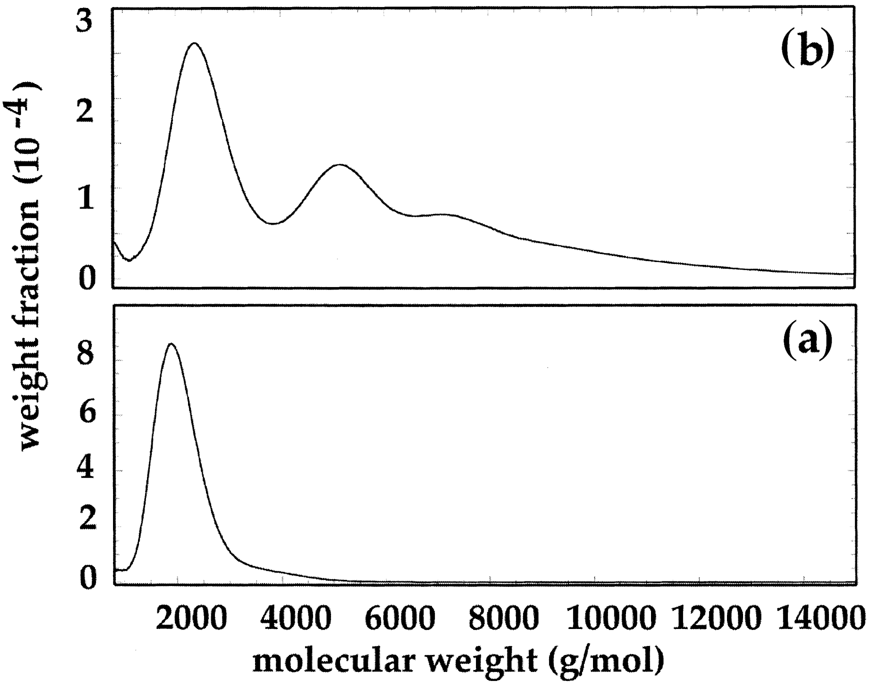

FIGURE 4 Weight distributions calculated for PPG and PPG* prepolymer reaction product.

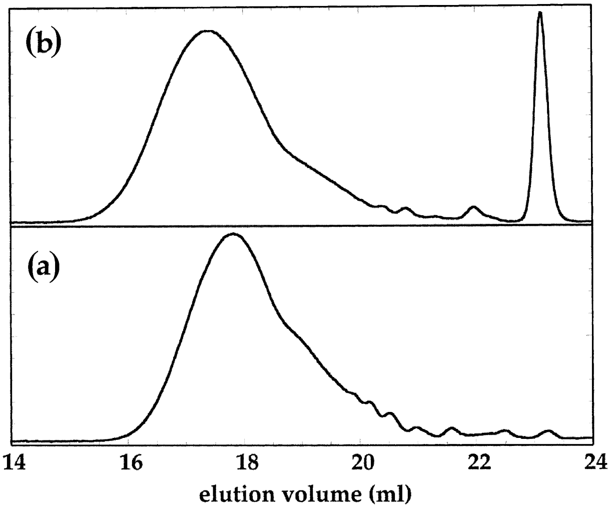

FIGURE 5 Chromatograms of (a) PHMA and (b) PHMA* prepolymer.

chromatograms of PHMA and PHMA*. Due to the broader molecular weight distribution of PHMA [13], resolution of the oligomers is not as clear as for PPG*. The relative shift in molecular weight is observed as the elution peak shifts from 17.80 to 17.38 ml. Elution peaks of the lower molecular weight chains between 20 and 24 ml shift as well, indicating formation of higher molecular weight prepolymer products. As indicated below, chemical and physical changes from prepolymer chemistry have a profound effect on the miscibility of these ternary polymer blends.

Phase Behavior

The effects of converting a diol to its prepolymer on the miscibility behavior of adhesive blends can be examined by comparing four ternary blend systems: (PPG, PHMA, P(MMAnBMA)), (PPG*, PHMA, P(MMAnBMA)), (PPG, PHMA*, P(MMAnBMA)), and (PPG*, PHMA*, P(MMAnBMA)). These four ternary systems allow examination of the effects of prepolymer structural differences on the miscibility of various ternary blends. It should be noted that a commercial system may be prepared in several steps and then blended together rather than synthesized in one step as suggested above. This is an important point, as the order of addition or reaction could produce blends with different morphologies and properties.

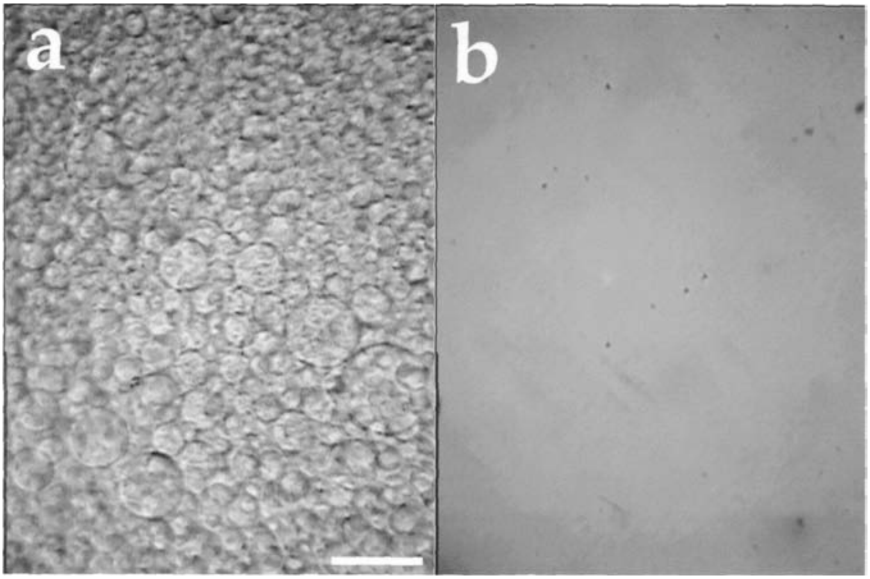

FIGURE 6 Optical micrographs of a ternary blends of 45, 45, and 10 wt% PPG, PHMA, Acrylic polymers in the melt at 115°C (a) before and (b) after the prepolymer synthesis. Scale bar = 200 μm.

The difference in the phase behavior of the three components before and after reaction is quite apparent, as shown in Figure 6 for a ternary blend composed of 45, 45, and 10 wt% PPG, PHMA, and P(MMAnBMA), respectively, at 115°C. It is clear that a phase-separated morphology exists before reaction, and a clear mixture is observed for ternary blends after synthesis of the functionalized polyethers and polyesters. Due to the presence of two reactive polymers, PPG and PHMA, the final miscibility of the system is determined by contributions from both polyester and polyether prepolymers. The role of each component needs to be examined separately.

Figure 7 shows a miscibility diagram for ternary blends of the starting materials, PPG, PHMA, and P(MMAnBMA) in the melt at 110°C. In the miscibility diagrams presented here, optically clear blends are denoted by open squares (□), turbid and translucent blends by gray squares (▨), and blends that rapidly phase separate or are completely opaque by filled black squares (■). This system denoting the character of the solution rather than strictly noting miscible or immiscible helps to illustrate where the phase separation boundaries are and how we are approaching them. As an immiscible mixture approaches a miscibility boundary in temperature or

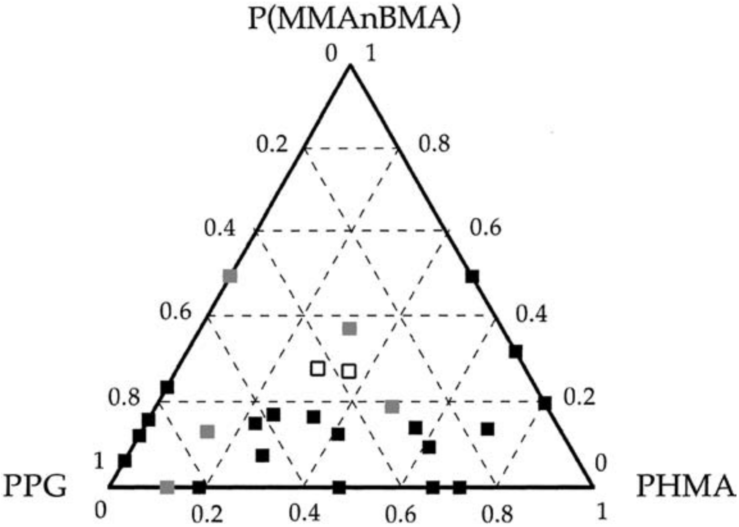

FIGURE 7 Miscibility map for ternary PPG, PHMA, and P(MMAnBMA) blends in the melt at 110°C.

composition space the interfacial tension tends toward zero, and the compositions of the coexisting phases become nearly identical and then optically clear.

This ternary system is composed of three partially miscible binary blends and displays a region of miscibility near the center of the composition map. The addition of the acrylic copolymer appears to promote compatibility of the polyether and polyester components. The centrally located compatible region in Figure 7 is an interesting feature. Islands and closed-loop regions of miscibility have been observed in other polymer systems and stem from a balance between the three polymer-polymer interaction parameters [19–21].

The miscibility behavior for blends containing PPG* (Figure 8) for this ternary blend in comparison with the starting material (Figure 7) is dramatic. A comparison of Figures 7 and 8 indicates that the region of compatible compositions in the ternary system involving PPG* has "opened up" compared with the initial materials. The binary polyether/acrylic and the polyether/polyester subsystems show the largest difference in compatibility upon altering the structure of the polyether. The result is an increase in the range of compatible ternary blend compositions upon inclusion of the PPG* prepolymer. The miscibility map for ternary blends prepared with the polyester prepolymer, PHMA*, is shown in Figure 9. Inclusion of PHMA* did not improve the

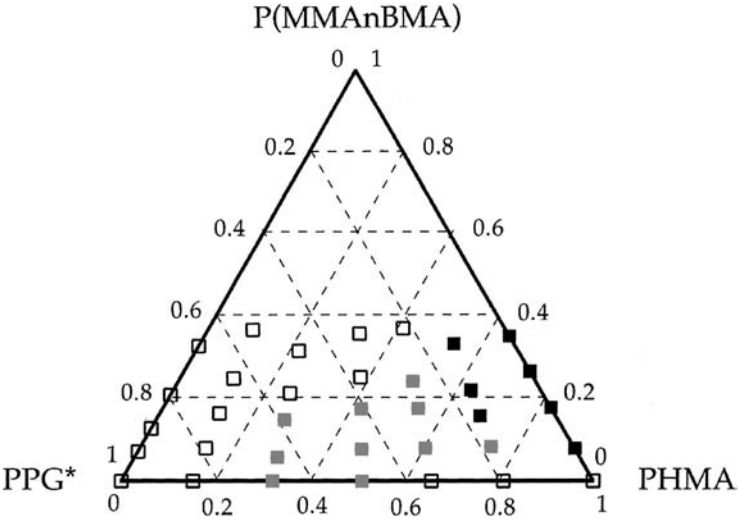

FIGURE 8 Miscibility map for ternary blends of PPG*, PHMA, and P(MMAnBMA) in the melt at 124°C.

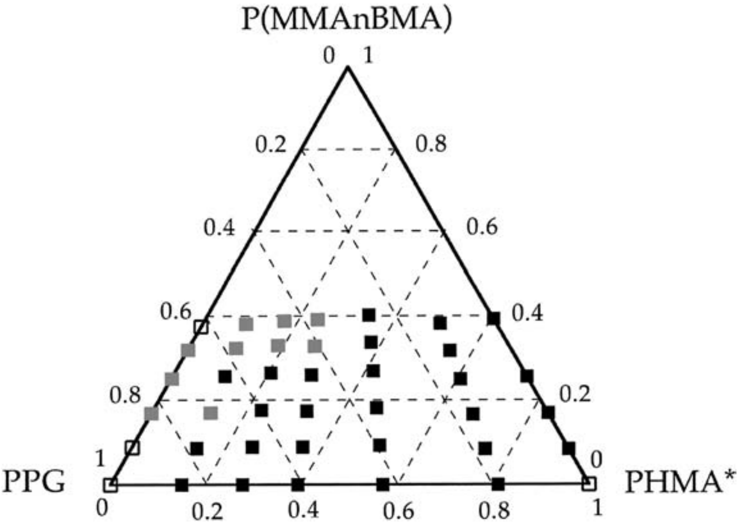

FIGURE 9 Miscibility map for ternary blends of PPG, PHMA*, and P(MMAnBMA) in the melt at 120°C.

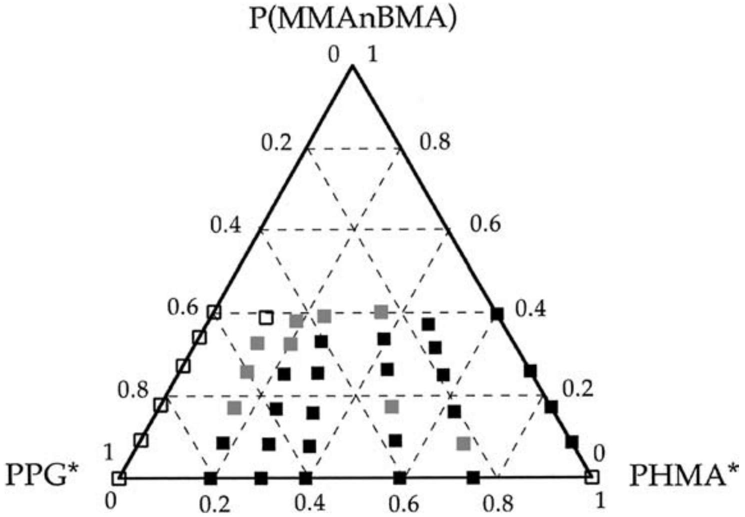

FIGURE 10 Miscibility map for ternary blends of PPG*, PHMA*, and P(MMAnBMA) in the melt at 120°C.

range of compatible compositions as the addition of PPG* did. In fact, based on the location of the unstable compositions, it appears that PHMA* destabilized some of the ternary blend compositions. A miscibility map of ternary blends containing both PPG* and PHMA* is shown in Figure 10. In this case, the ternary blends exhibit characteristics of the two previous systems shown in Figures 8 and 9. Compositions that lie on and abut the PPG*/Acrylic binary axis are stable. As the PHMA content increases, moving right across the diagram, the ternary blends become unstable. The extent of compatibility improvement gained from the PPG* (Figure 8) is compromised by inclusion of the PHMA*.

Effects of Specific Interactions and Molecular Weight Increase

Both the molecular weight and specific interactions were modified by prepolymer reaction. The free energy of mixing based on the lattice model was employed to model the phase behavior of this system in a quantitative fashion. Miscibility maps, in conjunction with simulation analyses, allow determination of these competitive effects [13]. Equations (1) and (2) represent the free energy of mixing (ΔG^{mix}) and the spinodal or stability condition for a ternary polymer blend, respectively. The spinodal represents the boundary between thermodynamically unstable compositions and metastable, stable compositions at a given temperature. Unstable compositions will spontaneously decompose into two or more coexisting phases. In Equations (1) and (2) ϕ_j is the volume fraction, n_j the degree of polymerization for each component, and g_{ij} is the binary interaction parameters for the system [22]:

$$\frac{\Delta G^{mix}}{NRT} = \left(\frac{\phi_1 \ln(\phi_1)}{n_1} + \frac{\phi_2 \ln(\phi_2)}{n_2} + \frac{\phi_3 \ln(\phi_3)}{n_3}\right) + (\phi_1\phi_2 g_{12} + \phi_1\phi_3 g_{13} + \phi_2\phi_3 g_{23}), \tag{1}$$

$$\left(\frac{1}{n_1\phi_1} + \frac{1}{n_3\phi_3} - 2g_{13}\right)\left(\frac{1}{n_2\phi_2} + \frac{1}{n_3\phi_3} - 2g_{23}\right) - \left(\frac{1}{n_3\phi_3} + g_{12} - g_{23} - g_{13}\right)^2 = 0. \tag{2}$$

Polymer miscibility results from a balance between entropic (ΔS^{mix}) and enthalpic (ΔH^{mix}) contributions to the free energy of mixing (ΔG^{mix}) given by Equation (3):

$$\Delta G^{mix} = \Delta H^{mix} - T\Delta S^{mix}. \tag{3}$$

The ΔS^{mix} and ΔH^{mix} are given by the first and second terms in Equation (1), respectively.

The chemical structure of polymer repeat units [23, 24], copolymer composition [25], copolymer sequence distribution [26], polymer branching [27], tacticity [28], end groups [29], and hydrogen bonding interactions [30, 31] can all modify this balance. Equation (2) shows that the stability of a ternary blend depends on the degree of polymerization (molecular weight) and the relative magnitude of all three binary interaction parameters. The prepolymer reaction changes both and contributes to blend miscibility by changing the entropic and enthalpic contributions through the statistics of the polyaddition reaction.

The increase in the range of miscible compositions observed in Figure 8 is attributed to the introduction of MDI and urethane groups. The favorable contribution to (ΔG^{mix}) from the urethane groups appears to exceed the unfavorable contribution from increasing PPG molecular weight. The SEC results for PPG* (Figures 3 and 4) show that the majority of PPG* products are trimer. However, compatibility is expected to decrease with increasing molecular weight, and the region of compatible compositions in Figure 8 will diminish if the molecular weight of PPG* were to increase significantly during synthesis. Surprisingly, PHMA* prepolymer did not enhance miscibility of the three component system as demonstrated for PPG* (Figure 8).

Table 1 presents experimentally determined binary interaction parameters [13] and critical interaction parameters calculated from Equation (3) for the PPG, PHMA, and P(MMAnBMA) system at 120°C:

$$g_{12}^{\text{critical}} = \frac{(n_1^{-1/2} + n_2^{-1/2})^2}{2}. \tag{4}$$

The critical interaction parameter represents the limiting value for a binary blend to maintain complete miscibility. A blend with an interaction parameter larger than its critical value at a particular temperature is partially miscible. The difference between the experimental and critical interaction parameter is a measure of how far a mixture is from being totally miscible. Table 1 shows that the PPG, P(MMAnBMA) binary blend has an interaction parameter closer to its critical value than other binary blends. The experimental miscibility maps show that the polyether, acrylic binary blend shows dramatic compatibility improvement upon reaction. This argues that the urethane groups reduce the interaction parameter for this blend by at least 0.0032, an 11% reduction. An equivalent 11% reduction in the other binary interaction parameters in Table 1 still leaves them higher than the critical values and consequently results in partial miscibility as observed in Figures 8 and 9.

This analysis is a simplistic evaluation of changes in the interaction parameters necessary to alter the miscibility diagram associated with polyether, polyester, and the polyester acrylic binary blends. The synthesis of polyurethane prepolymers involves a number of structural changes. The most important parameter seems to be associated with details of the specific molecular interactions embodied in the enthalpic binary interaction parameters. The stability of ternary blends is sensitive to the balance between all three binary interaction parameters

TABLE 1 Experimental and Critical Binary Interaction Parameters

Polymer 1	Polymer 2	g(1, 2)	g(crit.)
PPG	PHMA	0.0647	0.053
PPG	P(MMAnBMA)	0.0272	0.024
PHMA	P(MMAnBMA)	0.0233	0.019

g_{12}, g_{13}, and g_{23} as shown in Equation (2), which represents the boundary between positive and negative curvature of the free energy surface. Compositions and temperatures where the curvature is negative are unstable and are stable or metastable when the curvature is positive. The second term on the right-hand side of Equation (2) is always negative. The combination of the three enthalpic interaction parameters (g_{12}-g_{23}-g_{13}) and the entropic ($1/n_3\phi_3$) term determines the magnitude. For a ternary blend to be stable or metastable, the first term in Equation (2) must be positive and greater in magnitude than the second. This criterion means that introduction of specific interactions is not always commensurate with improvement in polymer compatibility for ternary blends. For example, immiscible binary blends can be compatibilized [32] or miscible blends destabilized [33] by the addition of a third component, depending on the sign and relative magnitude of the three interaction parameters. Incorporation of urethane functionalities in another polyurethane blend system based on poly(caprolactone), poly(vinyl chloride) increased the interaction parameter. The blends remain melt miscible, but the addition of specific interactions from the urethane groups competes with the interactions between the repeat units of the polymer chains [34].

CONCLUSIONS

It is clear that the presence of functional groups and molecular weight increase associated with prepolymer synthesis greatly affects the miscibility behavior of multicomponent polyurethane hot melt adhesives. Ternary blends containing the polyether prepolymer reaction products (PPG^*) display an increase in miscible ternary blend compositions in comparison with ternary blends of the starting material. However, blends containing the polyester reaction products ($PHMA^*$) did not improve the compatibility of ternary blends. The polyether-acrylic and polyether-polyester binary blends showed the most significant changes in miscibility due to the prepolymers formed. More detailed analysis of the changes in interchain interaction and molecular weight effects will be reported.

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