

Interpenetrating Polymer Networks Based on Polyol Modified Castor Oil Polyurethane and Poly(2-ethoxyethyl methacrylate): Synthesis, Chemical, Mechanical, Thermal Properties, and Morphology

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Received 7 October 2003; accepted 14 April 2004

DOI 10.1002/app.20930

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Interpenetrating polymer networks (IPNs) of glycerol modified castor oil polyurethane (GC-PU) and poly(2-ethoxyethyl methacrylate) poly(2-EOEMA) were synthesized using benzoyl peroxide as initiator and ethylene glycol dimethacrylate (EGDM) as crosslinker. GC-PU/poly(2-EOEMA) interpenetrating polymer networks were obtained by transfer molding. The novel GC-PU/poly(2-EOEMA) IPNs are found to be tough films. These IPNs are characterized in terms of their resistance to chemical re-

agents thermal behavior (DSC, TGA) and mechanical behavior, including tensile strength, Young's modulus, shore A hardness, and elongation. The morphological behavior was studied by scanning electron microscopy. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1029–1034, 2004

Key words: transesterification; glycerol modified castor oil; polyurethane; 2-ethoxyethyl methacrylate; interpenetrating polymer networks

INTRODUCTION

Interpenetrating polymer networks (IPNs) are defined as a combination of two polymers or more in network form, in which at least one component is polymerized and/or crosslinked in the immediate presence of the other.^{1–10} The preparation of simultaneous interpenetrating networks (SINs) involves the mixing of all components in an early stage followed by the formation of both networks via independent reactions proceeding in the same container. SIN systems like PU/poly(styrene)¹¹ and epoxy/acrylate,¹² have been reported already.

Due to the plentiful availability of natural oil at low cost, it has been widely used in the preparation of IPNs. Several researchers have reported castor oil/acrylate IPNs,^{13,14} wherein incorporation of castor oil has increased the toughness of acrylic resins.

Modification of castor oil has been attempted by familiar reactions, such as epoxidation, hydrogenation, hydroxylation, and bromination, to improve the toughness and flame retardance of cured systems.¹⁵

As a part of our free radical polymerization studies,^{16–20} we have reported earlier on the synthesis of

IPNs based on modified castor oil polyurethane/poly(2-hydroxyethyl methacrylate)²¹ GC-PU/poly(2-HEMA). We present here the complete synthesis and characterization of sequential IPNs based on glycerol-modified castor oil polyurethane/poly(2-ethoxyethyl methacrylate), GC-PU/poly(2-EOEMA). Studies on chemical, mechanical, thermal properties, morphology, and the effect of NCO/OH ratio of the polyurethane on these properties have been reported.

EXPERIMENTAL

Materials

Castor oil from the local market was found to contain a hydroxyl value of 168 mg KOH/g without any purification. Hexamethylene diisocyanate (HMDI) was obtained from E. Merck (Germany). 2-Ethoxyethyl methacrylate (2-EOEMA) and ethylene glycol dimethacrylate (EGDM) were from Aldrich (USA). Triethanolamine and benzoyl peroxide were obtained from S.D Fine (India). Glycerol was from Loba Chemie (India). Benzoyl peroxide was recrystallized from chloroform and monomer 2-EOEMA was freed from the inhibitor before use. All other reagents were analytical grade and used without further purification.

Synthesis of glycerol-modified castor oil

A resin kettle equipped with thermometer, stirrer, nitrogen inlet, and reflux condenser were charged

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TABLE I
Data on Reed Composition (Individual) Polyurethane (PU) and 2-Ethoxy ethyl methacrylate for IPNs Synthesis

Polymer code	NCO/OH ratio of MDI and castor oil	Prepoly urethane (wt %)	2-Ethoxyethyl meth acrylate (wt %)	Density (g/ml)	T_g (K)
IPN-1	1.8	25	75	1.0004	279
IPN-2	1.8	35	65	1.0568	260
IPN-3	1.8	45	55	1.9582	240
IPN-4	2.0	25	75	1.0658	266
IPN-5	2.0	35	65	1.1346	258
IPN-6	2.0	45	55	1.9994	241
IPN-7	2.2	25	75	1.2591	271
IPN-8	2.2	35	65	1.0259	250
IPN-9	2.2	45	55	1.7956	248
Pure- 2-EOEMA	—	—	—	—	290
Pure GC-PU	—	—	—	—	223

with one equivalent each of castor oil and glycerol along with catalyst litharge (0.05%). The reaction was carried out at 240–250°C for 2 h. Progress of the reaction was monitored by thin layer chromatography.²² The resultant polyol was dried at 80°C under vacuum and had hydroxyl value of 223 mg KOH/g, acid value of 2.0 mg KOH/g, and viscosity (at 30°C) of 486 cP.

Synthesis of polyurethane

Glycerol-modified castor oil was added slowly with stirring to HMDI of varying ratios of NCO/OH. The reaction was carried out at 45°C for 1 h. The resulting polymer product was isolated as a thick liquid.

Synthesis of IPNs

Series of sequential IPNs (Table I) were synthesized by charging the isocyanate terminated polyurethane prepolymer (PPU) in different proportions and different NCO/OH ratios along with 1% triethanol amine (for chain extension and curing) to the mixture of 2-EOEMA, 1%EGDM crosslinker, and benzoyl peroxide (0.5% based on 2-EOEMA) in a reaction kettle. The mixture was stirred at room temperature for 15 min to form a homogeneous solution. The temperature was increased to 60°C to initiate 2-EOEMA polymerization. After stirring for 1 h, the solution was poured into a glass mold kept in a preheated oven maintained at 60°C. It was kept at this temperature for 24 h and at 120°C for 4 h to facilitate the complete network formation. The film thus formed was cooled slowly and removed from the mold (Scheme 1).

Characterization methods

IPNs were characterized according to the following standard methods: resistance to chemical reagent, ASTM specification D543 (1978); tensile strength,

ASTM specification D638 (1971); and hardness measurements, ASTM specification D1531 (1962).

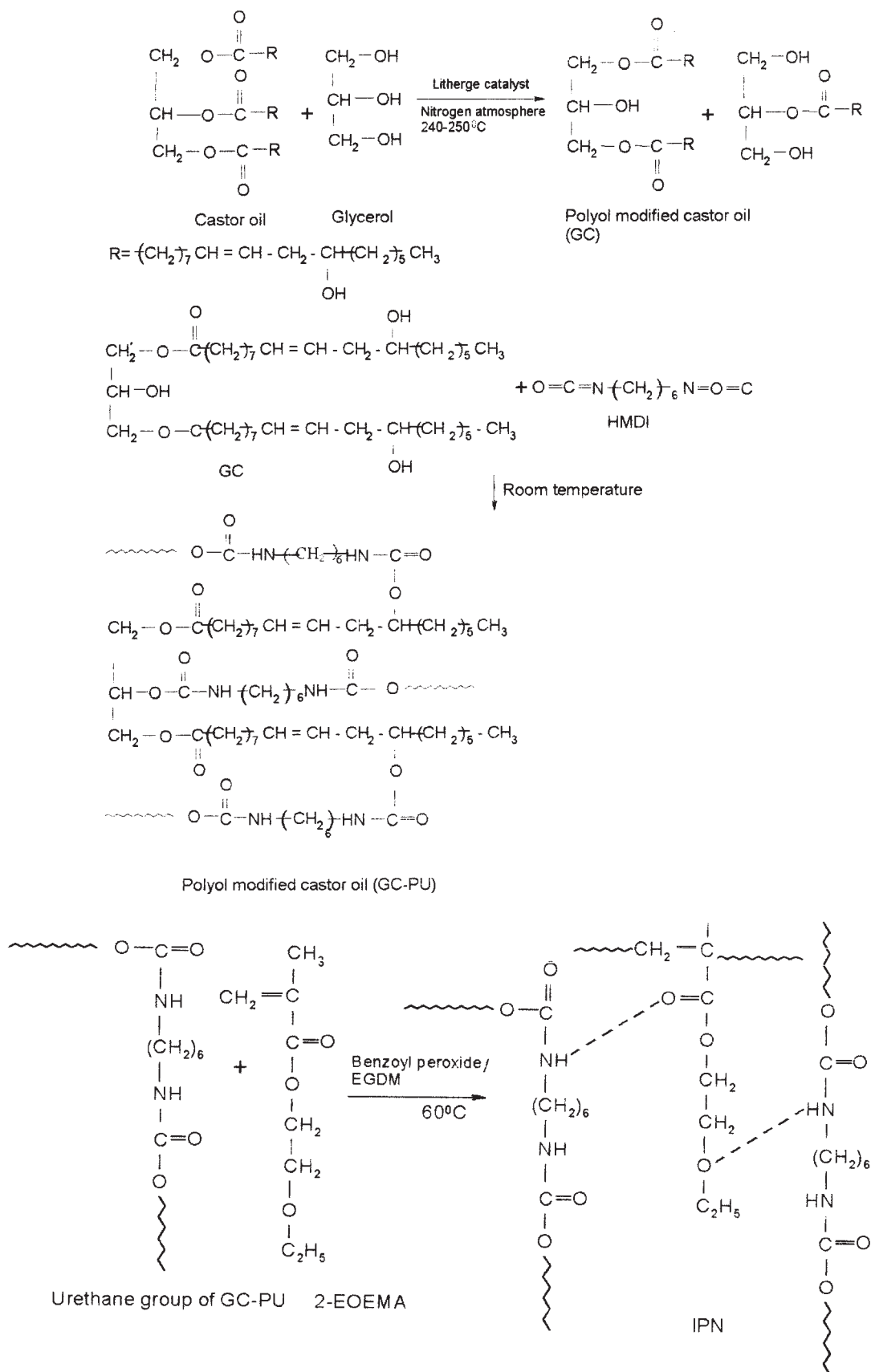
The glass transition temperatures were determined on a Mettler TA4000 DSC. Temperature and energy calibrations were carried out with indium. Samples weighing between 12 and 15 mg were used in all cases, with a scanning rate of 10°C/min in N₂ gas. The glass transition temperature (T_g) was calculated as the midpoint of the inflection point in heat capacity. The viscosity of the modified castor oil was determined with a Brookfield viscometer DVII+ with thermostat attachment. Scanning electron micrograph (SEM) observations were made with the Philips em-400 equipped with S (T) EM system PW-65585 scanning attachment. The cryogenically fractured film in liquid N₂ was mounted vertically on the SEM stub by Ag adhesive paste. The specimen was coated with gold using vacuum system EPS/CrI Zeiss at about 10⁻⁵ Torr. Thermograms were obtained on a Mettler TA 4000 TGA at a heating rate of 10°C/min in air.

RESULTS AND DISCUSSION

GC-PU/PEOEMA

Trans-esterification of castor oil has a very high advantage for preparation of PU because crosslinking density increases due to increase in OH content from 160 to 253 mg KOH/g as reported earlier.¹⁶ In the present work all PPUs were prepared by reacting modified castor oil with 4,4-diphenyl methane diisocyanate with different NCO/OH ratios. IPNs were synthesized by charging PPU along with 1% triethanolamine mixture to 2-EOEMA and subsequent heating at 60°C. All IPNs were synthesized as tough films from molding. The IPNs are almost insoluble in the following solvents such as acetone, carbon tetrachloride, chloroform, methanol, ethylacetate, dimethylformamide, tetrahydrofuran, diethyl acetamide, dioxane,

Preparation of GC-PU/poly(2-EOEMA)IPNs.



Scheme 1 Preparation of GC-PU/poly(2-EOEMA) IPNs.

TABLE II
Chemical Resistance Test of IPNs (% wt Loss on Treatment with Different Reagents)

Chemical reagent	IPN-1	IPN-2	IPN-3	IPN-4	IPN-5	IPN-6	IPN-7	IPN-8	IPN-9
25% CH ₃ COOH	3.9823	11.524	5.982	4.0372	5.248	7.613	4.982	7.968	5.983
25% H ₂ SO ₄	2.162	1.794	1.273	2.234	1.893	1.486	1.948	1.893	1.748
25% HCl	0.605	0.821	0.693	0.708	0.9612	0.792	1.592	0.928	0.832
5% HNO ₃	0.6427	0.3421	0.762	0.8374	0.3792	0.334	0.6524	0.531	0.234
10% NaOH	1.098	0.3679	1.786	2.2346	0.421	1.297	1.234	3.073	1.839
MEK	7.612	0.216	5.660	5.818	5.887	5.780	4.213	5.916	5.994
CCl ₄	8.923	6.6212	4.732	9.678	7.733	4.782	7.6312	5.932	4.932
Toulene	9.292	6.612	4.638	6.283	7.613	5.292	8.293	5.292	3.462

pyridine, benzene, xylene, etc. and their densities are higher than water (Table I).

IR spectra of PPU showed characteristic absorption at 1,740 and 3,410 cm⁻¹ corresponding to urethane amide (-NH stretching). As the prepolymer is isocyanate terminated, an intense and sharp band due to NCO is observed at 2,260 cm⁻¹. IR spectra of IPNs showed a broad peak at 3,220 cm⁻¹ corresponding to the unreacted -OH groups of castor oil or glycerol. Further, IPNs do not show any band at 2,260 cm⁻¹ corresponding to NCO, because of the reaction of curing agent 1% trietanolamine with the terminal NCO.

Chemical resistance

Chemical resistance in a series of standard reagents was studied as per ASTM D 543 (1978) and the results are furnished in Table II. The pieces of IPNs (20 × 20 × 0.78 mm) were kept in 100 mL standard reagents for 7 days. The percentage change in weight loss of some of the IPNs was measured. All these IPNs irrespective of NCO/OH ratio and PU/poly(2-EOEMA) composition were stable in all acid alkali and solvents. The present IPNs are much better in terms of chemical resistance due to higher crosslinking densities resulting from hydrogen bonding (Scheme 1) and conformed to IPNs of GC-PU/poly(methyl methacrylate) (GC-PU/poly (MMA))²³ and GC-PU/(2-HEMA).²⁰

Mechanical properties

Patel and Suttar,⁹ Riordan et al.,²⁴ and Padma et al.¹³ reported synergistic behavior of IPNs obtained from castor oil with different acrylates. The castor oil PU/acrylate IPNs exhibited modified properties of their individual components. Mechanical properties such as elongation at break (%), tensile strength, and Young's modulus were investigated according to ASTM D638 (1968) and shore A hardness with ASTM D1531 (1968) and the data obtained are recorded in Table III. It shows higher mechanical properties than their individual component networks and castor oil PUs.

It is observed from mechanical properties of these IPNs that incorporation of low T_g poly(2-EOEMA) into a GC-PU has given modest improvement in the Young's modulus value from 3 to 84 MN/m² depending upon the content of 2-EOEMA. GC-PU/poly(2-EOEMA) showed higher tensile strength with less elongation and better hardness compared to GC-PU/poly(2-HEMA)²¹ and GC-PU/poly (MMA).²³ It can be concluded that GC-PU/poly(2-EOEMA) IPNs exhibit better mechanical properties. Present IPNs under investigation show lesser elongation, maybe due to the fact that glycerol modification of castor oil results in more crosslinking and stiffer IPNs due to good compatibility. Compatibility can also be expected by hydrogen bonding between ether and carboxyl groups of poly(2-EOEMA) and a secondary amine of urethane.²⁵ (Scheme 1)

Thermal analysis

Frisch and coworkers²⁶⁻²⁸ assessed the thermal stability of various IPNs and found that they possessed greater stability than their component networks. The thermal stability of IPN-4, IPN-5, and IPN-6 of different monomer content were compared with homopolymer poly(2-EOEMA) in terms of percent loss in weight at different temperatures. Results obtained from TGA

TABLE III
Mechanical Parameters of IPNs

Sample code	Tensile strength (N/mm ²)	% Elongation	Young's modulus (MN/m ²)	Shore A hardness
IPN-1	9	49	2.9	56
IPN-2	9	17	84	45
IPN-3	5	41	59	58
IPN-4	3	23	17.6	49
IPN-5	16	25	63	57
IPN-6	12	21	7.9	66
IPN-7	11	29	47	72
IPN-8	5	40	7.2	59
IPN-9	12	40	3.8	41

TABLE IV
TGA Data of IPNs

Sample code	200°C	250°C	300°C	350°C	400°C	450°C	500°C	Degradation temperature (°C)
IPN-4	—	4.05	11.48	26.35	37.8	55.04	86.48	535
IPN-5	—	0.586	14.18	30.40	45.2	57.4	79.7	525
IPN-6	—	2.7	13.5	21.62	41.2	54.05	87.83	531
Pure EOEMA	16.89	47.29	94.59	—	—	—	—	307

are reported in Table IV. It is evident that all the IPNs are stable up to approximately 200°C and lose weight rapidly above 450°C and decompose completely beyond 550°C. However, there is not much change in thermal stability of all the IPNs with the increase in the content of poly(2-EOEMA) content. Thermal properties of all the IPNs are found to be much better than that of the homopolymer poly(2-EOEMA).

As per the previous findings,^{29–31} the synergistic effect of IPNs can be attributed to two factors: (1) the interpenetration between poly(2-EOEMA) and PU increases the cohesion and makes intimate contact between the two phases, (2) the depolymerization product of poly(2-EOEMA) acts as a radical scavenger and retards the degradation of the material. Figure 1 and Table IV show that the thermal stability of these IPNs is better than that of both the polyurethane and poly(2-EOEMA) networks. They exhibit a distinct synergistic effect.

The glass transition temperature (T_g) of synthesized IPNs lies between the T_g s of the GC-PU and poly(2-EOEMA) (Table I). The appearance of a single T_g indicates the formation of IPNs.

Phase morphology

The morphology of the IPNs were studied from their micrographs shown in Figure 2. Three IPNs were chosen at random: IPN-1, IPN-4, and IPN-7. The observed homogeneity in each specimen indicates the interpenetration of the phase domains of GC-PU and poly(2-EOEMA).

CONCLUSION

IPNs prepared by modified castor oil show improved properties over unmodified castor oil due to more crosslinking density due to an increase in hydroxyl

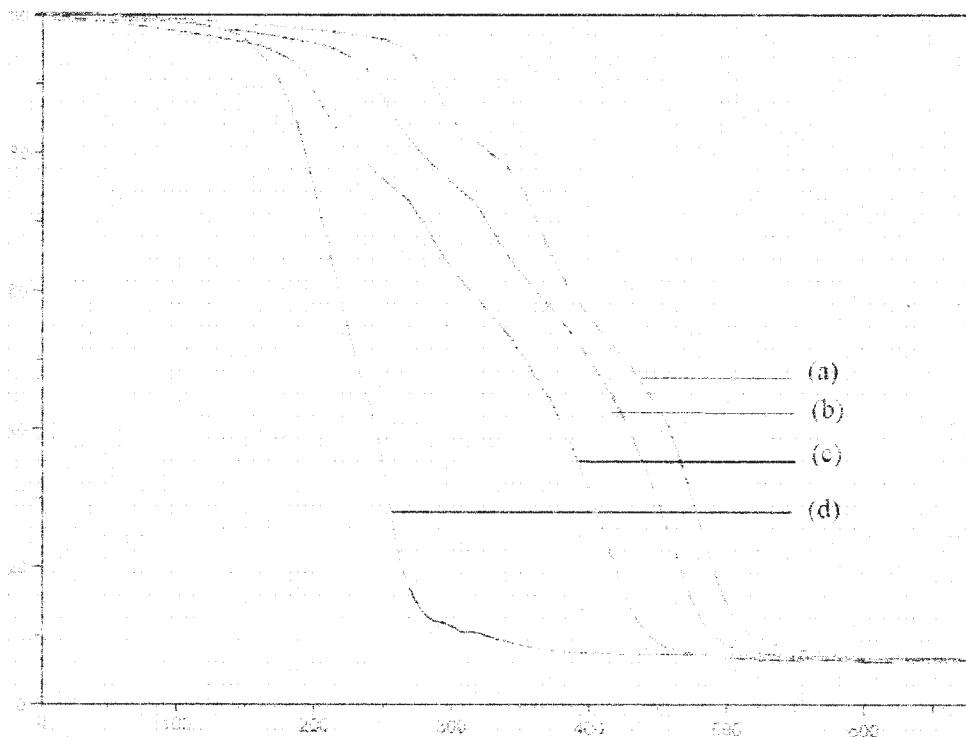


Figure 1 TGA thermograms: (a) IPN-1, (b) IPN-4, (c) IPN-7, (d) pure poly(EOEMA).

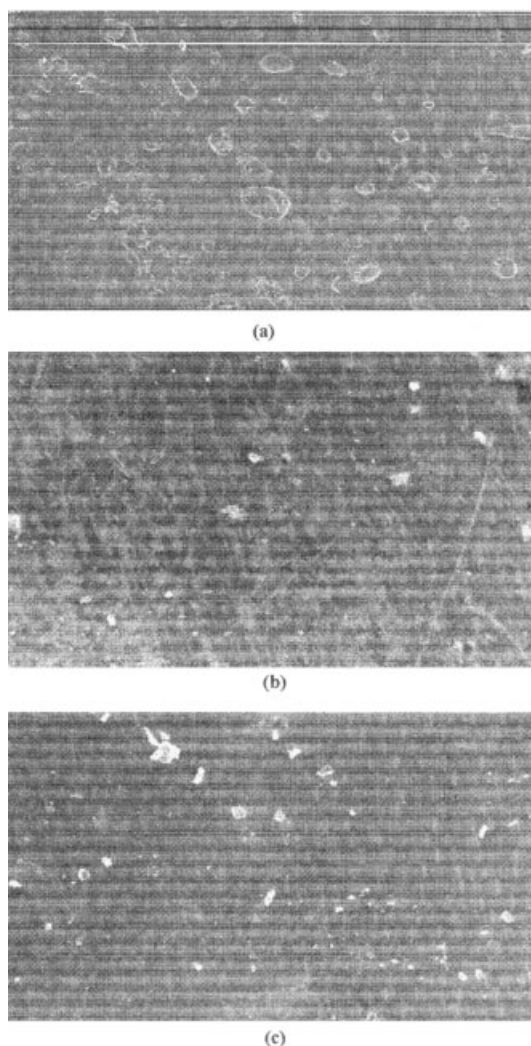


Figure 2 Scanning electron micrographs with $\times 1,200$ magnification: (a) IPN-1, (b) IPN-4, and (c) IPN-7.

content. Incorporation of low T_g poly(2-EOEMA) to GC-PU increased the toughness, decreased the elongation, and improved the thermal stability. Excellent chemical resistance and lower hardness and elongation could be due to higher compatibility. Hence it can be concluded that it is possible to obtain GC-PU IPNs with good toughness and low temperature resistance by incorporating poly(2-ethoxyethyl methacrylate) in the network.

C. S. Sanmathi is grateful for a fellowship awarded by Kuvempu University.

References

1. Sperling, L. H.; Mansona, J. A.; Quareshi, S. A. *Ind Eng Chem Prod Res Dev* 1981, 20, 163.
2. Sperling, L. H. *J Polym Sci* 1977, 60, 175.
3. Hourston, D. J.; Huson, M. G.; Mcluskay, J. A. *J Appl Polym Sci* 1986, 31, 709.
4. Lenz, R. W. *Organic Chemistry of Synthetic High Polymers*; Wiley: New York, 1967; p. 189.
5. Yenwo, G. M.; Mansona, J. A.; Pulido, L. H.; Sperling, L. H.; Conde, A.; Devia, M. N. *J Appl Polym Sci* 1977, 12, 1531.
6. Devia, N.; Mansona, J. A.; Sperling, L. H. *Macromolecules* 1977, 12, 360.
7. Kim, S. C.; Klempner, D.; Frish, K. C.; Radigam, W.; Frish, H. C. *Macromolecules* 1976, 9, 2258.
8. Liptav, Y. S. *J Polym Mater* 1987, 4, 173.
9. Patel, M.; Suttar, B. *Eur Polym Mater* 1987, 23, 399.
10. Patel, M.; Suttar, B. *J Appl Polym Sci* 1987, 34, 2037.
11. Kim, S. C.; Klempner, D.; Frish, K. C.; Frisch, H. C.; Ghiradella, K. *Polym Eng Sci* 1976, 1115, 339.
12. Touhsaent, R. E.; Thomas, D. A.; Sperling, L. H. *J Polym Sci* 1974, C46, 175.
13. Padma, L. N.; Lekha, S.; Panda, K.; Pattnain, T. *J Appl Polym Sci* 1993, 47, 1089.
14. Patel, P.; Shah, T.; Suthar, B. *J Appl Polym Sci* 1990, 40, 1037.
15. Weidiong, X.; Peixin, H.; Benqin, H. *J Appl Polym Sci* 2002, 86, 2530.
16. Sherigara, B. S.; Yashoda, M. P.; Nayak, P. V.; Padmalatha. *J Phys Org Chem* 1999, 12, 605.
17. Rai, K. S.; Shivakumar, K.; Sherigara, B. S. *Eur Polym Mater* 2000, 36, 2000.
18. Yashoda, M. P.; Sherigara, B. S.; Venkateshwaran, G. *Polymer* 2000, 41, 7381.
19. Yashoda, M. P.; Sherigara, B. S.; Venkateshwaran, G. *J Macromol Sci Pure Appl Sci* 2001, 37a, 1487.
20. Sanmathi, C. S.; Prasannakumar, S.; Sherigara, B. S. *Bull Mater Sci* 2004, 28, 243.
21. Prashantha, K.; Vasanthakumar Pai, K.; Sherigara, B. S.; Prasannakumar, S. *Bull Mater Sci* 2001, 24, 535.
22. Das, P.; Nirvan, Y. *Paint India* 1994, 44, 50.
23. Athawale, V.; Kolekar, S. *Eur Polym Mater* 1998, 34, 1447.
24. Riordan, D.L.; Song, M.; Schafer, F. U.; Pollock, H.M.; Ham-miche, A. *Polymer* 1999, 40, 4769.
25. Hill, D. J. T.; Whittaker, A. K.; Wong, K. W. *Macromolecules* 1999, 32, 5285.
26. Frisch, K. C.; Klempner, D.; Mukherjee, S. K. *J Appl Polym Sci* 1974, 18, 689.
27. Frisch, K. C.; Klempner, D.; Midgal, S. *J Polym Sci Polym Chem Ed* 1974, 12, 885.
28. Frisch, K. C.; Klempner, D.; Midgal, S. *J Appl Polym Sci* 1975, 19, 1893.
29. Kim, S. C. *J Polym Sci* 1977, 21, 1289.
30. Bolyakov, N. K. *Polym Sci USSR* 1968, 10, 700.
31. Zhang, L. C.; Liu, Y. L. *Macromolecules* 1979, 12, 360.