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# Characterization of Simultaneous Interpenetrating Polymer Networks from Methyl Methacrylate and Castor Oil

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The synthesis and characterization of simultaneous interpenetrating polymer networks (SINs) based on methyl methacrylate and castor oil are reported. A mixture of 50/50 in weight of HDI/N-100 was employed for the polymerization and crosslinking of the polyurethane phase. The SINs over the whole composition range have only one single glass transition temperature  $T_g$ , as determined by TMA (thermomechanical analysis) which suggests a single phase morphology even though the linear chain blends are completely immiscible. This is also supported by scanning electron microscopy observations. The SINs exhibit a higher heat resistance than pure PMMA but lower than N-100. They also exhibit a maximum tensile strength and impact strength at a composition of PU around 30%. This synergistic effect resulted from a strong entanglement between two networks as well as chain transfer phenomenon.

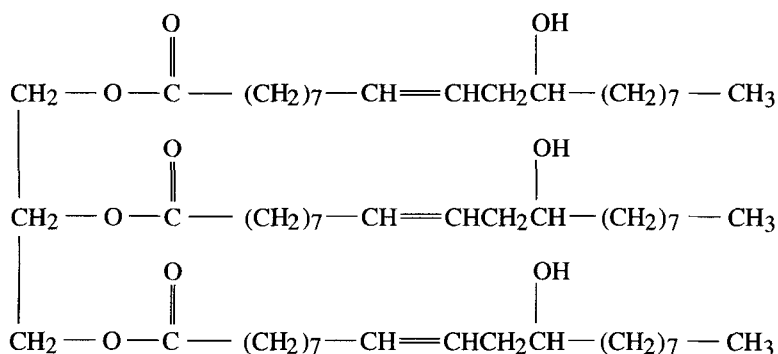
*Keywords:* Thermomechanical analysis; thermogravimetric analysis; scanning electron microscopy; impact test; tensile test; interpenetrating polymer networks

## 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. IPN and semi-IPN are characterized by their bi-continuous structure: two polymers are brought into intimate contact, although there is no chemical linkage between them. In sequential IPN a monomer is added, polymerized and crosslinked in the presence of a polymer network. 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.<sup>1-2</sup> Polymerization and crosslinking lead to a reduction in the entropy of mixing and tend to induce phase separation. In IPN this tendency is counterbalanced by the physical constraint imposed on diffusion by the development of interlocking networks, so that phase separation is limited.<sup>3</sup> This constraint results in structures that are much finer than those of mechanically blended polymers.<sup>4</sup>

The combination of rubbery and glassy polymers in IPN and semi-IPN can produce materials with properties ranging from reinforced elastomers, to damping materials, to high-impact plastics.<sup>5</sup> In 1986, there were approximately 150 IPN patents and 15 products identified as interpenetrating polymer networks.<sup>6</sup> This compared to 1979, when there were approximately 75 patents and only three IPN products. Amongst these IPN systems, the PMMA/PU system by bulk polymerization can be used for shapable polymeric articles.<sup>7</sup> Simultaneous IPN (SINs) formed from poly(methyl methacrylate)/polyurethane (PMMA/PU) were prepared and characterized by several authors using different polyols for the PU phase.<sup>8-11</sup> One of the naturally occurring polyols most useful for the synthesis of the PU phase in the IPN is castor oil due to its three reactive hydroxyl groups.<sup>12-17</sup> The chemical structure of castor oil is as follows:<sup>6-7</sup>



In those syntheses, three main isocyanate compounds were frequently used: hexamethylene diisocyanate (HDI), 2,4-toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI).

In a previous work,<sup>18</sup> a polymeric isocyanate based on HDI, Desmodur N-100, was used together with HDI at various proportions for the synthesis of PU from castor oil. Results from density measurement and swelling test

have shown that N-100 played an effective role as a crosslinking agent for the obtained PU; this greatly affected its tensile and impact properties. The purpose of this work is to synthesize simultaneous IPN from methyl methacrylate (MMA) and castor oil at different compositions. In these systems, the polymerization of MMA is initiated following a free radical mechanism by 2,2' Azobisisobutyronitrile (AIBN), and then crosslinked by ethylene glycol dimethacrylate (EGDMA). Meanwhile, the polyurethane phase is formed by reacting castor oil with a 50/50 mixture of HDI and N-100 (in weight) where the latter acts as an effective crosslinking agent.<sup>18</sup> The SINs obtained are then characterized using scanning electron microscopy (SEM), thermomechanical analysis (TMA), thermogravimetric analysis (TGA), tensile tests, and instrumented impact tests.

## 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 supplied from Aldrich and its NCO equivalent weight is 84 g. They were used as received without further purification.

Methyl methacrylate was supplied by Aldrich. It was washed with an aqueous solution of KOH (5%) to remove inhibitors and then dried over molecular sieve prior to use. AIBN and EGDMA were provided by Aldrich. AIBN was purified by recrystallization in methanol.

### Synthesis

Castor oil and a corresponding amount of MMA for a fixed SIN composition were introduced into a flask equipped with a reflux accessory. The mixture was heated to 65°C and continuously stirred with a poly(tetrafluoroethylene)-coated magnetic stir bar. Predetermined amounts of HDI, N-100, AIBN and EGDMA were then simultaneously introduced into the flask, and the vigorous agitation continued for about 1.5 h until the mixture became vis-

cous. It was then poured into molds made of poly(tetrafluoroethylene) according the ASTM D638 for tensile test specimens and disk shaped specimens for impact testing.<sup>18-19</sup> A slight vacuum was rapidly applied to the molding system to remove air bubbles prior to carefully covering the molds with a poly(tetrafluoroethylene) sheet in order to prevent loss of MMA monomer through evaporation. The SIN samples were cured overnight in an oven at 65°C and then in a vacuum oven at 100°C for about 6 hrs. The products obtained were transparent and colorless or slightly yellow depending on the PU composition in the SINs. The loss of MMA monomer through the synthesis process was approximately 5%. This was checked by the difference of the total weight of chemical reactants and that of SINs products. Table I lists the amounts of different compounds used in the syntheses of the SINs systems. These amounts are sufficient to produce at least five tensile test specimens and five impact test specimens for each SIN composition.

## Characterization

### Scanning Electron Microscopy (SEM)

Electron micrographs were taken on a Joel JSMT100 scanning electron microscope using different magnifications.

### Thermomechanical Analysis (TMA)

The glass transition temperatures of SINs were determined by TMA using a Mettler TA-4000 with a TMA 40 measuring cell linked to a processor TA 11. The approximate sample dimensions were 3 mm thick in the direction of measurement and 6 mm in diameter. Measurements were carried out in

TABLE I Amounts of the Compounds Used in the SINs Syntheses and  $T_g$  Values of SINs as a Function of Composition with NCO/OH = 1.25

PMMA/PU (Wt %)	Phase I-PMMA			Phase II-PU			$T_g$ (°C)
	MMA* (g)	AIBN (g)	EGDMA (g)	Castor Oil (g)	HDI (g)	N-100 (g)	
0/100	0	0	0	71.91	14.05	14.05	-29.0
20/80	20.70	0.10	0.20	57.53	11.24	11.24	-3.5
50/50	51.80	0.25	0.50	35.95	7.02	7.02	38.0
70/30	71.70	0.35	0.70	21.57	4.21	4.21	78.2
100/0	103.50	0.50	1.00	0	0	0	85.7

\*These values accounted for 5% loss through evaporation

the range of  $-100$  to  $200^{\circ}\text{C}$  at  $10^{\circ}\text{C}\cdot\text{min}^{-1}$ , and a constant probe force of  $0.02\text{ N}$  was applied to the sample. A low-temperature accessory was used with liquid nitrogen as refrigerant.

### ***Thermogravimetric Analysis (TGA)***

The heat resistance of SInS, as well as crosslinked PMMA and PU, was 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  $5\text{ mg}$  were thermally degraded under inert atmosphere starting from  $200^{\circ}\text{C}$  until  $500^{\circ}\text{C}$  at a heating rate of  $10^{\circ}\text{C}\cdot\text{min}^{-1}$ .

### ***Tensile Testing***

Tensile tests were performed on an Instron tester (model 4206, fully digitalized, equipped with a computer), at room temperature with a cross-head speed of  $10\text{ mm}/\text{min}$ . The gauge dimensions of specimens were  $(25 \times 10 \times 3.0)\text{ mm}$  where the thickness varied from one sample to another and were precisely measured with an electronic micrometer.

### ***Impact Testing***

Impact tests were performed using a Rheometrics Drop Weight Tester (RDT-5000), at room temperature. A high-speed dart weighing  $3.73\text{ kg}$  was employed. All the tests were carried out using a probe with a hemispherical end,  $12.7\text{ mm}$  in diameter. A force-sensing load cell in the dart had a full range of  $1134\text{ kg}$ . The impact test specimens were cast in a disk shape  $37.0\text{ mm}$  in diameter and  $3.0\text{--}3.1\text{ mm}$  in thickness. The specimens were held in place on an annular stainless steel ring with an internal diameter of  $25.4\text{ mm}$ . The set impact speed was  $7.6\text{ m}\cdot\text{s}^{-1}$ . The impact force displacement traces were recorded in order to characterize the impact properties of the specimens.

## **RESULTS AND DISCUSSION**

The selected synthesis temperature of  $65^{\circ}\text{C}$  yielded similar reaction times for the PMMA and PU phases which were determinant for the interpenetration extent of both phases in the total network. When MMA was polymerized alone

by bulk method, its reaction time was greatly affected by the auto-acceleration phenomenon. However, in the case of SIN synthesis, the presence of castor oil and other ingredients have significantly attenuated that phenomenon so that the polymerization patterns of both phases became similar to each other.

Figures 1 and 2 show scanning electron micrographs for SINs at two different PMMA/PU compositions, 70/30 and 50/50, respectively, with a NCO/OH ratio equal to 1.25 for the PU phase. There was no phase separation observed in SINs because of permanent entanglements between the two crosslinked networks of PU and PMMA. Furthermore, this one-phase behavior noted for the PMMA/castor oil-based polyurethane SINs might be due to chain transfer promoting miscibility between two network polymers which thermodynamically are less miscible than a blend of two linear polymers. This chain transfer may have occurred due to the presence of three  $-C=C-$  groups in the castor oil structure, which are able to initiate a free radical polymerization. This morphology of SINs is confirmed by the values of  $T_g$  obtained from TMA shown in Table I. All SINs exhibited a single glass transition temperature which is in the range between the pure crosslinked PU ( $-29.0^\circ\text{C}$ ) and PMMA ( $85.7^\circ\text{C}$ ). The  $T_g$  values were greatly increased with increasing PMMA content.

The heat resistance properties of SIN samples are compared with those of pure PMMA and PU in Table II and Figures 3 and 4. The data presented in Table II and in Figure 4 were deduced from Figure 3 by means of derivation of the weight loss percentage with respect to temperature. The temperatures T1, T2 and T3, called peak temperatures, represent the temperature where the degradation rate is maximum, for each degradation step. Due to the more complex chemical structure of PU which consists of castor oil, HDI and N-100, the thermal degradation of PU is composed of three steps. The first one, T1, is attributed to that of castor oil, the second one, T2, belongs to HDI and finally N-100, T3, has the highest heat resistance. These steps were checked by the thermal degradation patterns of each individual compound.<sup>20</sup> Meanwhile, the thermal degradation of PMMA is nearly one step and its heat resistance is much lower than that of HDI and N-100. Owing to the entanglement of two crosslinked networks, the heat resistance of all SINs considerably increased compared to that of pure PMMA. According to Figure 3, this increase seemed to be independent of SINs composition. This phenomenon can be explained in terms other than interpenetration.<sup>7,21</sup> The more easily degradable polymer PMMA, absorbs free radicals and stabilizes the less easily degradable polymer, PU. The

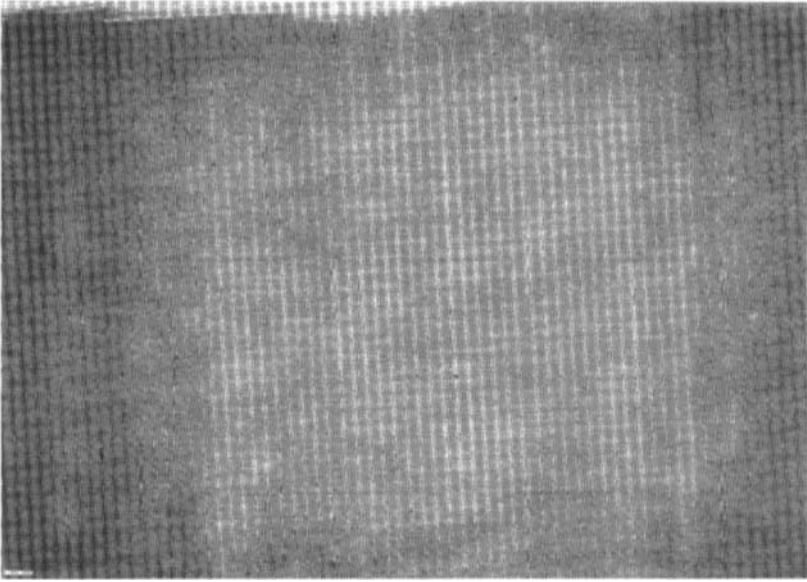


FIGURE 1 Scanning Electron Micrograph of SIN at PMMA/PU = 70/30 ( $\times 1500$ ).

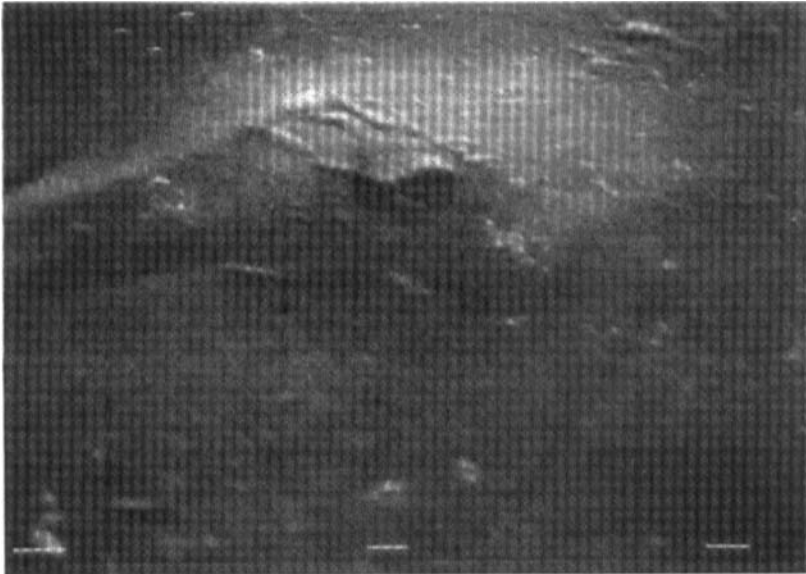


FIGURE 2 Scanning Electron Micrograph of SIN at PMMA/PU = 50/50 ( $\times 1500$ ).



TABLE II Peak Temperatures of PMMA/PU SINs as a function of composition with NCO/OH = 1.25

Composition PMMA/PU	T1 (°C)	T2 (°C)	T3 (°C)
100/0	nil	352	nil
70/30	315	385	408
50/50	320	410	422
20/80	322	nil	428
0/100	327	412	440

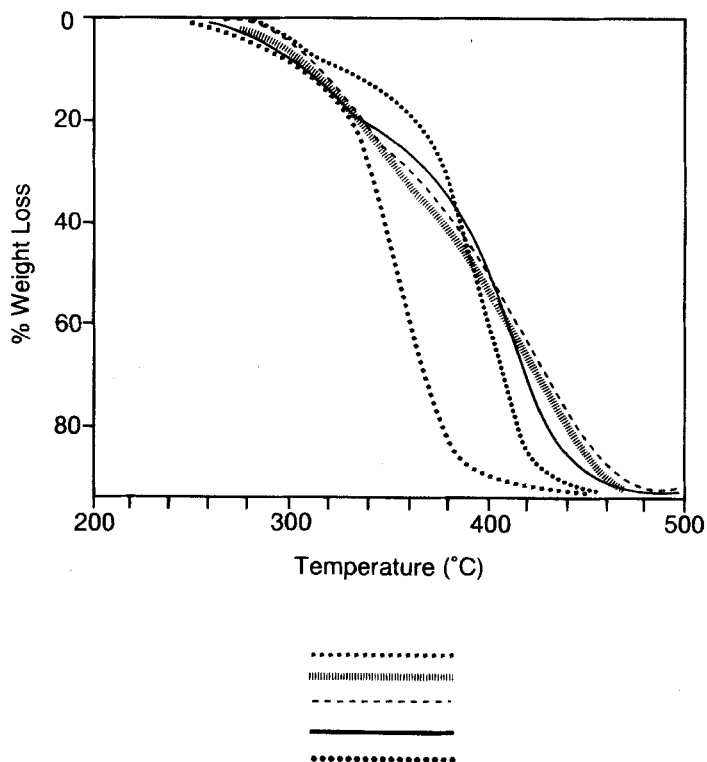


FIGURE 3 TGA Thermograms of: (◆◆◆) Pure Crosslinked PMMA; (----) Pure PU; (.....) SINs of PMMA/PU = 70/30; (—) 50/50; and (▨▨▨) 20/80.

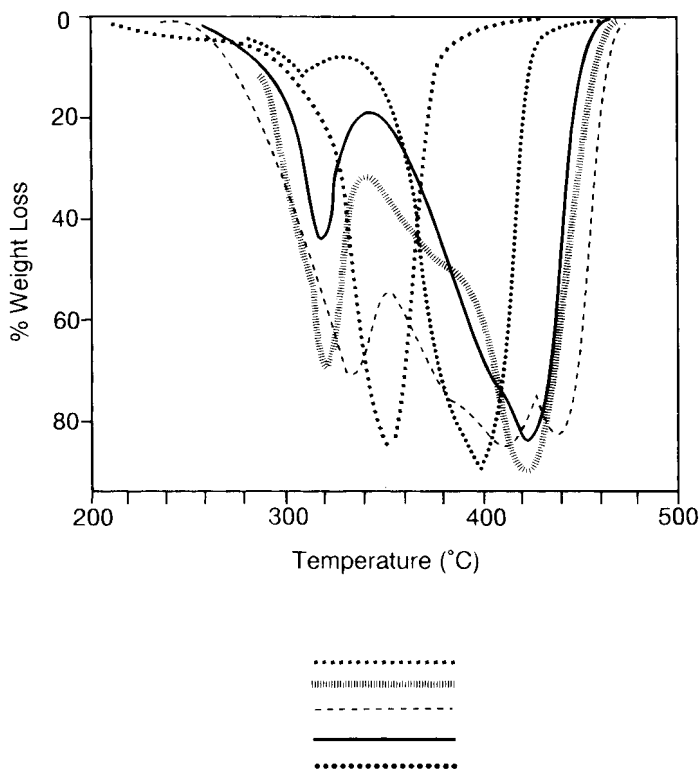


FIGURE 4 Thermal Degradation Rates as a Function of Temperature of: (◆◆◆◆) Pure Crosslinked PMMA; (----) Pure PU; (●●●●) SINs of PMMA/PU = 70/30; (—) 50/50; and (||||) 20/80.

close juxtaposition of the IPNs allows the PMMA and its degradation products to act as free-radical scavengers for the PU.

Tensile strength, elongation at break and Young's modulus data are presented in Table III for various SINs. It is noted that the SINs exhibited a maximum in tensile properties versus composition at around 30% by weight of PU. This maximum has been observed in many other IPNs.<sup>22-25</sup> Figures 5 and 6 illustrate the effect of the NCO/OH ratio on the Young's modulus and the elongation at break, respectively, for SINs samples of composition 50/50. This ratio is related to the crosslinking density in the PU phase which had to directly affect the interpenetrating extent of IPN's. It is likely that increasing NCO/OH ratio made the SINs stiffer while their elongation at break remained nearly the same.

TABLE III Tensile Properties of PMMA/PU SINs as a Function of Composition with NCO/OH = 1.25

Composition PMMA/PU	Tensile strength (MPa)	Elongation (%)	Modulus (MPa)
0/00	1.1	47	1.9
20/80	9.2	85	6.6
50/50	28.4	56	27.3
70/30	33.8	12	56.0
100/0	nil	nil	nil

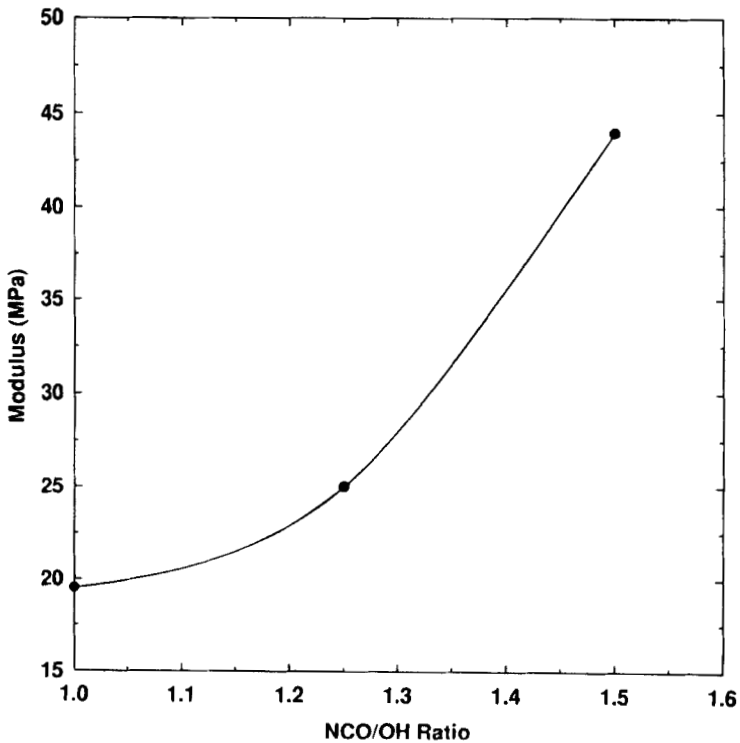


FIGURE 5 Effect of NCO/OH Ratio on the Young's Modulus of SINs Samples of Composition 50/50.

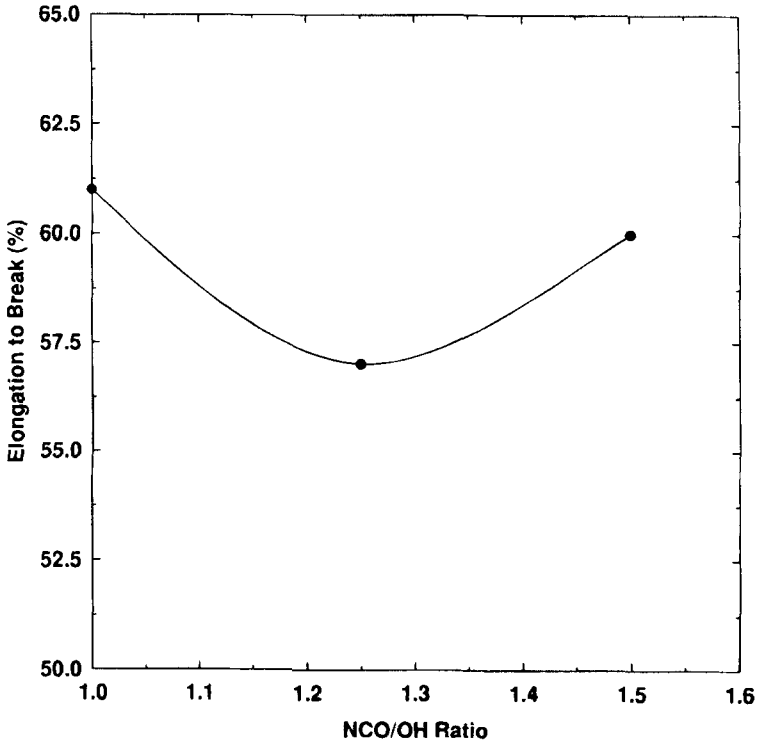


FIGURE 6 Effect of NCO/OH Ratio on the Elongation to Break of SINs Samples of Composition 50/50.

A typical impact-deformation trace for the pure PU sample (with  $NCO/OH = 1.25$ ) is shown in Figure 7. Some main parameters of the impact event can be measured from this trace:  $F_m$  the maximum force,  $D_m$  the displacement at maximum force,  $D_t$  the final displacement where no resistance to impact remains,  $U_m$  the absorbed energy up to the maximum force and  $U_t$  the total absorbed energy. The impact strength of plastic materials is usually characterized by the total impact energy  $U_t$ , which in the case of instrumented impact testing, is measured by the area under the force-displacement curve.<sup>18</sup> Data on total impact energy of SINs are presented in Table IV. Similarly to the tensile properties, the impact strength of SINs also exhibited a maximum at around 30% in weight of PU. Figure 8 shows a large effect of increasing NCO/OH ratio on the impact strength of SINs which once again is attributed to the

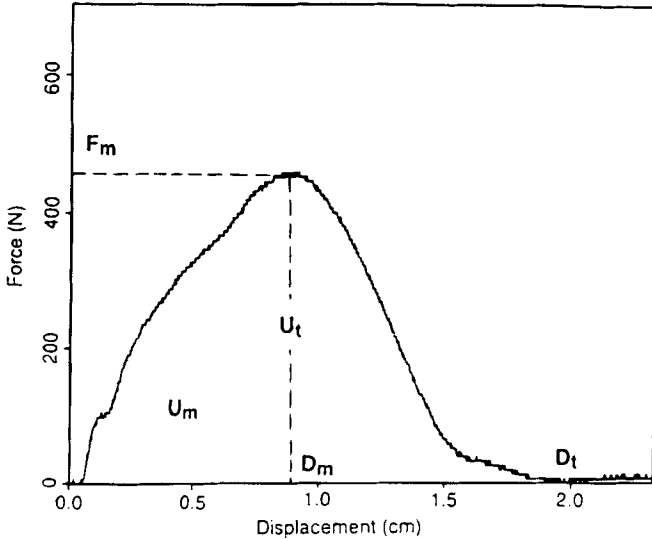


FIGURE 7 Typical Impact Force-displacement Curve for Pure PU of NCO/OH = 1.25.

TABLE IV Total Impact Energy of PMMA/PU SINs as a Function of Composition with NCO/OH = 1.25

Composition PMMA/PU	0/100	20/80	50/50	70/30	100/0
Energy (J)	4.0	3.3	6.2	11.7	1.2

increase in crosslinking density of the PU phase leading to a better interpenetration between two networks as well as a chain transfer between them.

## CONCLUDING REMARKS

The simultaneous synthesis of IPN carried out with castor oil and MMA using a mixture of HDI and Desmodur N-100 at 65°C produced transparent samples of good morphology. This is supported by their electron micrographs as well as their single glass transition temperatures detected by TMA. The interlocking between two crosslinked networks, PMMA and PU, combined with a chain transfer mechanism, produced some synergistic

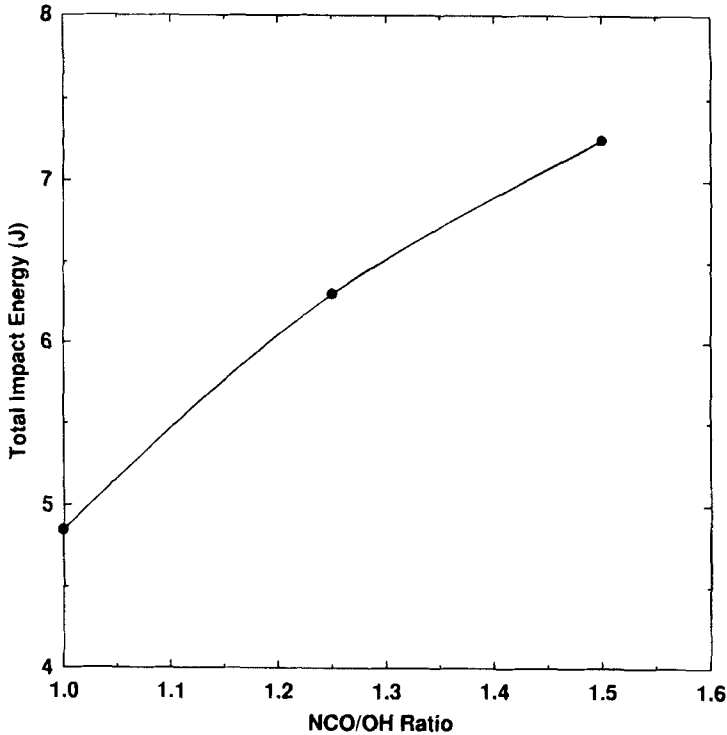


FIGURE 8 Effect of NCO/OH Ratio on the Total Impact Energy of SInS Samples of Composition 50/50.

effect on the heat resistance of SInS compared to that of PMMA and pure castor oil. This effect is clearly seen in the tensile and impact properties of SInS, mostly around the composition of 30% in weight of PU. Finally, the reinforcement of the crosslinking density of PU by means of increasing NCO/OH ratio gave rise to a slight increase in Young's modulus and total impact energy of SInS.

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