Study on the Properties, Morphology, and Applications of Castor Oil Polyurethane–Poly(methyl methacrylate) IPNs

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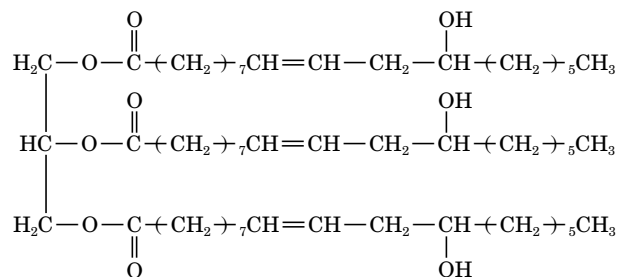
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ABSTRACT: A series of castor oil polyurethane–poly(methyl methacrylate) interpenetrating polymer networks (IPN COPU/PMMA) were produced from castor oil, toluene diisocyanate, and methyl methacrylate. The properties and morphology of the IPNs were estimated. The adhesives based on the IPN COPU/PMMA prepolymer were prepared and the influence of the composition on the adhesion strength was studied. The experimental results showed that the adhesives have an effective adhesive power for metals and these adhesives have good prospects in a practical project. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 1393–1401, 1997

INTRODUCTION

Castor oil is a naturally occurring monomer, which is a triglyceride of rincinoleic acid containing three hydroxyl groups and three double bonds:

$$\begin{array}{l} H_2C-O-\overset{O}{\overset{\|}{C}}\text{+}CH_2\text{+}_7CH=CH-CH_2-\overset{OH}{\overset{|}{CH}}\text{+}CH_2\text{+}_5CH_3 \\[4pt] HC-O-\overset{O}{\overset{\|}{C}}\text{+}CH_2\text{+}_7CH=CH-CH_2-\overset{OH}{\overset{|}{CH}}\text{+}CH_2\text{+}_5CH_3 \\[4pt] H_2C-O-\underset{O}{\underset{\|}{C}}\text{+}CH_2\text{+}_7CH=CH-CH_2-\underset{OH}{\underset{|}{CH}}\text{+}CH_2\text{+}_5CH_3 \end{array}$$

Commercial castor oil consists of triglycerides that contain 90% rincinoleic acid residues and 10% nonfunctional acid residues, so that castor oil has an effective hydroxyl functionality of 2.7.[1] Castor oil is thus a fine candidate for making interpenetrating polymer networks (IPNs). The double bonds of the oil may be crosslinked to form an elastomeric material by a chain-growth reaction, and the hydroxyl functionality can be used to form polyester or polyurethane networks by a step-growth reaction.

The extensive use of castor oil in IPN research began in 1977 with sulfur-crosslinked castor oil that was swelled with styrene and divinylbenzene[2] or methyl methacrylate and glycol dimethacrylate.[3] Castor oil polyester and polyurethane-based IPNs were studied at Lehigh University during the late 1970s and early 1980s.[4–9]

Yenwo et al.[3] were the first to utilize castor oil to synthesize sequential IPNs, and the dynamic mechanical properties of the IPNs were studied.[8] The experimental data show extensive but incomplete molecular mixing of the two networks.

Devia et al.[7] studied the synthesis of simultaneous IPNs based on elastomeric polymers derived from castor oil and crosslinked polystyrene. The elastomers included crosslinked polyurethane with toluene diisocyanate (TDI) and crosslinked polyester–polyurethane from castor oil, sebacic acid, and TDI. The morphology and glass transition behavior of the simultaneous IPNs were studied using electron microscopy and dynamic mechanical spectroscopy techniques, respectively.[9] A two-phase morphology was revealed by electron microscopy. Dynamic mechanical spectroscopy studies showed two well-defined glass transition temperatures near respective homopolymer glass
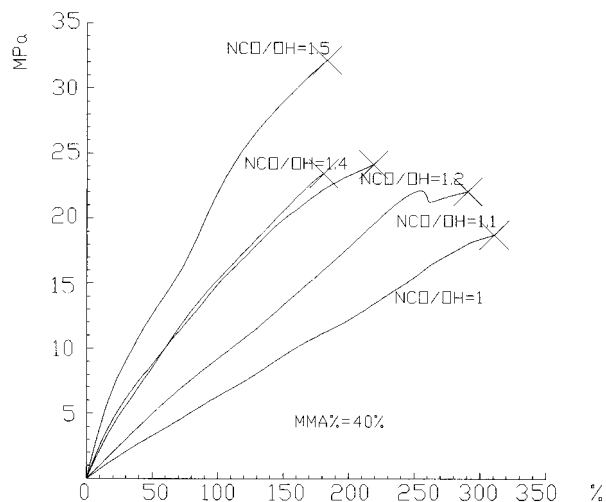

Figure 1   Influence of NCO/OH ratio on the mechanical properties.

transition temperatures but shifted inward to a greater or lesser extent.

These materials proved to be tougher than their corresponding homopolymer networks. The toughness of these simultaneous IPNs increased with a decreasing domain size of the dispersed phase.[10]

Xie et al.[11,12] synthesized simultaneous IPNs at room temperature from castor oil polyurethane and copolymers of viny monomers including styrene, methyl methacrylate, and acrylonitrile using a redox initiator without a crosslinker agent and both the rates of crosslinking and grafting on phase separation were examined. These IPNs exhibited good properties, including high strength, good resilience, anticorrosion, oil, and solvent resistance, and high abrasion resistance.

Barrett et al.[13] made semi-IPNs of castor oil and poly(ethylene terephathalate). The castor oil improves the crystallization rate of poly(ethylene terephthalate), and after the polymerization of castor oil, it offers a mechanism for toughening the materials.

Liu et al.[14] reacted castor oil and other monomers and oligomers with diisocyanate and eventually with 2-hydroxyethyl acrylate to make a series of AB crosslinked polymers (ABCPs). The morphologies and dynamic mechanical properties of an ABCP and an IPN with the same composition were compared. The results showed that the degree of phase separation of the ABCP is lower than that of the IPN.

Recently, research on castor oil polyurethane IPNs became an active field in China.[15–18] Al-

though castor oil polyurethane IPNs have been investigated and reviewed by many authours, reported investigations on the application of castor oil polyurethane IPNs are still limited in the literature, and the details of the relationship between composition, structure, and properties of these IPNs are still incomplete. The castor oil polyurethane–PMMA IPN used as adhesives have not been reported yet. In this article, the castor oil polyurethane–PMMA IPNs used as adhesives were synthesized and the properties and morphology were studied.

EXPERIMENTAL

Raw Materials and Treatment

Castor oil (chemically pure) was dried by azeotropic distillation with chemically pure tolutene. Toluene diisocyanate (TDI; ratio of 2,4-TDI/2,6-TDI is 80/20 by weight), had a purity $> 97\%$. Methyl methacrylate (MMA; analytically pure) was purified by reduced pressure distillation to remove any inhibitors. Dibutyltin dilaurate (DBTL; chemically pure) was used as received. Benzoyl peroxide (BPO) was dried in a vacuum desicator. Dimethylaniline (DMA; chemically pure; purity $> 98\%$) was used as received. All other reagents were analytically pure.

Polymerization

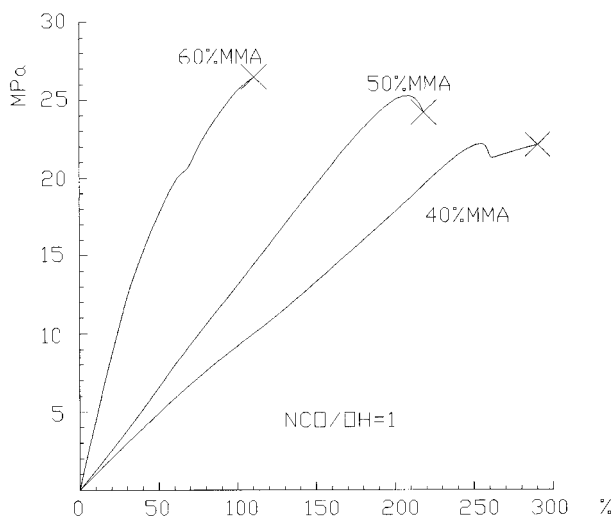The polymerization was carried out in a 250 mL, tetraneck bottle in a nitrogen atmosphere. To the

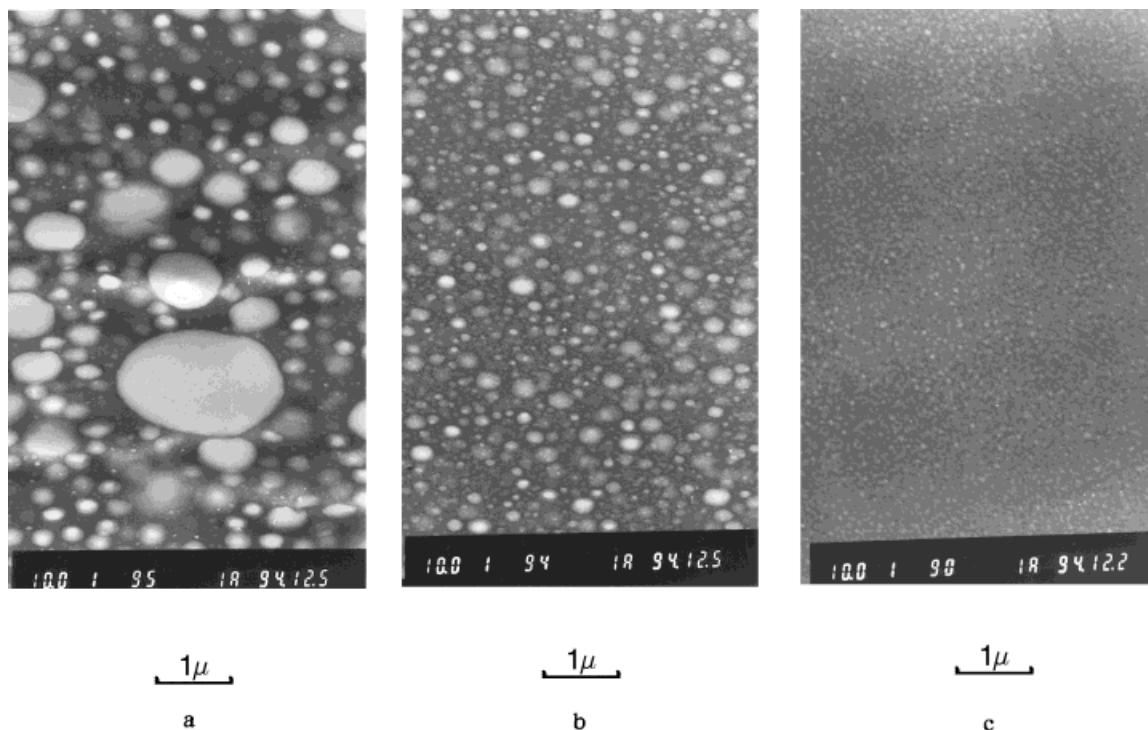**Figure 2**   Influence of MMA content on the mechanical properties.

Figure 3 Transmission electron micrographs of IPN COPU/PMMA. Magnification: 10,000; NCO/OH = 1.4: (a) 60% MMA; (b) 50% MMA; (c) 40% MMA.

reaction vessel equipped with a stirrer, the calculated amount of castor oil, MMA, and DBTL was added. After being stirred, TDI was added and reacted at 25°C under stirring for 1 h. After that, the initiators (BPO + DMA) were added and reacted for 1 h under stirring at 25°C and in a nitrogen atmosphere. Then, the reaction mixture was degassed and the prepolymer of the IPN COPU/ PMMA was thus synthesized. Then, the prepolymer was poured into a glass mold, using silicone oil as the release agent, and cured at room temperature for 24 h. The IPN COPU/PMMA was thus prepared.

Characterization of IPN COPU/PMMA

The morphology was studied on a transmission electron microscope (Hitachi H-800). The sample

Table I Influence of MMA Content on the Domain Size

	MMA Content (wt %)		
	60	50	40
Average domain size (nm)	273	61	27

was microtomed under refrigeration (−60°C) and stained with osmium tetroxide; then, the transmission electron micrographs were taken.

The glass transition temperatures (T_g's) were determined using a thermomechanical analyzer (Model TM-700, Japan) at heating rate of 5°C/ min; the temperature range was −100 to 200°C. The thermal stability of the IPNs was measured using a thermal analyzer (type LCT) in a nitrogen atmosphere. The heating rate was 15°C/min and the temperature range was 0–600°C.

Adhesive Power Measurement

The lap shear strength of adhesion for metals was measured according to China standard HG2-151-65 using a tensile tester (type LJ-5000A). The samples prepared using metal (steel and aluminum) substrates were coated with the adhesive (prepolymer of IPN COPU/PMMA) and the lap length was about 25.0 mm. The samples were cured for 1 week at room temperature under a pressure of about 1 kg/cm^2; then, the lap shear strength was measured.

Peeling strength of 180° was measured according to China standard GB2790-81 with a tester (type CSS-1110). The substrates (aluminum)
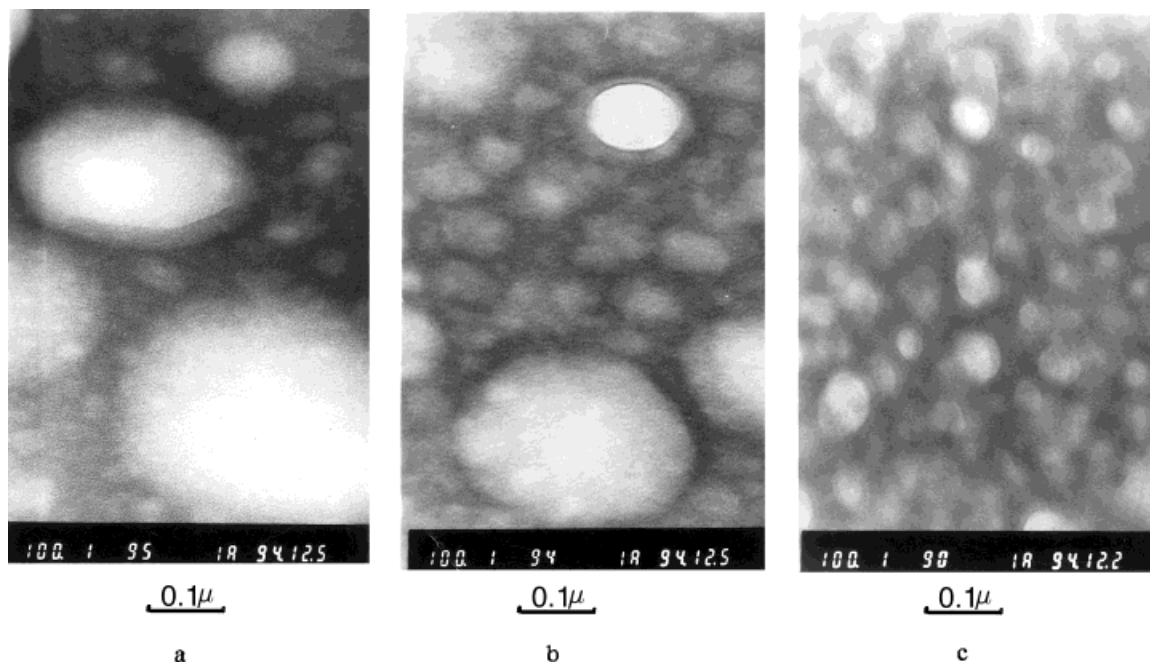
Figure 4   TEM of IPN COPU/PMMA; magnification: 100,000. These micrographs are the magnified images of Figure 3.

were coated with the adhesive and were joined under pressure and cured at room temperature for 1 week.

The cleavage resistance was measured according to China standard GB7749-87. The shear impact strength was measured according to China standard GB6328-86. The tensile strength of adhesion was determined according to China standard GB6329-86, and inhomogeneous clevage strength was determined according to China standard HB5166.
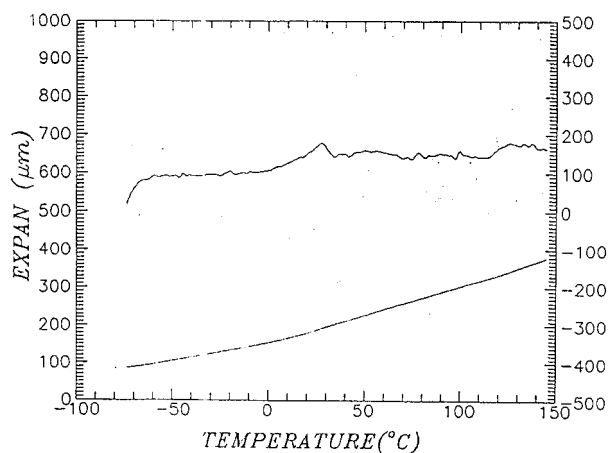

Figure 5   Thermomechanical analysis of IPN COPU/ PMMA (NCO/OH = 1.4; 50% MMA).

RESULTS AND DISCUSSION

Mechanical Propaties and Morphology

Experimental results indicated that the mechanical properties of the IPN COPU/PMMA depend on the NCO/OH ratio and MMA content, as shown in Figures 1 and 2.

Figure shows that the tensile strength is enhanced and, in contrast, the elongation at break is decreased as the NCO/OH ratio increases. For the NCO/OH ratio increased from 1.0 to 1.5, the tensile strength is increased from 16.45 to 33.30 MPa; in contrast, the elongation at break is decreased from 210 to 158.8%. These results are consistent with the reference data.[19]
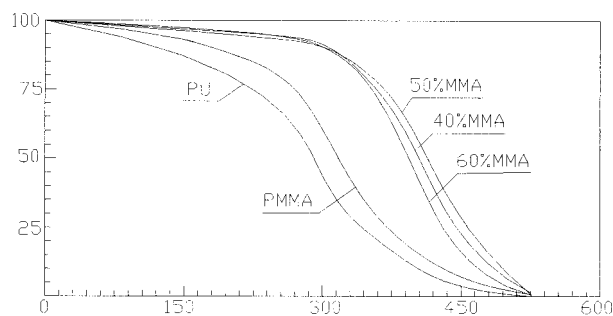

Figure 6   TGA thermograms of IPN COPU/PMMA (NCO/OH = 1.4).

Table II TGA Data of Figure 6

MMA Content	250°C	300°C	350°C	400°C	450°C	525°C	Degradation Temp °C
60%	3.80	6.96	19.6	53.2	92.4	99.4	314
50%	6.10	7.60	18.3	35.9	87.8	99.2	337
40%	5.00	6.52	20.7	42.1	85.5	98.6	307
Pure PU	15.0	67.0	77.0	90.0	98.0	—	—
Pure PMMA	7.50	35.0	80.0	97.0	—	—	—

From Figure 2, it can be seen that the tensile strength is enhanced and the elongation at break is decreased with MMA content. No maximum tensile strength exists at an MMA content of about 50%. This was different from that reported in the literature,[12,14] which may be attributed to the different compositions and reaction conditions in this article.

Figure 3 is the transmission electron micrographs of the IPN COPU/PMMA stained with OsO_4. The castor oil polyurethane exists as a dark continuous phase (the unreacted double bonds of castor oil can be stained with OsO_4) and the PMMA exists as bright domains.

According to the methods reported by Allen et al.[20] the average domain size can be estimated from the transmission electron micrographs. The results are included in Table I.

From Figure 3 and Table I, it can be seen that the domain size increases with MMA content and no phase inversion occurs when the MMA content increased from 40 to 60%. The domain size increase with MMA content can be attributed to the following: The components are initially miscible and then phase-separate as the polymerization and crosslinking occur. It is the relationship between crosslinking and phase-separation kinetics that controls the final IPN morphology. Generally, the morphology and structure of the IPN are controlled by competition between thermodynamic and kinetic factors. The promoting force for phase separation is thermodynamic, the main criterion of which is thermodynamic miscibility of the constituents. All factors that promote miscibility decrease the domain dimension and enhance the extent of the interpenetrating of phases. However, the extent of phase separation is controlled by the kinetic factors, where the basic criterion is the rate of viscosity increase relative to the kinetics of phase separation. All factors that enhance the viscosity tend to reduce the rate and extent of phase separation. As the MMA content
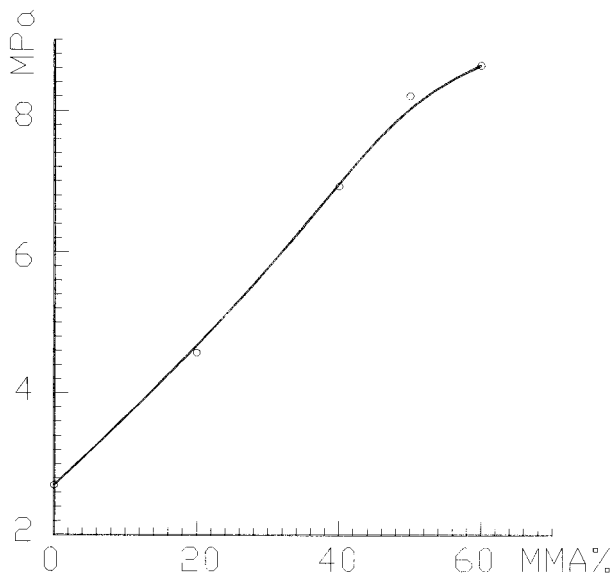

Figure 7 Influence of MMA content on the lap shear strength of adhesion. Substrates: 45# steel–45# steel; NCO/ON = 1.4.
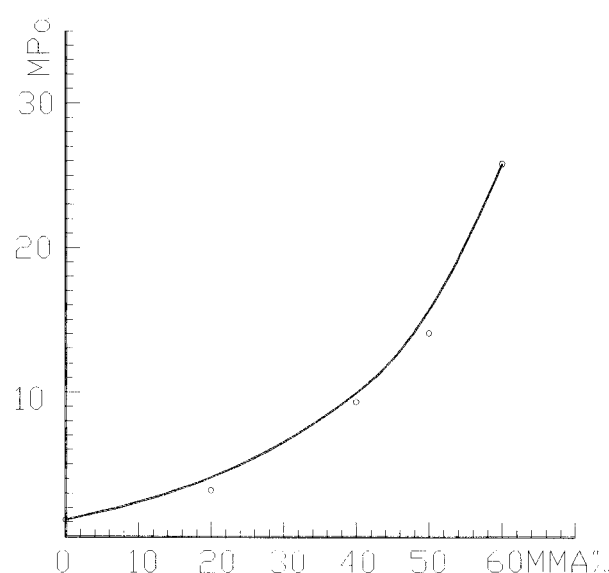

Figure 8 Influence of MMA content on the tensile strength of adhesion. Substrates: 45# steel–45# steel; NCO/ON = 1.4.
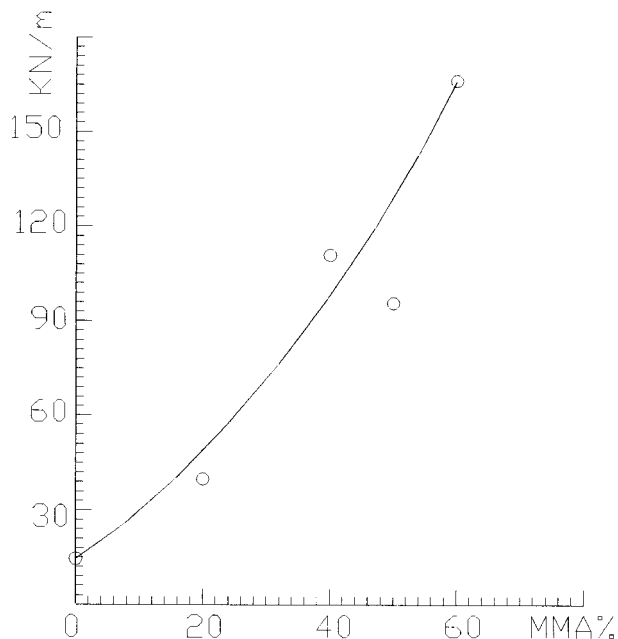
Figure 9   Influence of MMA content on the cleavage strength of adhesion. Substrates: 45# steel−45# steel; NCO/ON = 1.4.

increases, the viscosity of the reaction systems decrease, so the rate and extent of phase separation increase and, thus, the domain size becomes larger.

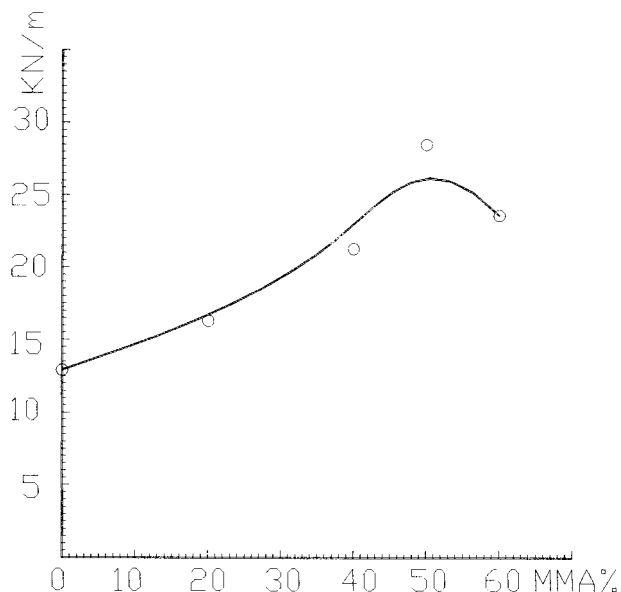It also can be seen from Figure 3 that the dispersed phase appears to be a spherical structure

Figure 10   The influence of MMA content on the inhomogeneous cleavage strength of adhesion. Substrates: 45 steel−alumium; NCO/ON = 1.4.

Table III   Influence of MMA Content on the Shear Impact Strength[a]

	MMA Content (%)				
	60	50	40	20	0.0
Shear impact strength (kJ/m²)	11.0	8.60	13.9	10.3	10.2

[a] NCO/OH = 1.4, substrate: 45# steel-45# steel.

with quite different domain sizes. The domains do not have clear boundaries as shown in Figure 4. A castor oil polyurethane (COPU) fine structure was found in the matrix and across the smaller dispersed domains, which implies that interpenetration occurred not only at the boundaries but also inside the domains. This fact can be attributed to the increase of miscibility owing to the occurrence of graft copolymerization. As pointed out by Tan,[21] castor oil not only reacts with diisocyanate in the formation of polyurethane networks, but also participates in the formation of vinyl copolymer chains and a grafted IPN was formed.

Thermal Analysis

Figure 5 presents the results of the thermomechanical analysis of the IPN COPU/PMMA. Two
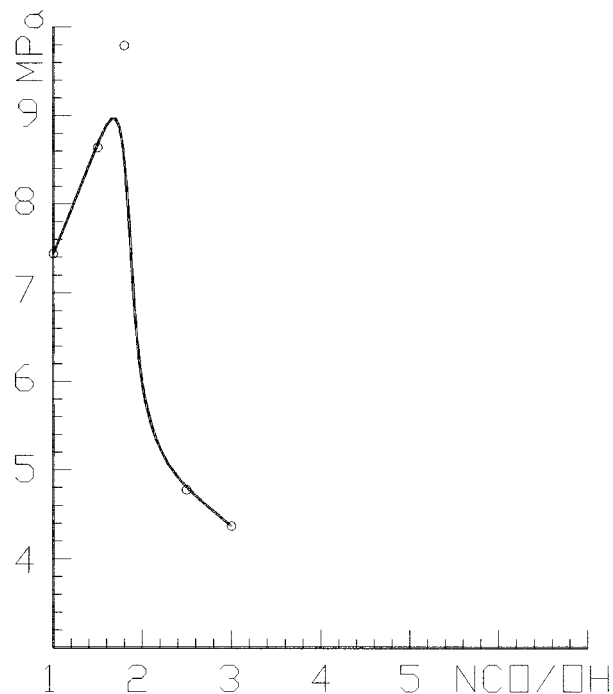

Figure 11   Influence of NCO/OH ratio on the lap shear strength. Substrate: 45# steel; 50% MMA.
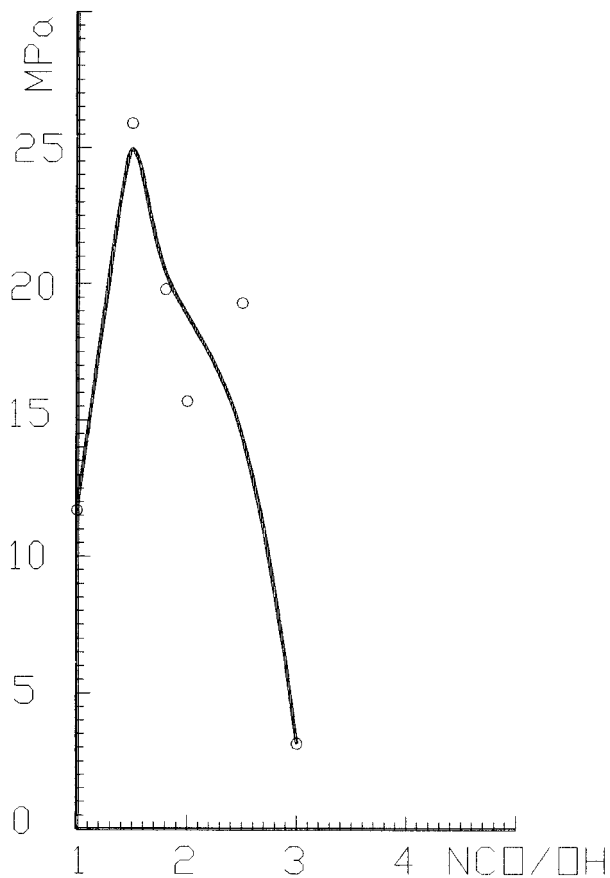
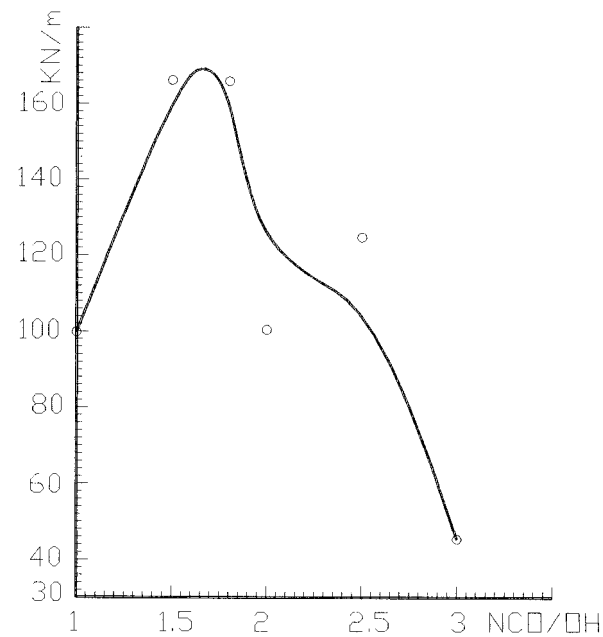**Figure 12** Influence of NCO/OH ratio on the tensile strength of the adhesion. Substrate: 45# steel; 50% MMA.

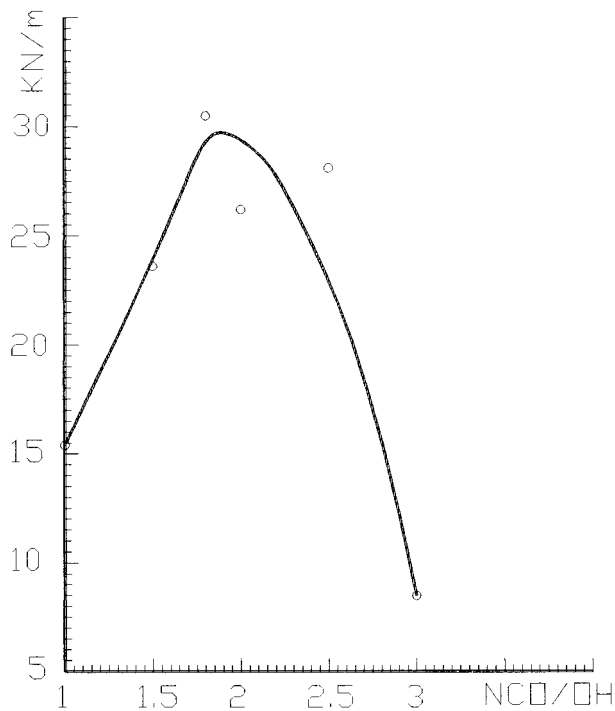**Figure 13** Influence of NCO/OH ratio on the cleavage strength. Substrate: 45# steel; 50% MMA.

Figure 14 Influence of NCO/OH ratio on the inhomogeneous claevage strength. Substrate: 45# steel; 50% MMA.

distinct glass transition temperatures (T_g's) were observed; one is 11°C and the other is 118°C. The two glass transition temperatures are near the respective homopolymer glass transition, but shifted inward for the lower one (11°C). This fact reveals the two-phase structure, which is consistent with the TEM analysis (see Fig. 3).

Thermogravimetric analysis (TGA) was carried out to estimate the thermal stability of the IPN. Figure 6 shows the TGA spectrum. The weight loss was calculated from Figure 6; the results are included in Table II.

Figure 1 and Table II illustrate that the thermal stability of the IPNs is better than of both polyurethane and PMMA networks and that they exhibit a distinct synergistic effect. According to

Table IV Influence of NCO/OH Ratio on the Shear Impact Strength

	NCO/OH				
	2.5	2.0	1.8	1.5	1.0
Shear impact strength[a]	8.6	7.0	7.7	11.0	12.6

[a] Substrate: 45# steel; 50% MMA; unit kJ/m^2.

Table V   Influence of MMA Content on the Peeling Strength (NCO/OH = 1.5)

Peeling Strength (N/mm)	MMA Content (Wt %)			
	50.0	40.0	20.0	0.0
For Fe—Al	1.40	1.60	2.10	1.50
For Al—Al	1.50	2.10	2.20	1.50

Kim[22] and Bolyakov,[23,24] this synergistic effect (i.e., the thermal stability of some IPNs is better than of any pure component) can be contributed to two factors: First, the interpenetration between PMMA and PU increases the cohesion and makes intimate contact between the two phases. Second, the depolymerization product of PMMA acts as a radical scavenger and retards the degradation of the material.

Adhesive Power

The influence of MMA content on the lap shear strength, tensile strength of adhesion, cleavage resistance, and inhomogeneous clevage strength are graphically shown in Figures 7–10, respectively. The influence of MMA content on the shear impact strength is tabulated in Table III.

Figures 7–9 illustrate that the lap shear strength, tensile strength, and cleavage strength increase with MMA content. But the maximum value is at about 40–50% MMA content for inhomogeneous cleavage and shear impact strength as shown in Figure 10 and Table III.

The influence of the NCO/OH ratio on the lap shear strength, tensile strength, cleavage strength, and inhomogeneous cleavage strength are shown in Figures 11–14, respectively, and the influence
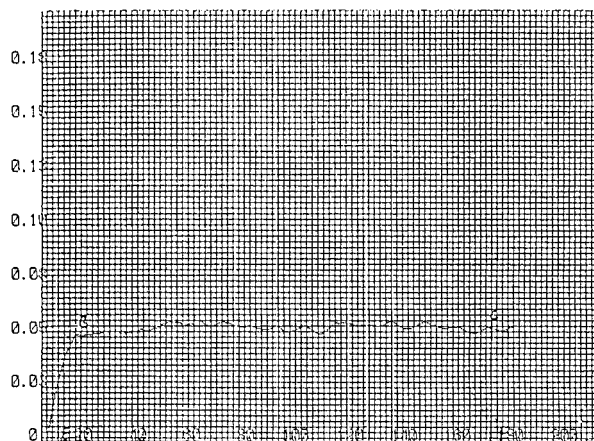

Figure 15   Peeling curve for aluminum–aluminum. Ingredients: NCO/OH = 1.5; MMA content 50%.

of the NCO/OH ratio on the shear impact strength is shown in Table IV.

From Figures 11–14 and Table IV, it can be seen that all the mechanical strengths of adhesion exist at a maximum value at a NCO/OH ratio about 1.4–1.5. Figure 15 shows the 180° peeling curve for aluminum to Aluminum. The influence of MMA content on the peeling strength is tabulated in Table V. Table V indicates that the peeling strength reaches the maximum value at about 20% MMA.

The above test results clearly indicate the excellent adhesive power of the adhesives made from the prepolymer of IPN COPU/PMMA. As compared with other generally used ahesives, as shown in Table VI, it is obvious that this type of adhesive is a good prospect for use in a practical project.

CONCLUSIONS

1. The IPN COPU/PMMA made here is a two-phase material which exhibits excel-

Table VI   Comparison with Other Generally Used Adhesives

Trade Name	Lap Shear Strength	Tensile Strength	Inhomogeneous Cleavage	Cleavage Strength	Shear Impact
Adhesive made in this article	8.64[a]	25.85[a]	23.6[a]	166.2[a]	11.0[a]
Great Wall 717	> 6.96[b]				> 9.8[a]
JQ-2	13.7[b]				
GH-201	12.0[a]				
AZ-1	14.7[a]		27.0[a]		
TeMo401	7.84[b]	18.36[b]			
AZN-501		14.7[a]			

[a] For steel–steel.
[b] For aluminum–aluminum.

lent mechanical properties and thermal stability.

2. The adhesives made from the prepolymer of IPN COPU/PMMA have good prospects in a practical project, especially for the adhesion of metals. The adhesive strength of the adhesive is excellent. The lap shear strength, tensile strength of adhesion, 180° peeling strength, cleavage strength, inhomogeneous cleavage strength, and shear impact strength reaches 9.79 MPa, 25.9 MPa, 2.2 kN/m, 166.2 kN/m, 30.5 kN/m, and 13.9 kJ/m^2, respectively.

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