Thermal and Rheological Characterization of Semi-II Interpenetrating Polymer Networks from Poly(methyl methacrylate) and Castor Oil-based Polyurethane

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The synthesis and characterization of semi-II interpenetrating polymer networks (IPN) based on poly(methyl methacrylate) (PMMA) and on castor oil polyurethane (PU) of composition 70/30 are reported. Various degrees of crosslinking of the PU phase were obtained by varying the weight ratio of HDI/N-100 while maintaining the NCO/OH ratio fixed at 1.5. Thermal characterization was performed by thermomechanical analysis (TMA), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Two distinct glass transition temperatures were observed, indicating a two-phase morphology. This was also supported by scanning electron microscopy (SEM) observations. Rheological characterization was performed using a capillary rheometer. Shear thinning flow behaviour and reprocessing were confirmed for all semi-II IPN. All the results demonstrate that a higher crosslinking level leads to better overall properties.

Keywords: Interpenetrating polymer networks; poly(methyl methacrylate); polyurethane; thermomechanical analysis; thermogravimetric analysis; scanning electron microscopy; capillary rheometer

INTRODUCTION

Interpenetrating polymer networks (IPN) typically comprise two crosslinked polymer networks that are physically interpenetrated. Semi-IPN consist of linear polymer chains threaded through a crosslinked polymer network. Depending upon whether the component I or II of the system

is crosslinked, the resulting semi-IPN is called semi-I or semi-II IPN. In all cases, two polymers are brought into intimate contact to create some extent of miscible morphology, although there is no chemical linkage between them. Factors affecting the IPN morphology and consequently their properties include polymerization sequence, composition, crosslink density, miscibility of the polymer in the monomer and polymer pair compatibility.[1-2] Polymerization and crosslinking lead to a reduction in the entropy of mixing and tend to induce phase separation. The crosslinking in the two networks provides to IPN a thermoset character that poses a practical limitation: IPN cannot be processed or reprocessed by thermoplastic methods and machinery. However semi-IPN may be processed, owing to the absence of crosslinking in one of the two components or phases. An understanding of rheology of semi-IPN is the key to effective design of their processing. In related work[3] involving full IPN based on crosslinked PMMA and crosslinked castor-oil based polyurethane (PU), it was found that their mechanical properties are synergistically high due to a fully developed network between the two phases, as well as a chain transfer phenomenon. However, this system has a fully thermoset behavior, making it infusible. It is expected that if the crosslinking density of one of the two phases is lowered, the overall properties of this IPN system will consequently be decreased for the benefit of making it reprocessable as the relevant phase becomes completely uncrosslinked.

The purpose of this work is to investigate the thermal and rheological behavior of semi-II IPN based on uncrosslinked PMMA and variably crosslinked PU produced from castor oil[4-9] and a mixture of hexamethylene diisocyanate (HDI) and Desmodur N-100.[10-11] The latter played the role of crosslinking agent where its composition with respect to HDI will vary the crosslinking density of PU. The PMMA phase used 2,2' azobisisobutyronitrile (AIBN) as the initiator. The semi-II IPN were produced using bulk polymerization process. As the polymerization time of MMA is longer than that of castor oil, HDI and N-100, the former was allowed to start first, therefore resulting in a sequential type of semi-II IPN.

Thermal characterization may be performed by analyzing two criteria: glass transition temperature (T_g) and heat resistance. The former may be used to evaluate the degree of miscibility of two components. A single and narrow peak on a thermograph indicates high miscibility. A very broad glass transition range or two distinct $T_g s$ represents a heterogeneous composition. Heat resistance as a function of thermal degradation may be used in the same fash-

ion. A uniform one-step degradation indicates high miscibility, whereas a two or multi-step one represents heterogeneity within the IPN/semi-II IPN system.

Several methods exist for measuring rheological properties, more specifically viscosity, of melted polymers. These techniques include solution viscometry, rotational and oscillatory methods, and controlled stress techniques.[12] To accurately study polymer rheology under the conditions with which these polymers will be processed in industry, certain requirements must be met. The technique must be capable of taking several multi-point measurements since single point measurements of non-Newtonian melt polymers can be misleading.[12] Temperature control and measurement must be very accurate since melt polymer viscosity is highly sensitive to temperature fluctuation. Lastly, the technique must be able to handle highly viscous polymer melts, requiring a plunger to exert an external and measurable force on the melt. The capillary rheometer is a popular method used throughout industry because it satisfies all the aforementioned requirements. This instrument forces polymer melts to flow through a capillary of known dimensions.

EXPERIMENTAL

Materials

Castor oil was obtained from Aldrich Chem. Co. Its equivalent weight per hydroxyl group is equal to 373.2 g. Desmodur N-100 is a clear, slightly yellow, viscous, and solvent-free liquid. It is composed of an aliphatic polyisocyanate resin based on HDI, and its equivalent weight per NCO group is 191 g. It was supplied by Mobay Co. through Bayer Canada. HDI was obtained from Aldrich and its NCO equivalent weight is 84 g. They were used as received without further purification.

Methyl methacrylate (MMA) was supplied by Aldrich. It was washed with an aqueous solution of NaOH (5%) to remove inhibitors and then dried over molecular sieves prior to use. AIBN was purchased from Aldrich.

Synthesis of Semi-II IPN PMMA/PU

MMA with 0.5% AIBN were introduced into a flask equipped with a reflux accessory. The mixture was heated to 67°C and continuously stirred with a poly(tetrafluoroethylene)-coated magnetic stir bar for 3 hrs. Predetermined amounts of castor oil, HDI and N-100 were then simultaneously introduced

into the flask. These were based on a NCO/OH ratio of 1.5. Table I shows the quantity of each constituent used in the synthesis based on 10 g of castor oil. The resulting global mass of the semi-II IPN produced was enough to conduct the rheological tests. The vigorous agitation continued for 3 hrs until the mixture became thick enough, before it was poured into poly(tetrafluoroethylene) molds. The samples were cured for 16 hrs in an oven at 70°C. The products obtained were semi-transparent and of golden color. The loss of MMA monomers through the synthesis process was approximately 5%. This was checked by the difference of the total weight of chemical reactants and that of semi-II IPN produced.

Characterization

Thermomechanical Analysis (TMA)

The glass transition temperatures were determined by TMA using a Mettler TA-4000 with a TMA 40 measuring cell linked to a processor TA 11. Approximate sample dimensions were 3 mm thick in the direction of measurement and 6 mm in diameter. Measurements were carried out in the range of –70 to 150°C at 20°C·min^{-1}, and a constant probe force of 0.02 N was applied to the sample.

Differential Scanning Calorimetry (DSC)

The glass transition temperatures were determined by DSC using a Mettler TA-3000 with a DSC 20 measuring cell linked to a processor TA 11. Measurements were carried out in the range of 30 to 200°C at 10°C·min^{-1}.

TABLE I   Quantity of constituents used in the synthesis of the semi-II IPN 70/30 PMMA/PU with an NCO/OH ratio = 1.5 in terms of equivalent-weight. Amounts are based on 10 g of castor oil

Phase I—PMMA		Phase II—PU		
MMA* (g)	AIBN (g)	% HDI (in eq.w.)	HDI (g)	N-100 (g)
41.20	0.21	20	0.68	6.14
39.10	0.19	40	1.35	4.61
37.00	0.18	60	2.03	3.07
34.90	0.17	80	2.70	1.54
32.80	0.16	100	3.38	0

*These values accounted for 5% loss through evaporation

A low-temperature accessory was not available for this DSC. Samples weighing between 5 and 10 mg were used.

Thermogravimetric Analysis (TGA)

The thermal stability of pure PU, uncrosslinked PMMA and semi-II IPN were determined by means of a Mettler TA-4000 with a TGA 50 module simultaneously linked to a processor TA10 and a computer. Samples of about 10 mg were thermally degraded under inert atmosphere over the range from 200°C until 550°C at a heating rate of $10°C·min^{-1}$.

Scanning Electron Microscopy (SEM)

Electron micrographs were taken on a Joel JSMT100 scanning electron microscope operated at 25 kV. Samples were frozen under liquid nitrogen, then fractured and mounted on a stub. They were coated with gold (100 Å) using the Edwards S150A Sputter Coater. Photographs were taken on Polaroid 52 film at a magnification of 1500x.

Rheological Analysis

The rheological properties of pure uncrosslinked PMMA and semi-II IPN samples were investigated using a capillary rheometer, the Instron Model 3210 Rheometer. This rheometer was used in conjunction with an Instron universal testing instrument that forces the fluid through the capillary at a constant volumetric flow rate, independent of load and fluid. It has some unique features such as the Command Shear Rate, providing excellent control over the plunger velocities, and a multi-point measurement capability, allowing for fast and accurate data acquisition. The operating temperature was 235°C ± 1°C with a charge load of 50 kN and the velocity schedule was 0.5, 1, 2, 4, 10, 20, 35 and 50 $mm·min^{-1}$. Two capillaries of the following dimensions were used: 50.912 mm and 50.965 mm in length, and 1.275 mm in diameter. This is important because of the sensitivity of viscosity to temperature change. Also, the absolute temperature profile from the top to the bottom of the rheometer, including the capillary, can be controlled within ±1°C.

RESULTS AND DISCUSSION

Thermal Analysis and Morphology of Semi-II IPN

Glass transition temperature analysis from TMA measurements revealed two different $T_g s$ for each sample, indicating two-phase morphologies in the semi-II IPN system. As shown in Figure 1, the first one, T_{g1}, was observed at approximately −31.7°C and corresponds to the PU not part of the semi-II IPN. This value falls within the same range as previously observed for pure PU made from the same compounds.[9-10] The second one, T_{g2}, is around 84.5°C and was corroborated by DSC analysis with a T_g at 84.8°C, clearly lower than that of PMMA (105°C). This value corresponds to the PU network interpenetrated with PMMA. The influence and behavior of the thermoplastic phase are responsible for this glass transition. However the interpenetration is not complete since two $T_g s$ are present. Both of them tend to decrease as the percentage of HDI increases, while the opposite effect is observed for the phase separation. Although not always obvious, the SEM photographs in Figure 2 show this tendency.

The TGA trend is similar to that of observed for a full PMMA/PU IPN reported in the preceding paper.3 The thermograph in Figure 3 compares the thermal degradation of pure PMMA, pure PU (50% HDI) and a semi-II PMMA/PU (30% HDI). The uniform (one-step) degradation of the PMMA comes from its single monomer-constituted polymer chains. Its wide broadening may be explained by a high polydispersity resulting from free radical polymerization. The multi-step degradation of pure PU is more complex since it involves three monomers: castor oil, HDI and N-100. From studying individually the degradation of these components, the PU degradation may be explained in the following manner. The castor oil and HDI would degrade first because of their lower thermal stability than that of N-100. The latter would then degrade, the PU chains being completely destroyed. As far as the degradation of the semi-II IPN is concerned, the first step represents the PMMA that separates from the PU network during the heating process, as its heat resistance is much lower than that of HDI and N-100. The second step is the remaining PU.

Owing to the entanglement of two crosslinked networks, the heat resistance of all semi-II IPN increased considerably compared to that of pure PMMA. This phenomenon can be explained in terms other than interpenetration.[13-14] The more easily degradable polymer, PMMA, absorbs free radicals and stabilizes the less easily degradable polymer,
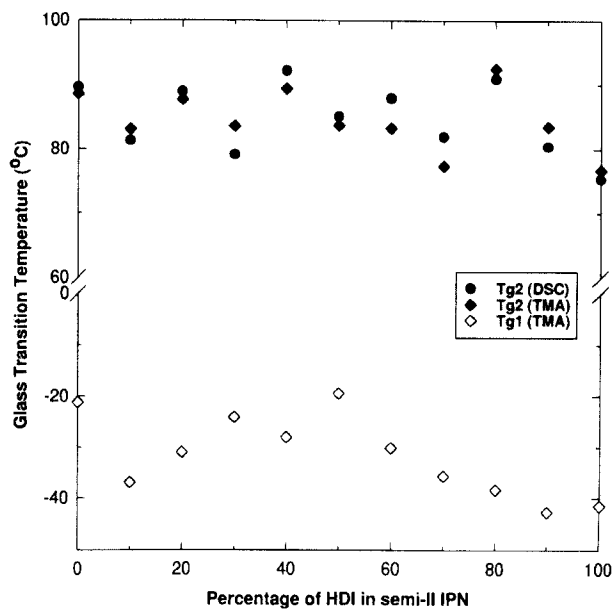
FIGURE 1   Glass Transition Temperature vs. Percentage of HDI in Semi-II IPN.
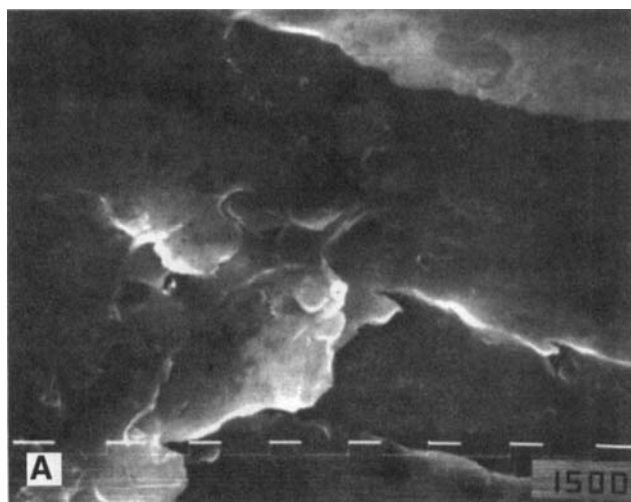

FIGURE 2   SEM photographs of semi-II IPN (×1500): (a) 0% HDI, (b) 20% HDI, (c) 40% HDI, (d) 60% HDI, (e) 80% HDI and (f) 100% HDI (Distance from the beginning of one line to the other is 10 μm).
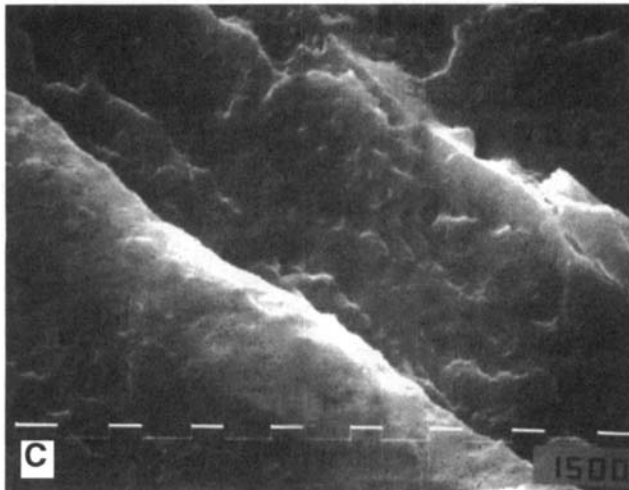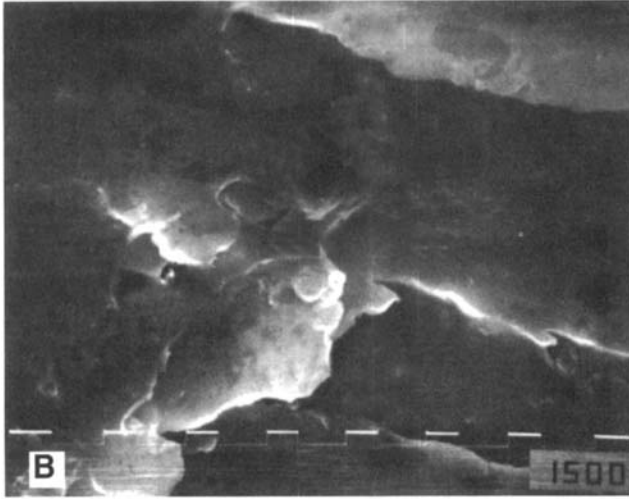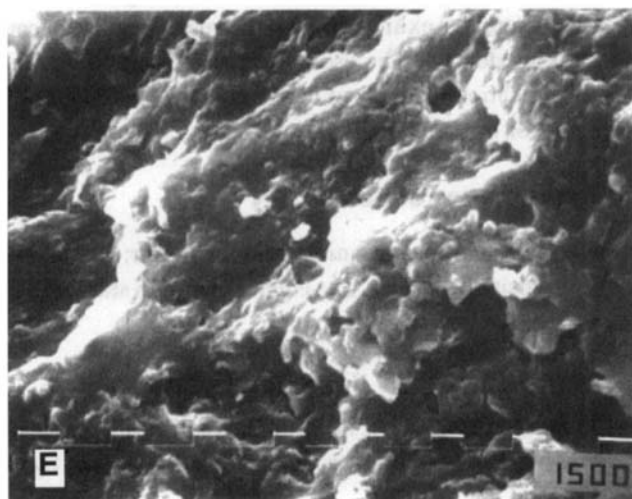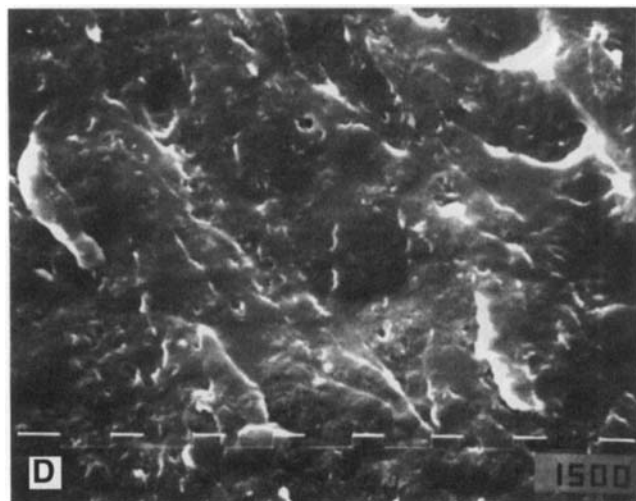
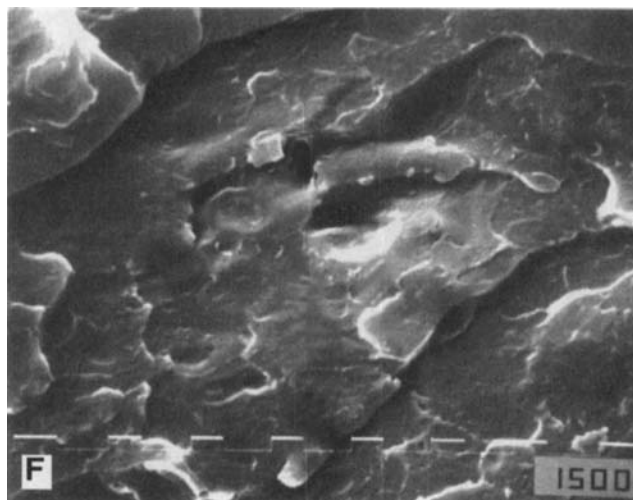FIGURE 2   (*Continued*)

FIGURE 2 (*Continued*)

FIGURE 2   *(Continued)*

PU. The close juxtaposition of the semi-II IPN allows the PMMA and its degradation products to act as free-radical scavengers for the PU. The heat resistance of the semi-II IPN may also be analyzed by plotting the half-life temperature (at which 50% of the weight has been lost) as a function of the percentage of HDI, as shown on Figure 4. Lower percentages of HDI tend to exhibit higher thermal stability because of a higher crosslinking density. The oscillation of the half-life temperatures obtained is an indication that part of the sample is constituted of pure PU which is not part of the semi-II IPN.

Rheological Properties of Semi-II IPN

Polymer melts exhibit shear-thinning flow behavior: as the shear rate increases, the viscosity decreases. The equation used to study this phenomenon is as follows:

$$\tau = \eta_a \dot{\gamma} \tag{1}$$

where τ is the shear stress (Pa), η_a is the apparent viscosity (Pa·s^{-1}) and $\dot{\gamma}$ is the shear rate. Modelling of polymer melts may also be done by using the power law (Ostwald law):[15]
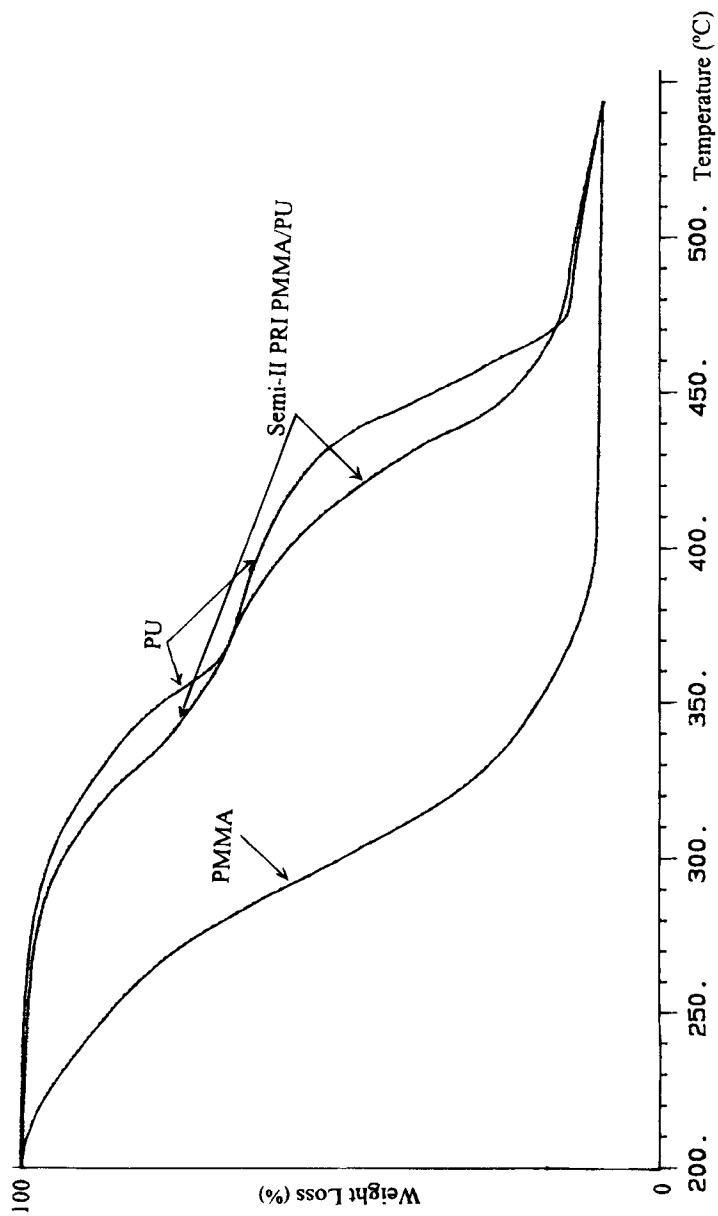
$$\tau = k\gamma^n \tag{2}$$

FIGURE 3   TGA Thermograph of PMMA, PU (50% HDI) and Semi-II IPN PMMA/PU (30% HDI).
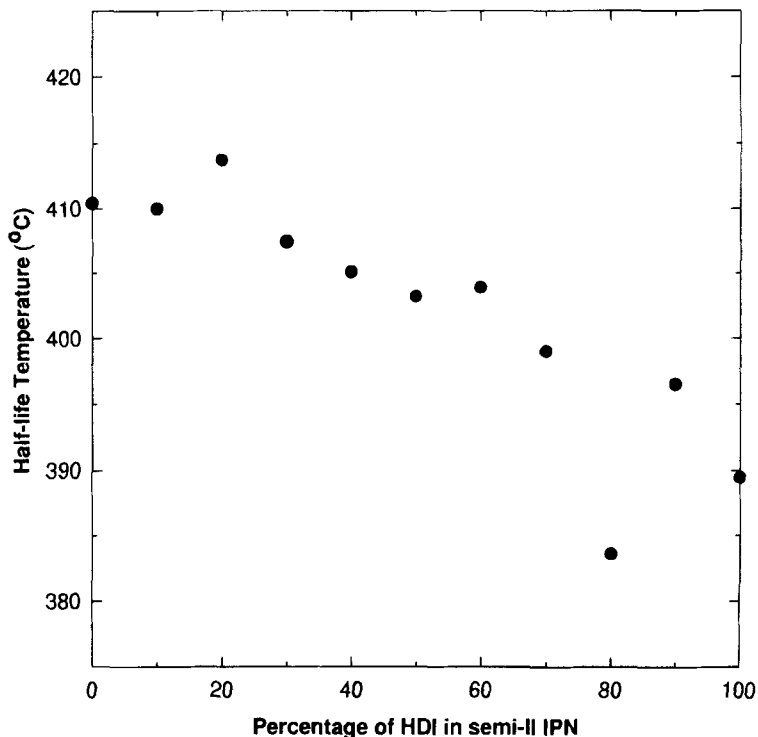
FIGURE 4   Half-life Temperature vs. Percentage of HDI in Semi-II IPN.

where k is the fluid consistency and n is the power law factor. For a shear thinning flow, $0 < n < 1$; ideal flow, $n = 1$. It is calculated from the slope of a *log* τ *versus log* $\dot{\gamma}$ plot such as the one shown in Figure 5. Power Law factors obtained for certain semi-II IPN are reported in Table II. The values confirm the overall shear thinning behavior of the semi-II IPN, as they vary between 0.10 and 0.28.

The forces required and corresponding plunger speeds during rheometric experiments were converted to shear stress and shear rate by mathematical calculations. This involved the geometry of the capillary and extruder, which were already entered into the software as a data file. The equations used by the software for calculating shear stress and shear rate are as follows:
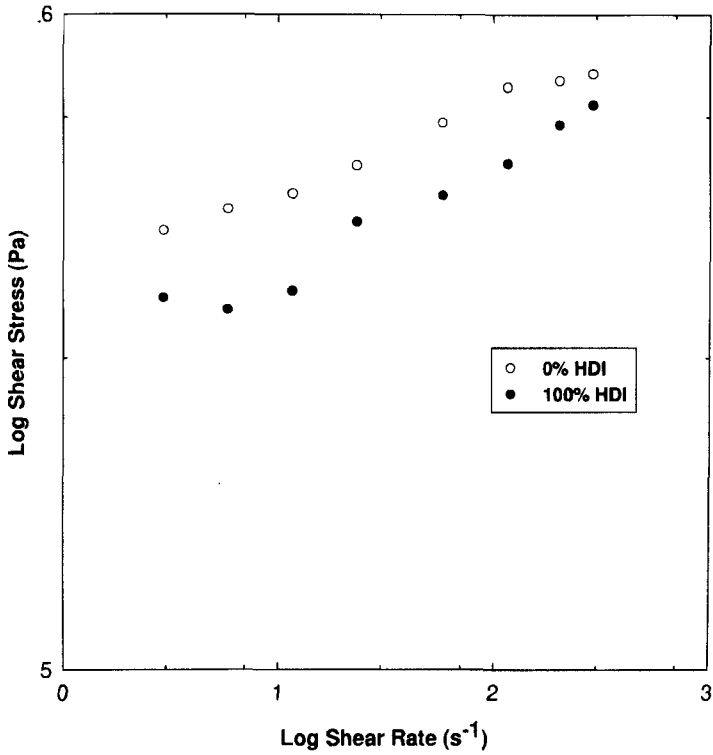
FIGURE 5   Power Law Factor: $Log\ \tau$ Versus $Log\ \dot{\gamma}$.

TABLE II   Power Law and Rabinowitsch Correction Factors as a Function of HDI Percentage of the Semi-II IPN

Percentage of HDI	Power Law Factor, n	Rabinowitsch Correction Factor
0	0.128	2.707
20	0.174	2.191
40	0.240	1.791
60	0.142	2.509
80	0.275	1.678
100	0.163	2.285

(1) Shear stress:

$$\tau = \frac{F}{4A_p(L_c/d_c)} \tag{3}$$

(2) Shear rate:

$$\dot{\gamma} = \frac{V_{xh}d_p^2}{d_c^3} \tag{4}$$

where F is the force (Pa) on the plunger of surface area A_p (m^2) and diameter d_p (m), L_c and d_c are the capillary length (m) and diameter (m) respectively, and V_{xh} is the crosshead speed (m·s^{-1}).

For each viscosity run, the test program reports shear rate, final load, shear stress, apparent viscosity and the remaining length of the rheometer barrel. Since polymer melts behave as non-Newtonian fluids, the calculated shear stress and rate are corrected using the Rabinowitsch correction factor $(3n + 1)/4n$,[15] as reported in Table I:

$$\dot{\gamma}_c = \frac{(3n+1)\dot{\gamma}}{4n} \tag{5}$$

where $\dot{\gamma}_c$ is the corrected shear rate and n is the power law factor.

The highlight of the rheological testing was that all the semi-II IPN were capable of being reprocessed. As the uncrosslinked PMMA begins to flow at 235°C, it coats the elastomeric PU particles and the whole system behaves in a similar fashion as observed with latex IPN.[16] The peculiar flow mechanism of the PU comes from its transformation into gel particles,[17] being an elastomer. These particles move through, slipping and rolling as a unit[18-19] in a two-phase flow system where the PMMA serves as a flow medium, carrying the particles. Due to the shearing effect, the semi-II IPN system could have undergone an irreversible change in morphology such that its properties after flow may be different form those of the original state.

Flow curves and viscosity vs. shear rate were plotted in Figures 6 and 7 respectively, using the corrected values of the shear rate and shear stress. The distinctive flow behavior of the semi-II IPN as described above explains why their viscosity and shear stress is much higher than that of pure PMMA. From these plots, shear thinning flow behavior of the semi-II IPN was confirmed. In fact, that specific behavior is initially observed and then becomes Newtonian as the shear rate reaches approximately 300 s^{-1}.

Below this shear rate, the force exerted by the plunger is not strong enough to properly align the polymer chains so that they can flow freely, one next to each other. As a general rule, the percentage of HDI seems to exert little influence on this behavior. The lower it is, the higher is the shear stress, for a given shear rate. This is the result of a lower crosslinking density for low percentages of HDI.

CONCLUDING REMARKS

The sequential synthesis of semi-II IPN carried out with MMA and castor oil, and using a mixture of HDI and Desmodur N-100 at 67°C, produced transparent samples of various morphology. This is supported by their elec-
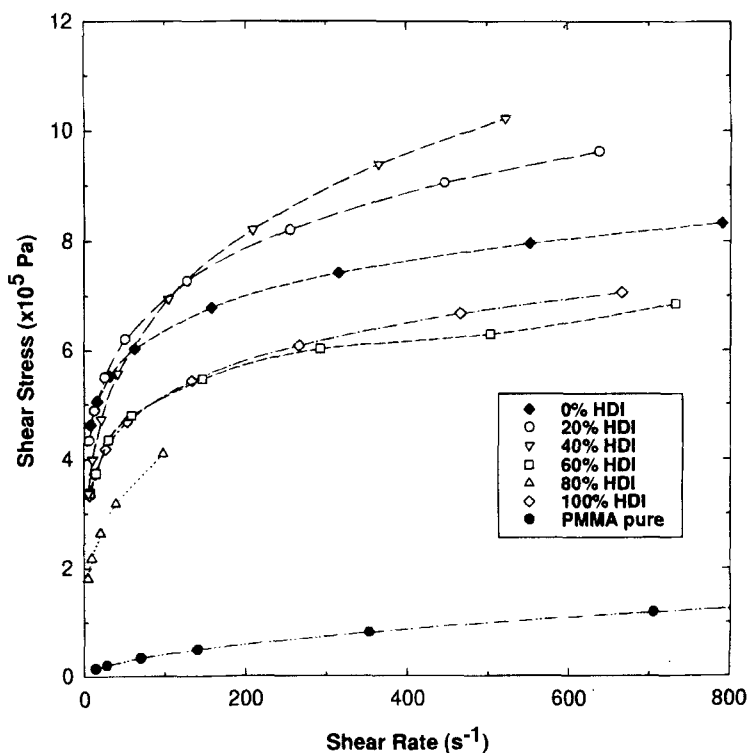

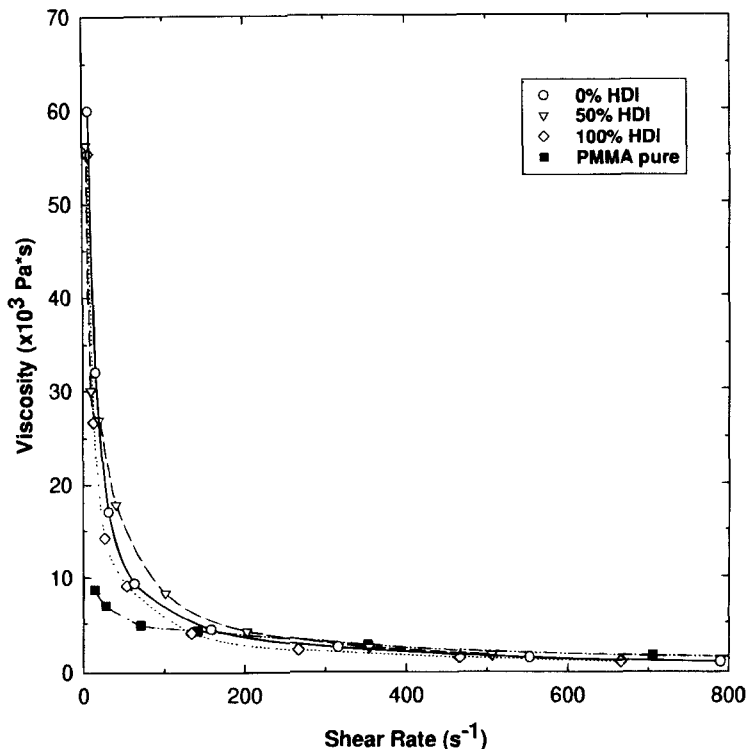FIGURE 6   Flow Curves of Semi-II IPN with Various Percentages of HDI.

FIGURE 7   Viscosity vs. Shear Rate for Semi-II IPN with Various Percentages of HDI.

tron micrographs as well as their single glass transition temperatures
detected by TMA. The interlocking between PMMA and the crosslinked
network of PU produced some synergistic effect on the heat resistance of
semi-II IPN compared to that of pure PU and PMMA. Shear thinning flow
behavior of all semi-II IPN was confirmed. All the samples were
reprocessed through a capillary rheometer, mainly due to the predominance
of the uncrosslinked PMMA.

Acknowledgments

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