

Semi- and Full-Interpenetrating Polymer Networks Based on Polyurethane Produced from Canola Oil and Poly(methyl methacrylate)

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ABSTRACT: Semi- and full-interpenetrating polymer networks (IPNs) were prepared using polyurethane (PUR) produced from a canola oil-based polyol with primary terminal functional groups and poly(methyl methacrylate) (PMMA). The properties of the material were studied and compared using dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and tensile measurements. The morphology of the IPNs was investigated using atomic force microscopy (AFM). Semi-IPNs demonstrated different thermal mechanical properties, mechanical properties, phase behavior, and morphology from full IPNs. Both types of IPNs studied are two-phase systems with incomplete phase separation. However, the extent of phase separation is significantly more advanced in the

semi-IPNs compared with the full IPNs. All the semi-IPNs exhibited higher values of elongation at break for all proportions of acrylate to polyurethane compared with the corresponding full IPNs. These differences are mainly due to the fact that in the case of semi-IPNs, one of the constituting polymers remains linear, so that it exhibits a loosely packed network and relatively high mobility, whereas in the case of full IPNs, there is a higher degree of crosslinking, which restricts the mobility of the chains. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 139–148, 2009

Key words: interpenetrating polymer networks; polyol with terminal functional group; mechanical properties; thermal properties; phase behavior; phase separation

INTRODUCTION

Interpenetrating polymer networks (IPNs) are a special class of polymer blends based on two or more polymers, with each polymer chemically crosslinked or at least one network being synthesized in the presence of the others.^{1–3} Ideally, the interpenetration is of a physical nature, with little or no chemical grafting between the two components.⁴ If both polymers are crosslinked, the material is called a full-IPN. In this type of IPNs, the entanglement of the two crosslinked polymers leads to forced compatibility compared with normal polymer blends and the resulting materials typically exhibit better mechanical properties, increased resistance to degradation and so on. Semi-IPNs differ from full IPNs in that they are composed of a noncrosslinked (thermoplastic) polymer entrapped in another polymer network

(thermoset) and unable to reptate out. All IPNs, similar to most polymer–polymer systems, generally are susceptible to phase separation as a consequence of low entropy of mixing, which leads to a positive Gibbs free energy of mixing.⁵ Generally, the synthesis of IPNs is carried out in a thermodynamically unstable condition. This process starts from thermodynamically equilibrium state with a mixture of the monomer(s) or polymer network swelled in another monomer(s). It is only upon polymerization that thermodynamic incompatibility occurs and the system begins to phase separate. The degree of phase separation observed will depend on the mobility of the polymer chains and on the time required for the chains to become permanently entangled. In other words, the extent of phase separation is a function of kinetics of formation of the growing constituent polymers.^{1,6}

Since IPNs were first prepared and studied by Millar in 1960,⁷ a significant body of literature has been published in this field.^{8–20} It has been found that the morphology and the mechanical properties of the IPN materials obtained depend on reaction kinetics, reaction conditions, and phase behavior. However, most of the polymer couples used for IPNs are traditionally industrially produced from petroleum-based monomers. There is a growing

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worldwide interest to develop novel bio-based products and innovative technologies that can lessen widespread dependence on fossil fuel. Vegetable oils and their derivatives are an important renewable resource for the preparation of monomers and polymers.^{21–26} Over the past few decades, many research groups have focused on the synthesis and characterization of IPN from natural products, such as castor oil, vernonia oil, and lesquerella oil.^{27–32} However, because most of the IPNs derived from renewable resources are full IPNs, there is a paucity of literature available in the area of natural products derived semi-IPNs. One of the more cited references that does examine the properties of semi-IPNs from natural products describes the preparation of semi-IPN from vegetable oils.^{8,33} These authors studied semi-IPNs made from polyethylene terephthalate (PET) with castor oil and vernonia oil based polyurethanes (PURs), respectively. In these semi-IPNs, network formation before or after crystallization of PET and phase separation were found to be the main factors that affect the crystallinity and phase morphology of the final materials, which in turn were the two parameters, which influenced the final physical properties. In addition, Zhang et al.^{34–37} studied semi-IPN materials prepared from castor oil-based PURs and derived variety of natural polymers, such as nitrocellulose, nitrokonjac glucomannan, and benzyl starch. These works demonstrated that the incorporation of the natural polymers into PURs can play an important role in accelerating curing and enhancing biodegradability.

Recently, a new type of polyol with terminal functional groups from vegetable oils using ozonolysis and hydrogenation technology has been invented.^{25,38} This type of polyol has been used successfully to produce full IPNs, which demonstrated significantly different physical properties and phase behavior when compared with full IPNs produced from castor oil.³⁹ In this article, we report on the properties of semi-IPNs prepared using polyol with terminal functional groups synthesized from canola oil and linear poly(methyl methacrylate) (PMMA) thermoplastics and compare them with full IPNs made from the same raw materials. The thermal properties and phase behavior of the IPNs were studied using dynamic mechanical analysis (DMA), and differential scanning calorimetry (DSC) techniques. The morphology of the IPNs was investigated using atomic force microscopy (AFM). It was found that semi-IPNs shown different thermal mechanical properties, mechanical properties, phase behavior and morphology from full IPNs. It was, however, demonstrated in this work that in both cases (semi and full IPNs), the combination of PUR with PMMA, is useful in extending the elastic properties of PUR and mitigating the brittleness of PMMA.

EXPERIMENTAL

Materials

Canola oil used in this study was a sample of “100% Pure Canola” supplied by Canbra Foods Limited. Canola oil-based polyol with terminal primary hydroxyl groups was synthesized using ozonolysis and hydrogenation-based technology and the procedure was reported in detail elsewhere.^{21,38} The hydroxyl number of the polyol was 237 mg KOH/g, as determined according to the ASTM D1957-86. The polyol contained 60.18 ± 1.16 wt %, 26.00 ± 0.48 wt %, and 4.72 ± 0.03 wt % of triol, diol, and mono-ol, respectively.²¹ The remainder about 9 wt % was composed of saturated triacylglycerols (TAGs). Aliphatic 1,6-hexamethylene diisocyanate-(HDI) based polyisocyanate (Desmodur N-3200) was sourced from Bayer Corporation, Pittsburgh, PA. Its functionality was 2.6 and equivalent weight was 183 as provided by the supplier. Benzoyl peroxide (BPO), 97%, and ethylene glycol dimethacrylate (EGDM), 98%, were obtained from Aldrich Chemical (USA). Methyl methacrylate (MMA, 99%) was purchased from Acros Organics (USA). BPO was recrystallized from methanol before use. MMA was washed twice with 5% aqueous NaOH and twice with distilled H₂O, dried with CaCl₂, filtered, kept at 5°C over MgSO₄ for 24 h and distilled at 100–101°C.

PUR and PMMA synthesis

The PUR prepolymer was prepared by fixing the molar ratio of the isocyanate (NCO) group to the OH group (NCO/OH) at 1.6/1.0. A suitable amount of polyol and HDI were weighed in a plastic container and mixed thoroughly at room temperature for 20 min. The prepolymer was isolated as thick syrup and was immediately used for IPN synthesis. Pure PUR specimens were also prepared using the same procedure followed by postcuring at 50°C for 24 hr.

Pure crosslinked PMMA specimens was prepared in the following procedure: a suitable amount of MMA, 0.5% of BPO initiator, and 1% of EGDM crosslinker (this compound was not included in the case of linear PMMA) was stirred at room temperature for 5 min to form homogeneous solution, followed by raising the temperature to 60°C. After stirring for 60 min, the solution was poured into a Teflon mold and was kept at 60°C for 24 h and then at 120°C for 4 h before demolding.

Semi- and Full-IPNs synthesis

Semi-IPNs were synthesized sequentially using various proportions of PUR and PMMA from 100 : 0 to 45 : 55, 35 : 65, 25 : 75 and 0 : 100. PUR prepolymer was poured in different mass proportions into a round bottom flask. To this, a suitable amount of

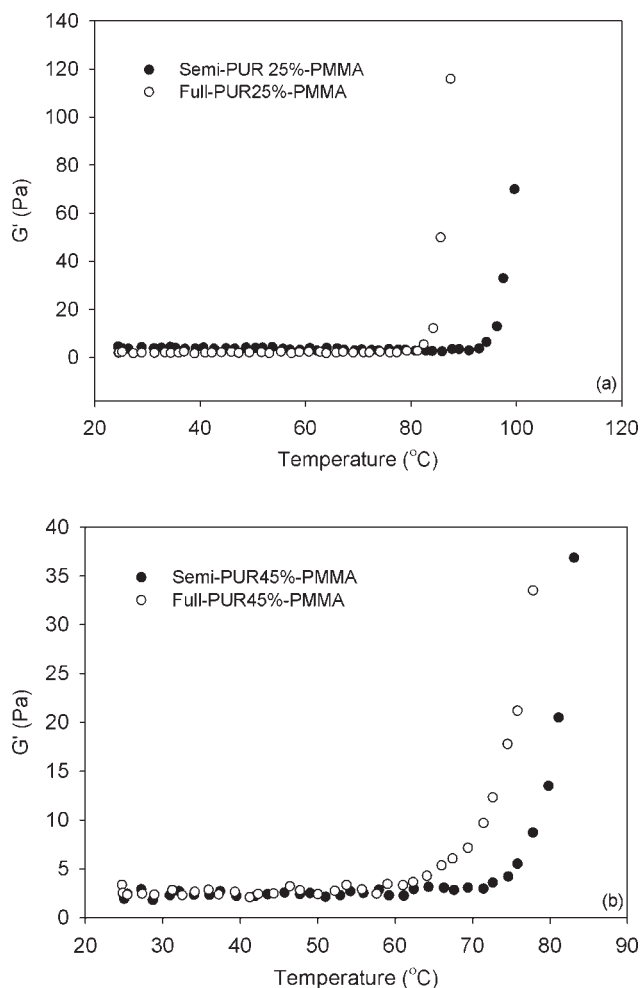


Figure 1 Storage modulus (G') as a function of temperature for the curing/polymerization process for both semi- and full IPNs with (a) 25% of PUR content and (b) 45% of PUR content.

MMA, and 0.5% of BPO initiator was added. The mixture was stirred at room temperature for 5 min to form homogeneous solution. Then the tempera-

ture was raised to 50°C to initiate the radical polymerization of MMA along with added crosslinker. After stirring for 30 min, the solution was poured into a Teflon mold kept in a preheated air circulating oven maintained at 60°C. It was kept at this temperature for 24 h and then at 120°C for 4 h before demolding. Full IPNs were synthesized in the same way as the semi-IPNs except that the 1% of crosslinker for PMMA, that is, EGDM, was added, thereby maintaining PMMA as a crosslinked polymer. The nomenclature used for these IPNs as listed in Table I are identified as follows: the number represents the weight percentage of PUR in the IPNs, whereas Semi- and Full- stand for the type of IPNs.

Degree of conversion

Degree of conversion measurements were carried out on a MDSC Q100 (TA Instruments, USA) equipped with a refrigerated cooling system. The procedure was as follows: the samples were transferred to DSC chamber immediately after the stirring procedure, heated to 60°C, and held isothermally until DSC could not detect any heat flow. The degree of conversion was calculated according to the following equation:

$$\alpha_t = \frac{\Delta H_t}{\Delta H} \quad (1)$$

where α_t is the degree of conversion of reaction, and ΔH_t is the heat generated up to time t , ΔH is the total exothermic heat involved in the reaction.

The glass transition temperature (T_g) of IPN samples was measured using the following DSC procedures: the samples were heated at a rate of 10°C/min from 25°C to 150°C to erase thermal history, cooled down to -60 °C at a cooling rate of 5°C/min then heated again to 150°C at a heating rate of 10°C/min. The second heating stage was selected to

TABLE I
Variable Manipulation and T_g of All the Semi-IPNs and Full IPNs Determined by DMA and DSC. Errors are Standard Deviations; $n = 3$

	PUR content (wt %)	PMMA content (wt %)	DMA			DSC	
			T_{g1} (°C)	T_{g2} (°C)	T_{g3} (°C)	T_{g1} (°C)	T_{g2} (°C)
Semi-Pure-PMMA	0	100			129 ± 1		112 ± 1
Semi-PUR15%-PMMA	15	85	55 ± 1		134 ± 1	27 ± 1	119 ± 1
Semi-PUR25%-PMMA	25	75	52 ± 1		137 ± 1	28 ± 1	120 ± 1
Semi-PUR35%-PMMA	35	65	53 ± 1		138 ± 2	26 ± 1	123 ± 1
Semi-PUR45%-PMMA	45	55	50 ± 1		138 ± 1	25 ± 0	123 ± 1
Full-Pure-PMMA	0	100			134 ± 1		115 ± 1
Full-PUR15%-PMMA	15	85	52 ± 1	113 ± 1	130 ± 1	25 ± 1	116 ± 1
Full-PUR25%-PMMA	25	75	50 ± 1		128 ± 1	30 ± 0	120 ± 1
Full-PUR35%-PMMA	35	65	36 ± 1		131 ± 2	34 ± 1	121 ± 1
Full-PUR45%-PMMA	45	55	26 ± 1	93 ± 1	135 ± 1	27 ± 1	123 ± 1
Pure-PUR	100	0	23 ± 1			20 ± 1	

be analyzed for the collection of heating data. All the DSC measurements were performed following the ASTM E1356-03 standard procedure under a dry nitrogen gas atmosphere.

DMA measurements

DMA measurements were carried out on a DMA Q800 (TA Instruments, USA) equipped with a liquid nitrogen cooling apparatus, in the single cantilever mode, with a constant heating rate of 1°C/min from -60°C to +150°C. The size of the samples was 18 × 7 × 2 mm. The measurements were performed following ASTM E1640-99 standard at a fixed frequency of 1 Hz and a fixed oscillation displacement of 0.015 mm.

Atomic force microscopy

Morphology analysis of the IPNs was done by AFM using a Digital Instruments Multimode Scanning Probe Microscope equipped with Nanoscope IIIa Controller (Digital Instruments, Veeco Metrology Group, USA) at ambient conditions. Sections of 500 nm obtained using ultramicrotome (MT6000, Sorvall Instruments) and placed on a silicon wafer were attached onto iron AFM substrate disks using double-sided tape. Images were obtained in tapping mode using commercial silicon microcantilever probes (MikroMasch, USA) with a tip radius of 5–10 nm and spring constant 2–5 N/m. The probe oscillation resonance frequency was ~ 120 kHz, and scan rate was 1 Hz. The operations were carried out at the hard tapping region such that in the phase images bright domains are attributed to PMMA phase and dark domains the PU phase.

Mechanical properties

The tensile property of the IPNs was conducted on an Instron 4202 according to ASTM D638 standard. Dumbbell-shaped specimens were cut out from the IPNs using an ASTM D638 Type V cutter. The measurements were performed at room temperature with crosshead speed of 50 mm/min and a load cell of 50 Kgf. The data presented were average of five different measurements. The reported errors are the subsequent standard deviations.

RESULTS AND DISCUSSION

The formation of IPNs is a complex process, because different chemical reactions are involved; the free-radical polymerization of MMA and the curing process of PURs. In the case of curing, gelation is the most significant phenomenon. Gelation occurs when the reaction products form a three-dimensional net-

work, which gives rise to a considerable increase in viscosity and the development of elastic properties that do not exist in the pregel materials. The rate of gelation process of PUR component in the reaction mixture is significantly affected by the presence of the second component.

The rheological properties during curing/polymerization process of the IPN samples were studied under nonisothermal conditions. Attempts to measure gel point for IPN samples using this method were not successful from a quantitative perspective, because evaporation of MMA monomer occurred during the period of measurement. However, modulus changes with temperature for semi-PUR25%-PMMA and full-PUR25%-PMMA are shown in Figure 1(a), and semi-PUR45%-PMMA and full-PUR45%-PMMA are shown in Figure 1(b), as examples. From both figures, it is clear that the storage modulus for full IPNs started to increase at lower temperatures compared with those of semi-IPNs, even if precise quantitative gel point data are lacking. This result suggests that full IPNs react faster than semi-IPNs, at least for these types of materials. Additionally, for both types of IPNs with higher PUR content, the storage modulus started to increase at lower temperatures, which indicated that the reaction rates increased with the increasing of PUR content. From these results, one can assume that the gelation process observed from rheological experiments performed at nonisothermal conditions involves both the PUR curing and also the MMA polymerization. This result could be further confirmed by analyzing conversion-time profiles.

The conversion-time profiles of semi- and full IPNs with PUR content of 25% and 45% are shown in Figure 2(a,b), respectively. It is obvious that the reaction rates of full IPNs are faster than those of semi-IPNs. As mentioned previously, the formation of IPNs is a complex process. The rates of formation of the two components in the IPNs are interconnected and are not equal to the reaction rates for pure components; the change in the reaction rate of one of the networks is reflected in the reaction rate of the other. Additionally, the change of reaction rates of both IPNs with the concentration of PUR content is significant: the reaction rates increased with the increasing of PUR content. By comparing Figure 2(a,b), it is obvious that the same component, depending on its concentration in the reaction mixture, can cause significant differences in the overall reaction rates in the case of the IPNs with 25% PUR content, or just slightly affect the overall reaction rates as in the case of the IPNs with 45% PUR content. This suggests that the presence of PUR network might promote chain extension of MMA. The earlier results could be further explained by considering the formation process of IPNs. The synthesis of both

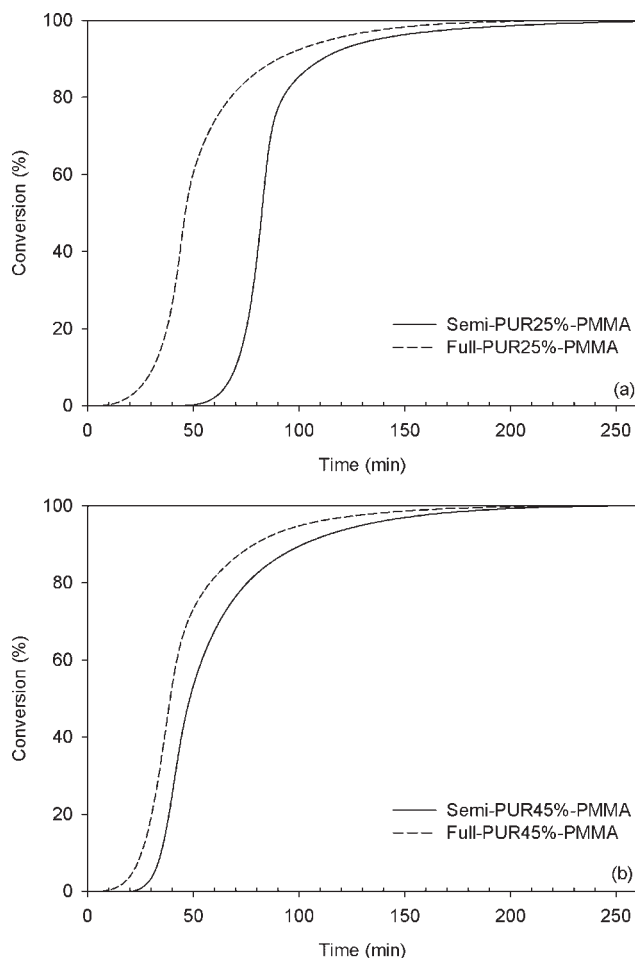


Figure 2 The conversion-time profiles of both semi- and full IPNs with (a) 25% of PUR content and (b) 45% of PUR content.

IPNs is carried out in the thermodynamically unstable conditions. It starts from a thermodynamically equilibrium state with a mixture of PUR network swelled with MMA monomer. During the process of polymerization, the combinatorial entropy of mixing of the system decreases significantly due to the transition of monomer molecules into polymer chains. As the Gibbs energy of mixing depends on the enthalpy and entropy of mixing, because of the decrease of entropy of mixing the Gibbs energy of mixing could become positive resulting in the phase separation of the system.⁵ The phase separation would then lead to diffusion of monomers, and MMA would start to polymerize. Whether or not MMA monomers are in the PUR network or separated phases, chain extension (reaction) would continue as long as free radicals exist. Nevertheless, the process of phase separation may be stopped at different stages with the increasing of system viscosity and the forming of permanent entanglements of the chains up to the gel point. In the case of full IPNs, the PMMA compound is a crosslinked network, and

therefore, once it is formed, it will act as a permanent entanglement restraining phase separation. Thus, the extent of phase separation in full-IPN systems is lower; the MMA monomers are better mixed with PUR network, which is further discussed in detail below by analyzing $\tan \delta$ spectra. Meanwhile, because chain extension of MMA could be promoted by the existence of PUR network, the reaction rates of full IPNs are faster than those of semi-IPNs.

The degree of phase separation of the IPNs is one of the most important factors, which determine the viscoelastic properties of these multicomponent materials. DMA was used to characterize indirectly the microstructure of the materials and to establish structure–property relationships. The dependences of $\tan \delta$ on temperature for semi- and full IPNs with various PUR/PMMA ratios are shown in Figure 3(a,b), respectively, and the maximum relaxation temperatures are listed in Table I. It is shown that PUR has one sharp relaxation peak corresponding to the α -relaxation (glass transition). Two relaxation peaks were detected for both pure linear PMMA and crosslinked PMMA: a small β -relaxation around 30°C corresponds to the rotation of ester groups in the PMMA, and a big α -relaxation, i.e., glass transition at 134°C due to the main chain segmental motions in PMMA. In the case of semi-IPNs as presented in Figure 3(a), the amplitude of the PUR α -relaxation peak increases with increasing PUR content, but the maximum value of this relaxation shifts to higher temperature (around 50°C) compared with that of pure PUR (23 °C). This shift suggests that a higher amount of energy is required to promote PUR chain segmental motions in the semi-IPNs, which are probably hindered by the PMMA phase. Simultaneously, the amplitude of PMMA α -relaxation peak decreases with the increasing of PUR content, but the location of this relaxation shifts to higher temperature (in the range of 134–138 °C) than that of pure PMMA (129°C). A confined PMMA chains environment inside the PUR network might be responsible for this increase of relaxation temperature. A similar behavior has been observed for polyisobutene/PMMA IPNs.⁴⁰ In the case of full IPNs as shown in Figure 3(b), features different to those of the semi-IPNs were obtained; the degree of phase separation depends not only on the IPN composition but also on the crosslinking characteristic of both components. Different from semi-IPNs, for which the maximum values of PUR α -relaxation are constant, the maximum value of PUR α -relaxation of full IPNs shifts from 52°C to 26°C with the increasing of PUR content. In addition, another relaxation peak located at 93°C, which was assigned to the interphase is observed for Full-PUR45%-PMMA. This “interphase” is the nonequilibrium transition zone from one phase to another; its size depends on

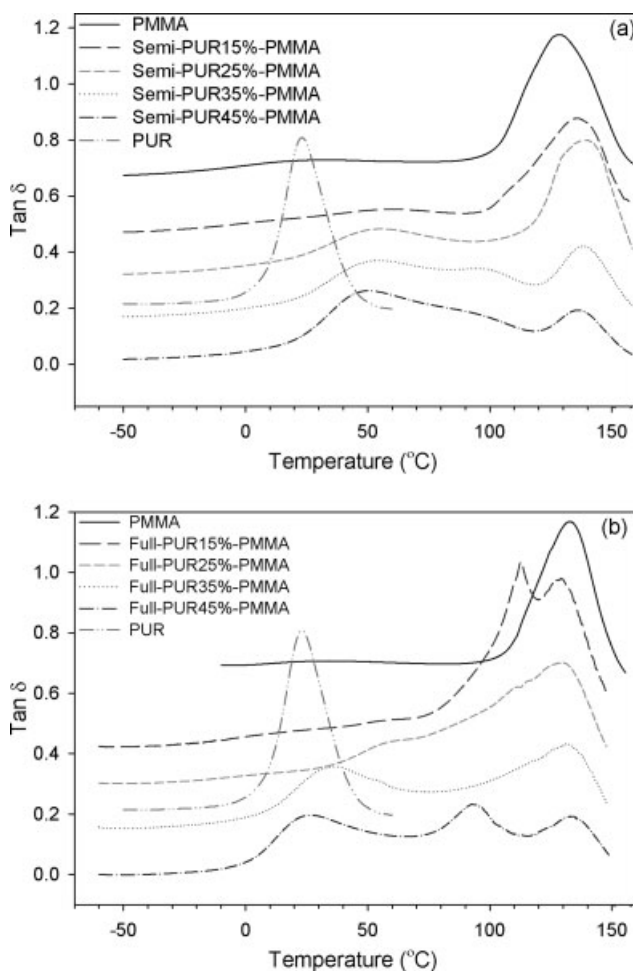


Figure 3 The dependences of $\tan \delta$ on temperature for IPNs with different PUR content (a) semi-IPNs, and (b) full IPNs. The curves were shifted vertically to discriminate peaks. The values in the bracket are the shifting degree of individual samples: PMMA (0.7), PUR15%-PMMA (0.45), PUR25%-PMMA (0.35), PUR35%-PMMA (0.15), and PUR (0.25).

the conditions of phase separation. It is worth pointing out that a vague relaxation peak (around 100°C) is also noticed for semi-PUR35%-PMMA and semi-PUR45%-PMMA. Nevertheless, this peak is not well resolved, which might be due to the fact that the sizes of these phases are too small to be detected. It was reported² that the domain dimensions at which the transition temperature could be detected by DMA has a lower limit of 15 nm. However, this interphase is well resolved in the full-PUR45%-PMMA sample, which is probably due to the crosslinking characteristics of both PUR and PMMA compounds, which prevents vigorous phase separation in the resultant IPNs. Another possible reason is the faster reaction rate of full-PUR45%-PMMA, which effectively prevents diffusion (caused by phase separation) of MMA components. In other words, it is a result of the balance between thermodynamics and

kinetics because thermodynamic equilibrium would be kinetically limited.

The existence of the interphase could be further explained by consideration of the formation process of IPNs. The formation of IPNs obeys the general rules of polymer network formation but is also much more complicated because the reaction is accompanied by phase separation. The main role in the process is played by the superposition of the chemical kinetics of the synthesis of two networks and of the physical kinetics of the phase separation; its driving force being the appearance of the thermodynamic incompatibility of two components at a defined conversion degree. Both processes proceed under nonequilibrium conditions. As discussed previously, during the transition of the system from the one-phase state into the metastable and unstable stages, the stable chain entanglements caused by physical or chemical crosslinking do not allow the full separation of network fragments and the system stays in the state of forced compatibility. This state makes an additional contribution to the free energy of the system. The contribution of the elastic energy is small at the onset of phase separation and increases with growth in the composition difference of phase-separated regions. As a result, the system is stabilized when the thermodynamic force of phase separation is balanced by the elastic forces from entanglements of the network fragment. Therefore, the system might remain in two states: a state of forced compatibility and a state of forced phase separation.¹ The formed phases may be considered as quasi-equilibrium with a molecular level of mixing. The degree of phase separation depends on the system composition and kinetic conditions of reaction. For full IPNs, both polymers are crosslinked, the entanglement of the two crosslinked polymers leads to stronger forced compatibility, therefore, less extent of phase separation. The incomplete phase separation leads to the formation of transition regions between two phases. This is the part of the system remaining for kinetic reasons in the unseparated state and preserving the structure of the reaction mixture before the onset of phase separation.

The phase behavior of semi- and full IPNs was also evaluated by DSC. The DSC curves of semi-IPNs with various PUR/PMMA ratios are shown in Figure 4 as an example. T_g s of these IPNs are listed in Table I. T_g s of full IPNs with various PUR/PMMA ratios are listed in Table I as well. The values are lower than those determined from DMA (usually up to 10°C lower) due to the dynamic nature of the test, but the trend is the same: with the increasing of PUR content, T_g s of PUR phase and PMMA phase in the semi-IPNs are slightly shifted toward higher temperatures compared with corresponding T_g s of pure PUR and linear PMMA.

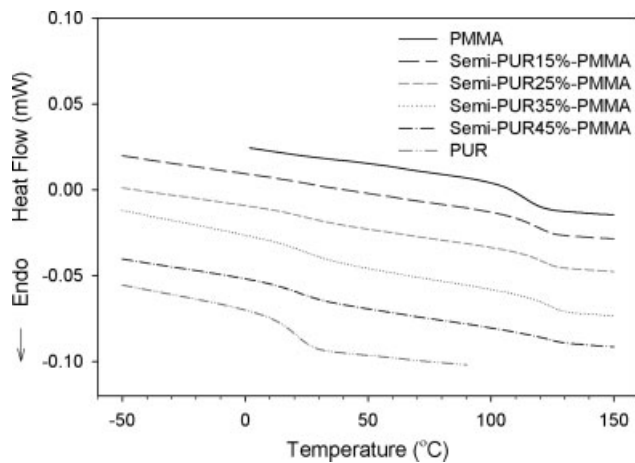


Figure 4 DSC curves of semi-IPNs with various PUR/PMMA ratios. The curves were shifted vertically to discriminate transitions.

However, in terms of full IPNs, the existence of the interphase was not observed owing to the low sensitivity of the DSC technique. DSC measures the change in heat capacity when chains go from the glassy to the nonglassy stage, which corresponds to a large scale of motion of whole molecules or groups of several molecules. In contrast, DMA measures the change in mechanical response of chain segments within these chains, which may be influenced to a much greater extent by phase continuity.⁴¹ In other words, a single T_g in the DMA spectrum indicates total segmental interpenetration, whereas a single T_g in the DSC analysis implies mixing at least on the level of small clusters of molecules. Thus, although DMA relaxation indicates there are phase separations with PUR, PMMA rich phases and interphase, DSC analysis shows that there is some mixing on a

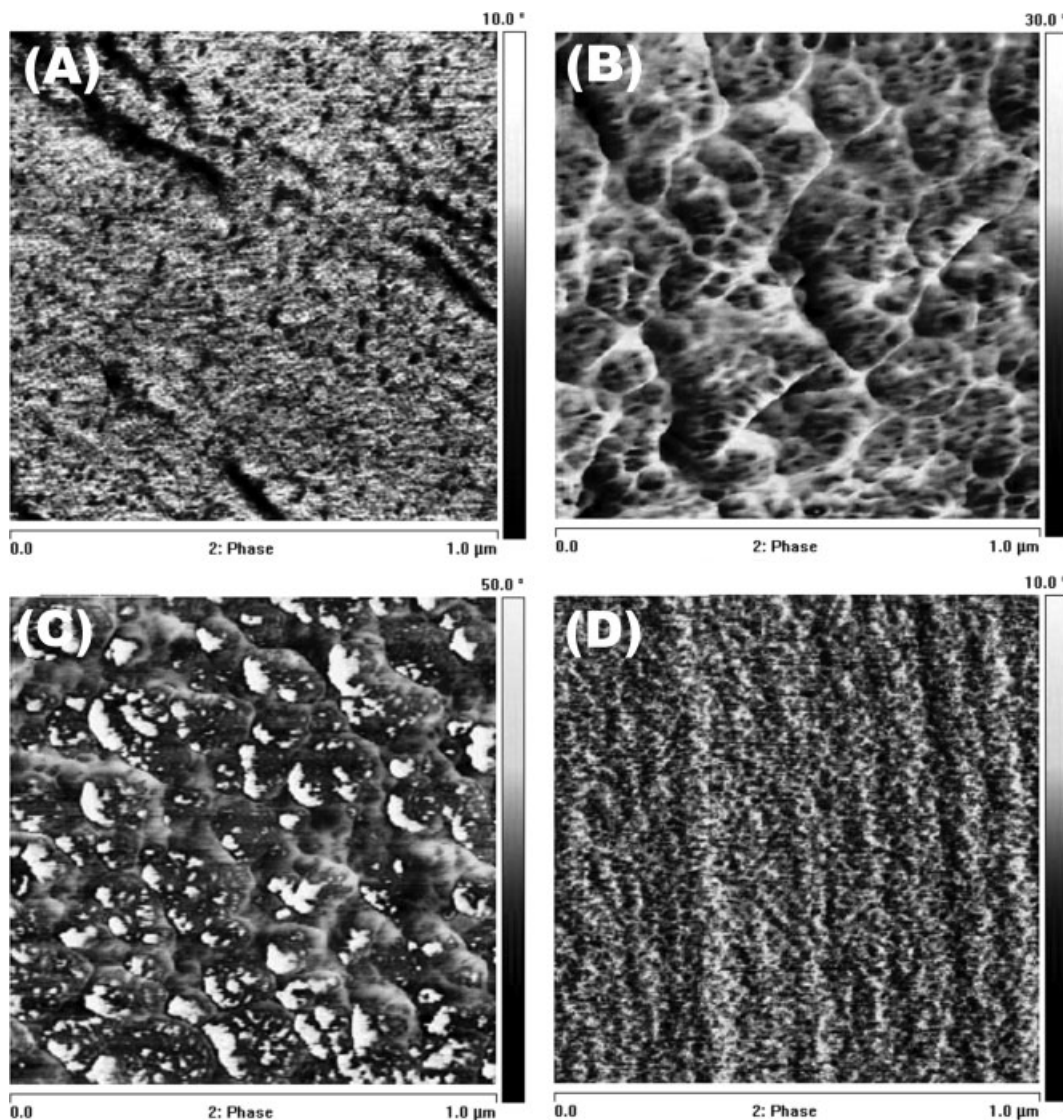


Figure 5 Atomic force micrographs for semi-IPNs with various PUR/PMMA ratios (a) semi-PUR15%-PMMA, (b) semi-PUR25%-PMMA, (c) semi-PUR35%-PMMA, and (d) semi-PUR45%-PMMA.

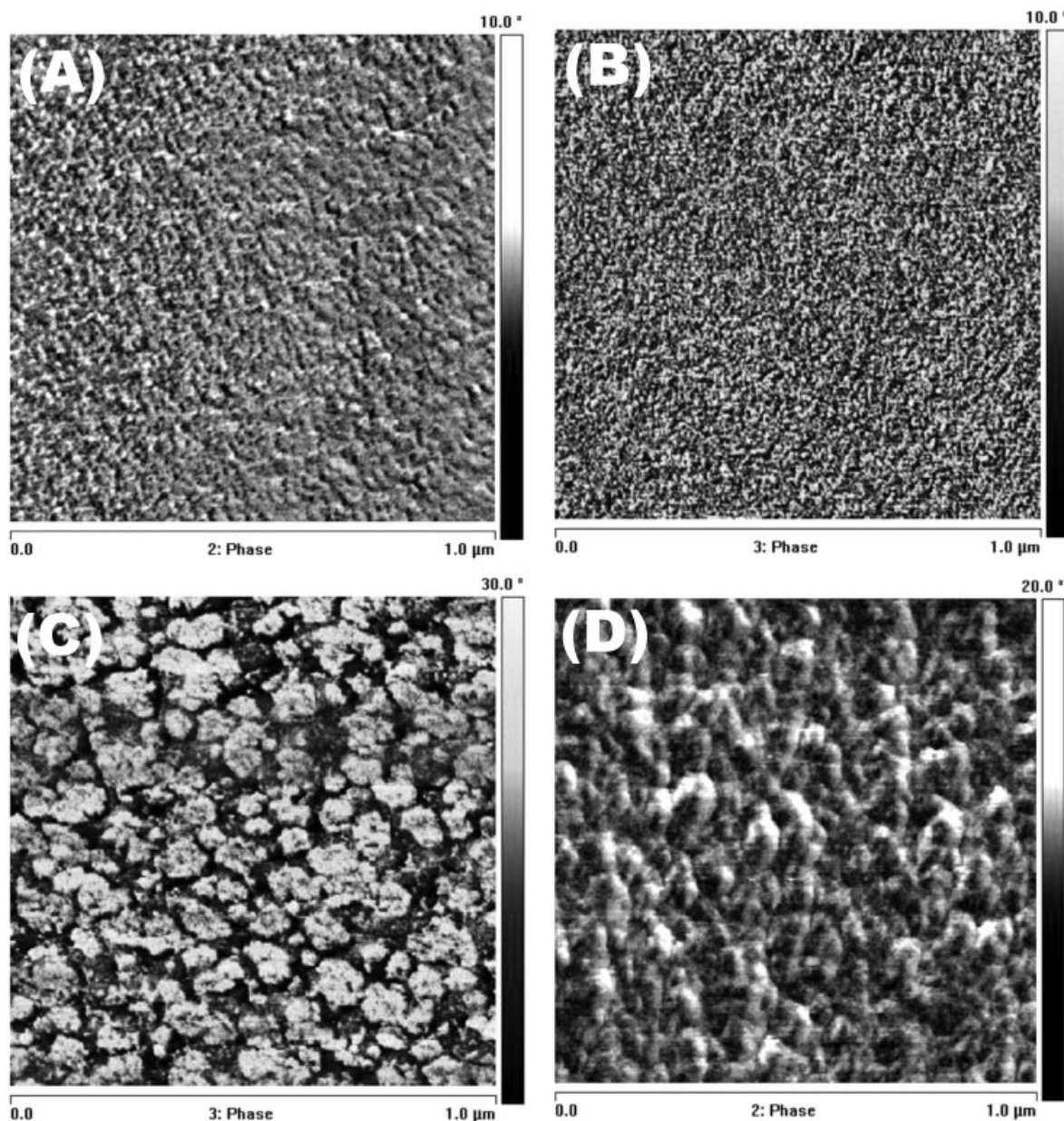


Figure 6 Atomic force micrographs for full IPNs with various PUR/PMMA ratios (a) full-PUR15%-PMMA, (b) full-PUR25%-PMMA, (c) full-PUR35%-PMMA, and (d) full-PUR45%-PMMA.

larger scale between interphase with PUR and PMMA rich phases. Therefore, the DMA technique provides more easily distinguishable values.

This system of polymers does not lend itself to an effective staining protocol, which can be used for transmission electron microscopy analysis. Therefore, in this study, we used AFM to study the morphological characteristics. It has been reported^{42–45} that via phase imaging under moderate tapping conditions a strong correlation could be revealed between phase shift of the oscillating AFM cantilever and local stiffness in multiphase polymer systems, which consists of, in our IPNs systems, plastic PMMA and elastic PUR domains. Because the same

AFM probe was used in these measurements, the contrast in the phase images strongly depends on the physical properties of the materials. The elastic PUR regions cause a stronger phase shift (dark in images), whereas the plastic PMMA domains generate less phase shift (bright in images). As presented in Figures 5 and 6, nanophase separation of PMMA and PUR is observed in all cases. It is noticed that the observed morphologies are quite different. Figure 5 shows representative phase images of semi-IPNs with various PUR/PMMA ratios. For semi-PUR15%-PMMA, PUR forms either spherical or cylindrical domains of 20–50 nm in the PMMA matrix. Cell structure with three phases: PMMA dominated

walls of 20 nm, spherical PUR dominated nuclei of ~ 50 nm, and PMMA/PUR coexisted phase was observed for the semi-IPNs containing 25% PUR. For semi-PUR35%-PMMA, phase reversion was observed, mostly with PMMA rich domains of 20–100 nm dispersed in PMMA/PUR coexisting matrix. For semi-PUR45%-PMMA, a defined morphology was observed. PUR became the continuous phase while PMMA became dispersed domains of ~ 20 nm confined in the continuous PUR phase.

For the full IPNs, apparently crosslinking of both components resulted in further inhibition of phase separation. For the two IPNs with PUR content of 15% and 25%, PMMA formed continuous matrix phase, whereas PUR formed small domains of ~ 15 nm dispersed in PMMA matrix. For full-PUR35%-PMMA, phase separation and inversion became more prominent; according to the phase contrast PUR formed a matrix phase and the PMMA formed dispersed domains of ~ 100 nm. For full-PUR45%-PMMA, we observed three-phase morphology—PMMA-rich, PUR-rich, and PMMA-PUR coexisting phases; all the phases interconnected together and formed a gradient contrast in the image.

The stress vs. strain curves of semi-IPNs with various PUR/PMMA ratios are presented in Figure 7. These curves indicate that the ultimate strength and Young's modulus increase with increasing of PMMA content in semi-IPNs. At the same time, the elongation at break decreases with increasing of PMMA content. The curve of PUR is a typical curve usually observed for elastomers. For semi-IPNs with content of PUR 25–45%, the polymers behave as a hard rubber with long elongation. For semi-PUR15%-PMMA and pure linear PMMA, the mechanical properties changed to a rigid and tough plastic. The mechanical properties for full IPNs have been reported in detail elsewhere.⁴⁶ The differences in mechanical proper-

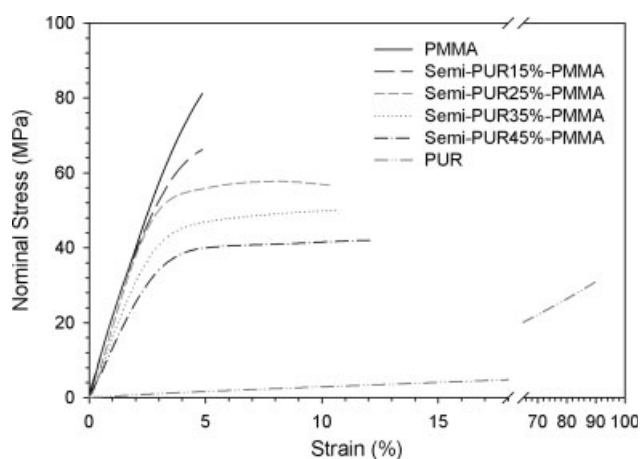


Figure 7 Stress vs. strain curves for semi-IPNs with various PUR/PMMA ratios.

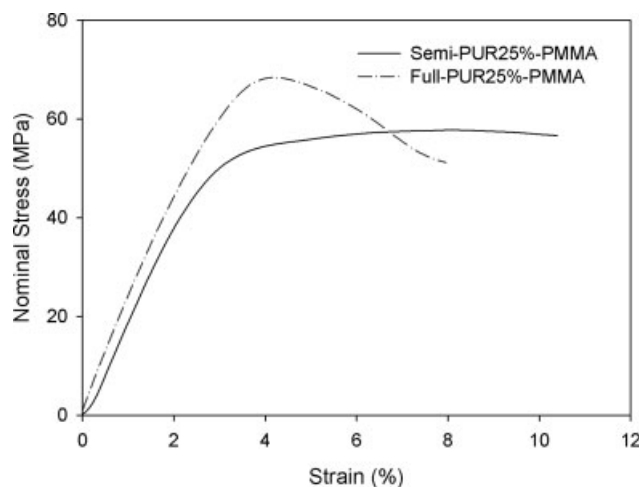


Figure 8 Comparison of stress vs. strain curves for semi-PUR25%-PMMA and full-PUR25%-PMMA.

ties between semi- and full IPNs could be clearly observed, especially for those IPNs with content of PUR 15–35%. It was found that all the semi-IPNs, exhibited higher values of elongation at break for all proportions compared with the corresponding full IPNs. The stress vs. strain curves of semi- and full IPNs with PUR/PMMA ratio 25/75 are presented in Figure 8 as an example. It is clear that Full-PUR25%-PMMA has a typical mechanical property of a ductile thermoset with a yield strength of 67 ± 1 MPa, whereas semi-PUR25%-PMMA has the typical mechanical properties of hard rubber with elongation at break of $10 \pm 1\%$. This is probably due to the different degree of phase separation and formation of different structures in semi- and full IPNs as shown in Figures 5 and 6. The full IPNs samples with early stage of phase separation demonstrate higher mechanical properties because of the finely divided rubber and plastic combination structures. Furthermore, this can be explained by considering the fact that in the semi-IPNs, because one of the constituting polymers (PMMA) remains linear, it exhibits a loosely packed network and high mobility, whereas in the case of full IPNs the higher degree of crosslinking restricts the mobility of the chains, because they are crosslinked.

CONCLUSIONS

Semi-IPNs have been successfully synthesized from canola oil-derived polyol with terminal functional groups and PMMA. The physical properties of these semi-IPNs are compared with those full IPNs made from the same materials. For both types of IPNs, the reaction rates increase with the increasing of PUR content. With the same components, the reaction rates of full IPNs are faster than those of semi-IPNs.

The morphology investigated by AFM demonstrates that the structures of the two types of IPNs are completely different, and these results are in agreement with mechanical properties of these IPNs. Both types of IPNs studied are two-phase systems with incomplete phase separation. However, the process of phase separation is more developed in the semi-IPNs compared with the full IPNs. The full IPNs exhibited better compatibility because of the enhanced interpenetration, as revealed by AFM. In both cases, the combination of PUR with PMMA is useful in extending the elastomeric properties of PUR and mitigating the brittleness of PMMA.

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