Simultaneous Full-Interpenetrating Polymer Networks of Blocked Polyurethane and Vinyl Ester. II. Static and Dynamic Mechanical Properties

CHIN-HSING CHEN, WE-JUI CHEN, MENG-HUEI CHEN, YUAN-MOU LI

Institute of Chemical Engineering, Chinese Culture University, Yang-Ming-Shan, Taipei, Taiwan, Republic of China

Received 11 March 1998; accepted 7 June 1998

ABSTRACT: Simultaneous full-interpenetrating polymer networks (full-IPNs) based on blocked polyurethane (PU) and vinyl ester (VE) have been prepared. The static and dynamic properties of these IPNs have been examined. Results show that the tensile strength and flexural strength of IPNs increased with blocked PU content to a maximum value at 7.5 wt % PU content and then decreased. The tensile modulus, flexural modulus, and hardness of IPNs decreased with increasing blocked PU content. The impact strength of IPNs increased with increasing blocked PU content. The tensile strength, flexural strength, tensile modulus, and flexural modulus of IPNs increased with filler (kaolin) content to a maximum value at 20 to 25 phr filler content and then decreased. The higher the filler content, the greater the hardness, and the lower the impact strength of IPNs. The tensile strength, flexural strength, tensile modulus, flexural modulus, and hardness of IPNs increased with increasing VE initiator content. The dynamic technique was used to determined the damping behavior across a temperature range. Results show that the glass transition temperature (T_g) of IPNs are shifted inwardly compared with pure PU and VE, which indicated that the blocked PU–VE IPNs showed excellent compatible. Meanwhile, the glass transition temperature was shifted to a higher temperature with increased filler content. The dynamic storage modulus (E') of IPNs increased with increasing VE and filler content. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1977–1985, 1999

Key words: interpenetrating polymer network; polyurethane; vinyl ester; static properties; glass transition temperature; dynamic storage modulus

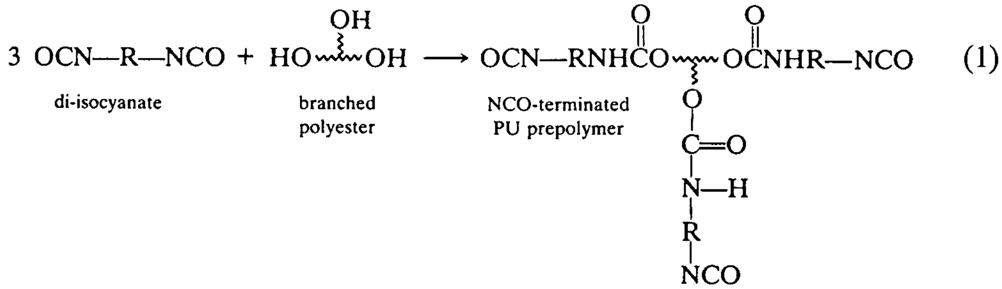
INTRODUCTION

Interpenetrating polymer networks (IPNs) were first synthesized by Miller in the 1960s.[1] Since that time, the jargon has been used to describe the combination of two or more different polymer networks, which consist of purely physical entanglements of the polymer chains synthesized either simultaneously or sequentially with respect to each other.[2–5] The objective of IPNs is to improve upon the properties of individual polymers. The IPNs are usually heterogeneous systems, in which one polymer exists above its glass transition temperature (T_g), which has a glassy microstructure at room temperature, while the other polymer exists below its T_g, which shows a rubbery microstructure at room temperature. By altering the relative amounts of each polymer in the IPNs, the individual polymer properties may be changed, in which the lower T_g component was shifted to a higher temperature, while the higher T_g component was shifted to a lower temperature.[6–11] The goal is an understand-

Correspondence to: C.-H. Chen.

Contract grant sponsor: National Science Council, Republic of China; contract grant number NSC 85-2216-E034-001.

Journal of Applied Polymer Science, Vol. 71, 1977–1985 (1999)
 CCC 0021-8995/99/121977-09



Scheme 1

ing of the important factors in determining the properties exhibited by the resulting IPNs so that materials with properties tuned to the required application may be produced.[1]

Polyurethane (PU) resin shows some unique properties, including excellent elasticity, excellent abrasion resistance and damping properties, high impact strength, and elongation, which have been widely used in adhesives, coatings, synthetic leather, construction, and automatic applications and as shoe soles.[12–14] However, PU could not be utilized in some applications for lack of mechanical modulus and thermal resistance. While vinyl ester possesses high mechanical modulus and thermal resistance, it is too brittle to be utilized in many instances.[15] Hence, a blending technique is applied utilizing IPNs of two polymer components that can improve the deficiencies of each individual resin.

In this study, the full-interpenetrating polymer networks (full-IPNs) based on blocked PU–vinyl ester (VE) were prepared from blocked NCO-terminated PU prepolymer with chain extender and VE prepolymer with initiator using a simultaneous polymerization (SINs) method.[16–18] This article presents the static and dynamic properties of blocked PU–VE IPNs. The effect of parameters on static mechanical properties included blocked PU content, filler content, and initiator content of VE. The dynamic technique was used to determined the damping behavior across a temperature range.

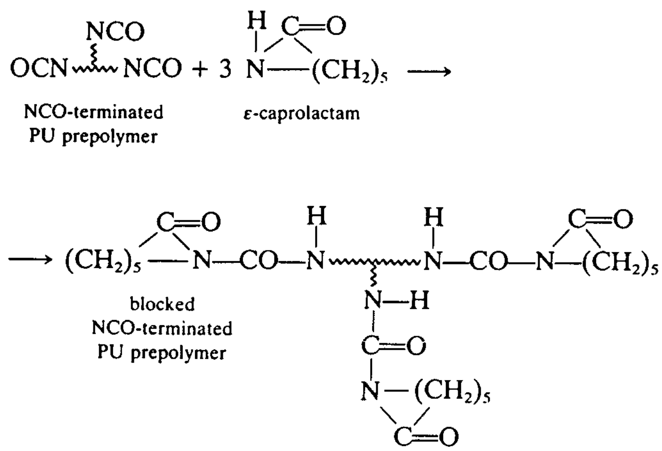
EXPERIMENTAL

Materials

A blocked NCO-terminated PU prepolymer was prepared from toluene di-isocyanate (TDI-80, 80/20 blend of 2,4 and 2,6 isomers) and from polyol (branched polyester) at the NCO-to-OH equivalent ratio of 2 to 1, and then was blocked by ε-caprolactam [the blocking reaction proceeds following eqs. (1) and (2)], which was supplied by the Bayer Co., Germany. It has a viscosity of 31000 mPa s, a weight-average molecular weight of 4230, and an equivalent weight with respect to 1410. The chain extender (curing agent) of PU used was aromatic diamine (ACR H-3486), a blend of 60% 4,4-methylene diamine, and 40% *m*-phenylene diamine, supplied by Shell Chemical Co., USA. It has a molecular weight of 266, a viscosity of 20,000 mPa s, and a specific gravity of 1.11. The vinyl ester (VE) prepolymer used was bisphenol-A-type [the chemical structure of which is described in eq. (3)] and was supplied by Swancor Co., Taiwan, ROC. It has a viscosity of 240 mPa s. The initiator used was C-type curing agent, which is a blend of 80% cumene hydroperoxide and 20% plasticizer, supplied by Swancor Co., Taiwan, ROC. It has a viscosity of 500 mPa s. The filler used was surface-treated kaolin and was supplied by Yin Chin Co., Taiwan, ROC, which has a specific gravity of 2.7 with a particle size of 325 mesh (see Schemes 1–3).

Equipment and Measurement

1. The tensile strength and modulus were measured on an Instron 1123 universal testing machine (Instron Co., USA) following the specification of ASTM D-638. The sample was dumbbell-shaped, with dimensions of 165 × 19 × 3.0 mm (length × width × thickness) and a crosshead speed of 10 mm/min.
2. The flexural strength and modulus were measured on an Instron 1123 universal testing machine (Instron Co., USA) following the specification of ASTM D-790. The sample dimensions were 127 × 12.7 × 3.0 mm (length × width × thickness), the span was 90 mm, and the crosshead speed was 2 mm/min.



(2)

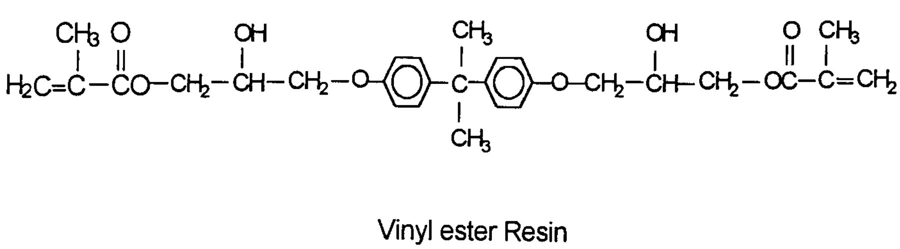
Scheme 2

3. The notched Izod impact strength was measured in a TMI-43-1 (Testing Machine Inc., USA) according to ASTM D-256. The sample dimensions were 63.5 × 12.7 × 3.0 mm (length × width × thickness), and the notched depth was 2.5 mm.
4. The surface hardness was measured by means of a Type-D Shore Durometer (Model No. 41-50, TMI Co., USA) according to ASTM D-2240.
5. The dynamic mechanical analyzer (DMA) utilized was a DuPont 9900 (DuPont Co., USA) from −150 to 250°C. The DMA system was a resonance-frequency-type, and the dried sample dimensions were 50 × 12.7 × 2.0 mm (length × width × thickness). The rate of heat was 5°C/min, and the amplitude of oscillation was 1 Hz. The Poisson's ratio was 1 to 2.

Preparation of Blocked PU–VE IPN Samples

The blocked NCO-terminated PU–VE IPN samples was prepared in four stages, as follows.

1. One equivalent of blocked NCO-terminated PU prepolymer was heated to 50°C and then mixed with one equivalent of aromatic diamine (ACR H-3486) homogeneously. The vinyl ester prepolymer was heated to 50°C and then mixed with 1.5 phr of initiator homogeneously. Then, the two mixtures were blended in various weight ratios at 50°C and mixed completely using a high-torque stirrer.
2. If necessary to discuss the effect of filler (kaolin) on the properties, the filler and the above two mixtures of blocked PU (15 wt %)–VE (85 wt %) were blended in various filler ratios at 50°C and mixed completely using a high-torque stirrer.
3. The above mixture (unfilled and filled) was molded in an ASTM standard stainless steel mold, and the surfaces of the stainless steel mold have been treated by chrome plating.
4. The mixture of mold was cured in an oven for 3 h, and the temperature was maintained at 140°C.
5. Finally, the samples were removed from the mold and kept in a desiccator, where the relative humidity and temperature were maintained at 50% and 30°C, respectively, for at least 2 days before they were tested.



(3)

Scheme 3

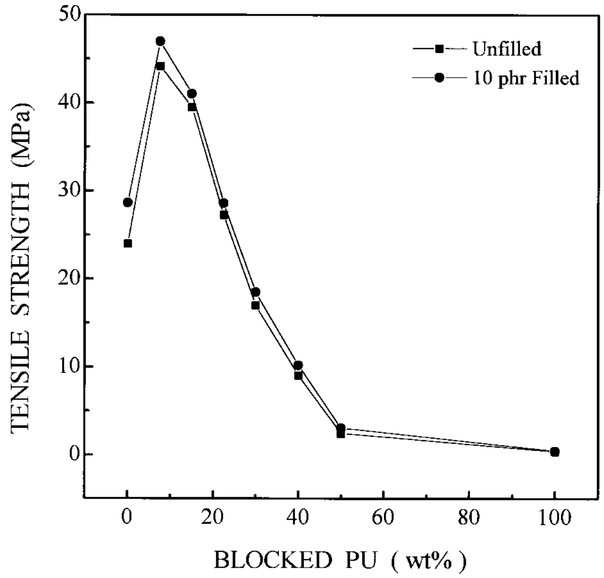


Figure 1 Tensile strength versus blocked PU content for unfilled (—■—) and 10 phr filled (kaolin) (—●—) of blocked PU–VE IPNs.

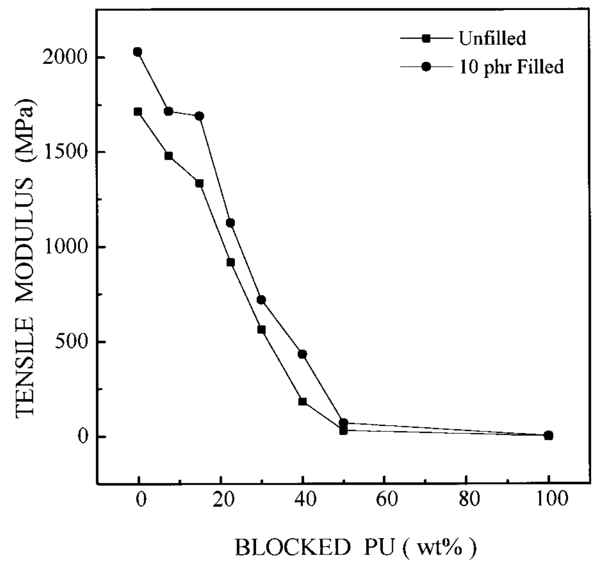


Figure 3 Tensile modulus versus blocked PU content for unfilled (—■—) and 10 phr filled (kaolin) (—●—) of blocked PU–VE IPNs.

RESULTS AND DISCUSSION

Static Mechanical Properties

Effect of Blocked PU Content

The initiator content is 0.5 phr in this section. Figures 1 and 2 showed the tensile strength and flexural strength versus blocked PU content for unfilled and 10 phr filled (kaolin) of blocked PU–VE IPNs. From these figures, one can observe that the tensile strength and flexural strength of IPNs increased with blocked PU content to a maximum value at 7.5 wt % blocked PU content and then decreased. This improvement in tensile strength and flexural strength may be due to the increase in the degree of the interpenetrating in the blocked PU–VE IPNs. Consequently, the physical entanglement would exist in the internetwork of both the blocked PU network and the VE network. The physical entanglement of the internetwork increased the crosslinking density of the matrix in the blocked PU–VE IPNs[19]; hence, the tensile strength and flexural strength of IPNs increased with increasing blocked PU content. However, as the blocked PU content is above 7.5 wt %, the tensile strength and flexural strength of IPNs showed no improvement and decreased with increasing blocked PU content. The tensile strength and flexural strength decreased, due to the soft segment content of the blocked PU, which is apparent in the blocked PU–VE IPNs when the blocked PU content is above 7.5 wt %. Figures 3–5 illustrated the tensile modulus, flexural modulus, and shore D hardness versus blocked PU content for unfilled and 10 phr filled (kaolin) of blocked PU–VE IPNs. As expected, it can be seen that the tensile modulus, flexural modulus, and shore D hardness all de-

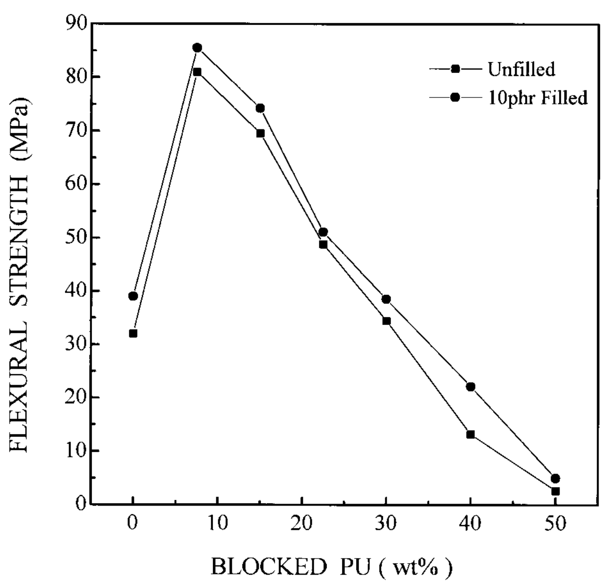


Figure 2 Flexural strength versus blocked PU content for unfilled (—■—) and 10 phr filled (kaolin) (—●—) of blocked PU–VE IPNs.

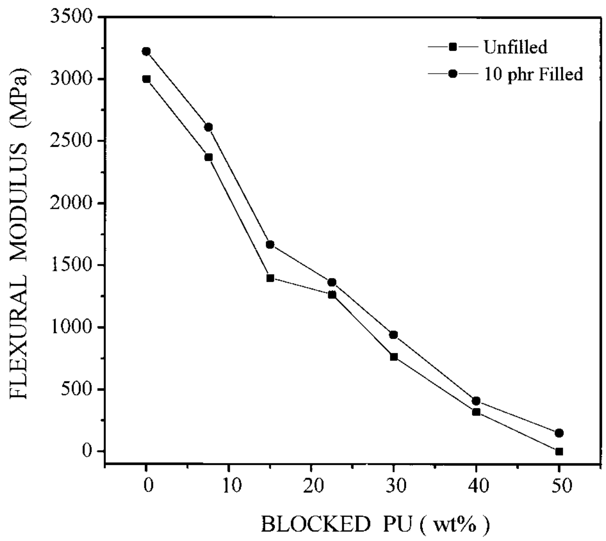


Figure 4 Flexural modulus versus blocked PU content for unfilled (—■—) and 10 phr filled (kaolin) (—●—) of blocked PU–VE IPNs.

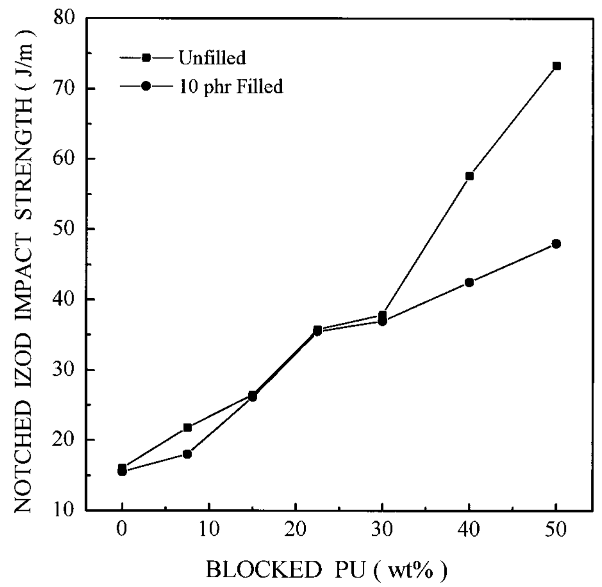


Figure 6 Notched Izod impact strength versus blocked PU content for unfilled (—■—) and 10 phr filled (kaolin) (—●—) of blocked PU–VE IPNs.

creased with increasing blocked PU content. This may be explained that the hard segments of VE appeared to have higher modulus properties, and the soft segments of blocked PU appeared to have lower modulus properties; hence, the higher the blocked PU content, the lower the tensile modulus, flexural modulus, and shore D hardness of IPNs. The notched Izod impact strength versus blocked PU content for unfilled and 10 phr filled (kaolin) of blocked PU–VE IPNs is shown in Figure 6. It can be found that the IPNs exhibited a higher impact strength when the blocked PU content increased, as the PU be dissolved in the VE matrix and the soft segments of blocked PU will toughen the matrix of the blocked PU–VE IPNs. The ductility of the matrix plays a very important role in toughening at high shear rate fracturing (that is, notched Izod impact strength).

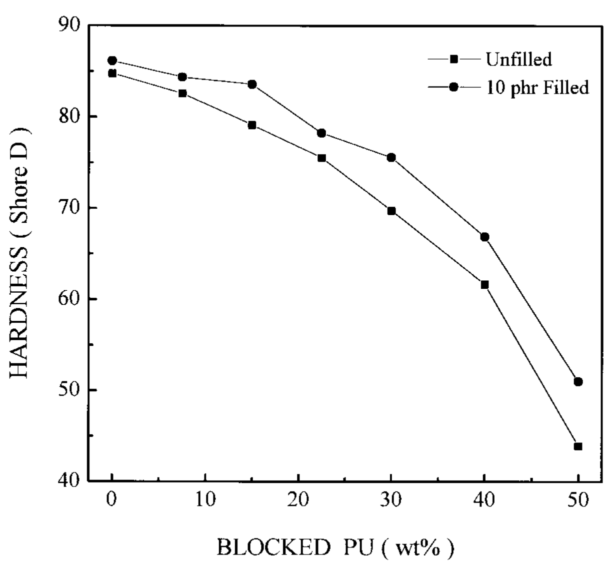


Figure 5 Shore D hardness versus blocked PU content for unfilled (—■—) and 10 phr filled (kaolin) (—●—) of blocked PU–VE IPNs.

Effect of Filler (Kaolin) Content

The initiator content is 0.5 phr in this section. The tensile strength and flexural strength versus filler (kaolin) content for blocked PU (15 wt %)–VE (85 wt %) IPNs is shown in Figure 7. It is observed that the tensile strength and flexural strength of IPNs increased with filler content to a maximum value and then decreased. The maximum tensile strength and flexural strength occurred at 20 phr filler content. Figure 8 shows the tensile modulus and flexural modulus versus filler (kaolin) content for blocked PU (15 wt %)–VE (85 wt %) IPNs. It was found that the tensile modulus and flexural modulus of IPNs also increased with filler content to a maximum value and then decreased. The maximum tensile modulus and flexural modulus occurred at 25 phr filler content. Figure 9 showed the shore D hardness versus filler (kaolin) content for blocked PU

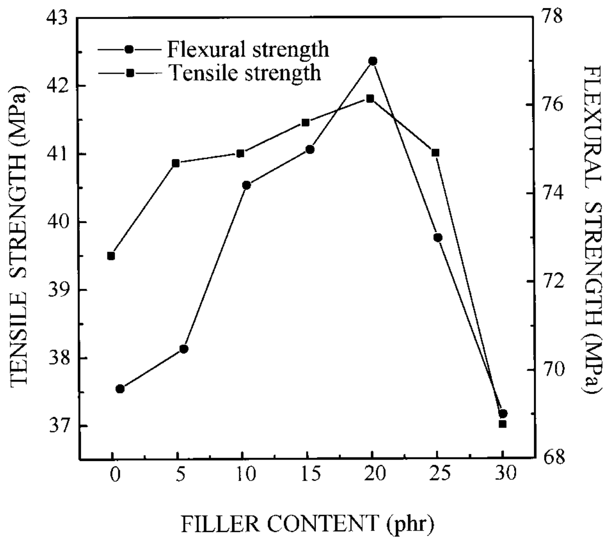


Figure 7 Tensile strength and flexural strength versus filler (kaolin) content for blocked PU (15 wt %)–VE (85 wt %) IPNs.

(15 wt %)–VE (85 wt %) IPNs. It can be seen that the hardness of IPNs increased when the filler content increased. Property improved with higher filler content. However, as the filler contents are above 20, 20, 25, and 25 phr, the tensile strength, flexural strength, tensile modulus, and flexural modulus decreased with increasing filler content, respectively. Figure 10 illustrated the notched Izod impact strength versus filler (kaolin) content for blocked PU (15 wt %)–VE (85 wt %) IPNs. From the figure, one can observe that the notched

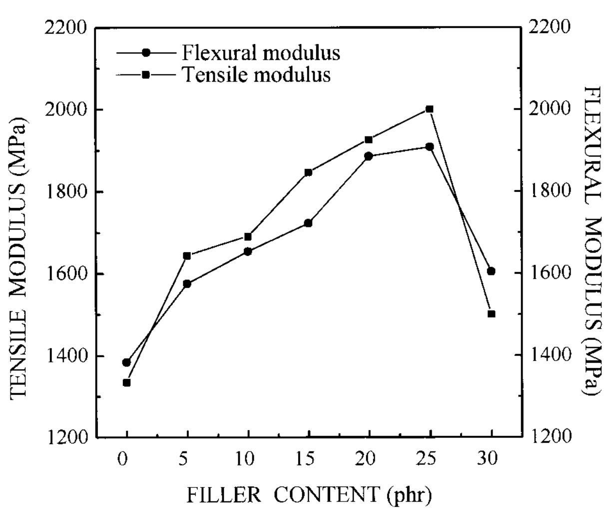


Figure 8 Tensile modulus and flexural modulus versus filler (kaolin) content for blocked PU (15 wt %)–VE (85 wt %) IPNs.

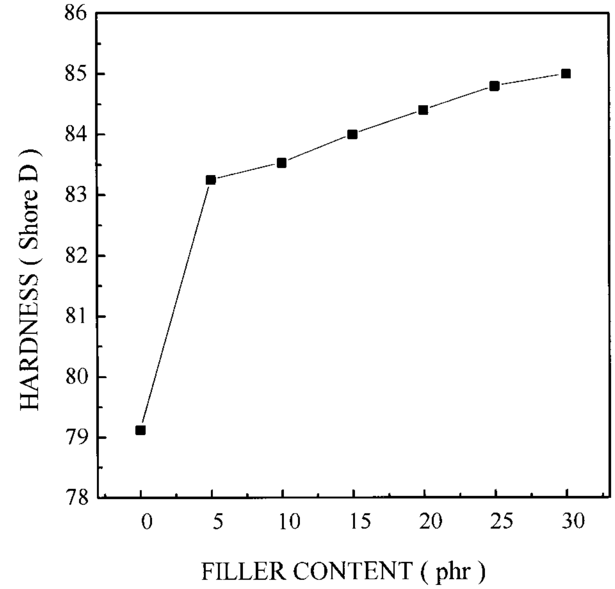


Figure 9 Shore D hardness versus filler (kaolin) content for blocked PU (15 wt %)–VE (85 wt %) IPNs.

Izod impact strength decreased with increasing filler content.

Effect of VE Initiator Content

The tensile strength, tensile modulus, flexural strength, flexural modulus, and shore D hardness versus the initiator content of VE for blocked PU

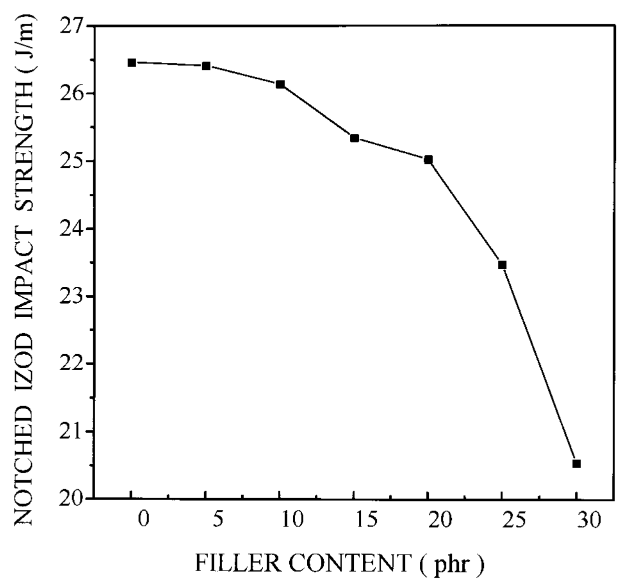


Figure 10 Notched Izod impact strength versus filler (kaolin) content for blocked PU (15 wt %)–VE (85 wt %) IPNs.

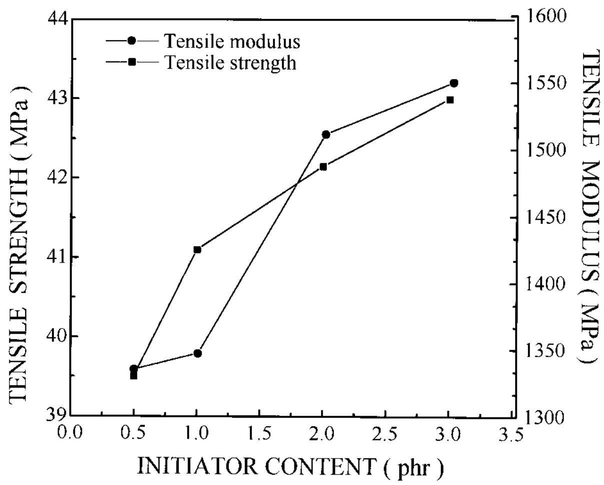


Figure 11 Tensile strength and tensile modulus versus initiator content of VE for blocked PU (15 wt %)–VE (85 wt %) IPNs.

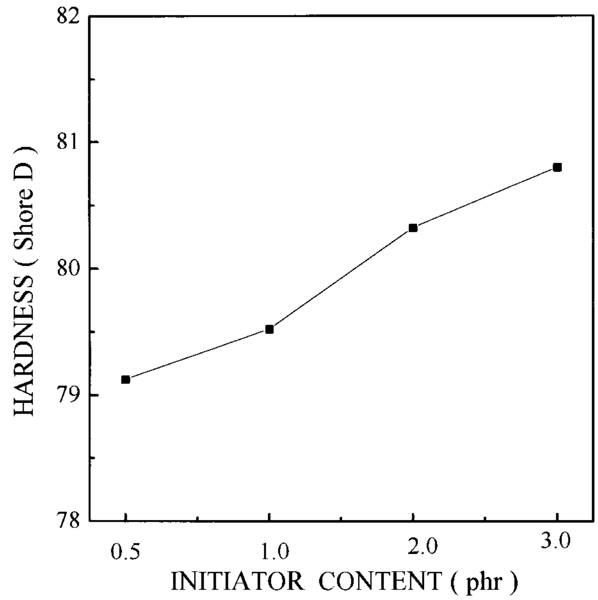


Figure 13 Shore D hardness versus initiator content of VE for blocked PU (15 wt %)–VE (85 wt %) IPNs.

(15 wt %)–VE (85 wt %) IPNs are shown in Figures 11–13. All of the properties investigated increased with increasing VE initiator content. As expected, this can be explained by assuming that the higher the VE initiator content, the higher the degree of the crosslinking density in the IPNs. Therefore, the tensile strength, tensile modulus, flexural strength, flexural modulus, and shore D hardness of the blocked PU–VE IPNs increased with increasing VE initiator content.

Dynamic Mechanical Properties

The glass transition temperature (T_g) was measured from the peak temperature of tan δ by DMA. The behavior of the dynamic damping curve (tan δ) over a range of temperatures for 0.5 phr initiator blocked PU–VE IPNs at various blocked PU content is shown in Figure 14. From Figure 14(a) and (e), one can observe that the peak temperature of tan δ of pure component VE

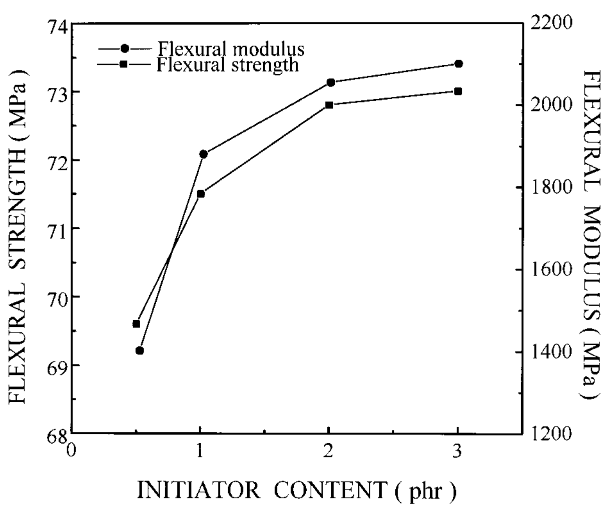


Figure 12 Flexural strength and flexural modulus versus initiator content of VE for blocked PU (15 wt %)–VE (85 wt %) IPNs.

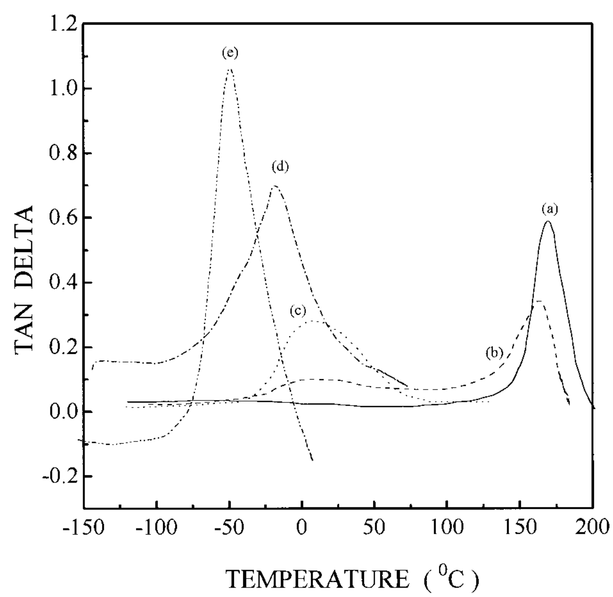


Figure 14 Dynamic damping curve (tan δ) versus temperature for blocked PU–VE IPNs at various blocked PU–VE compositions (wt %), as follows: (a) 0/100; (b) 30/70; (c) 50/50; (d) 65/35; (e) 100/0.

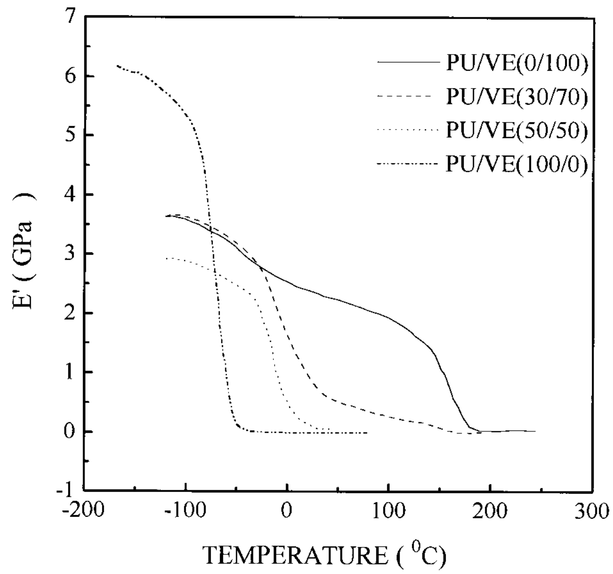


Figure 15 Dynamic storage modulus (E') versus temperature for blocked PU–VE IPNs at various blocked PU–VE compositions (wt %).

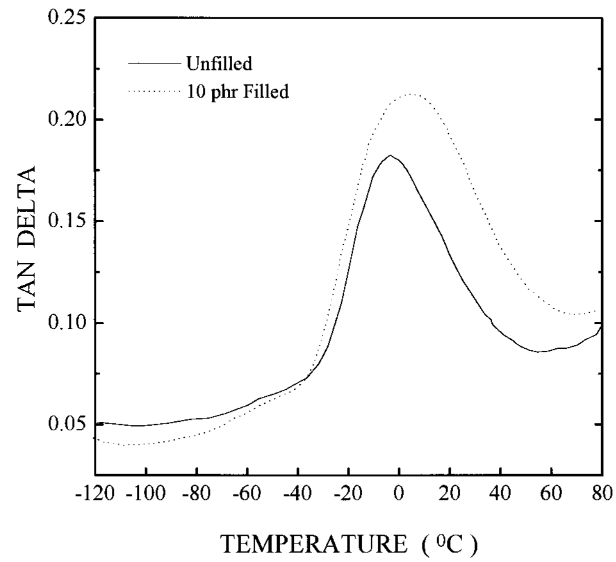


Figure 16 Dynamic damping curve (tan δ) versus temperature for unfilled (——) and 10 phr filled (kaolin) (· · ·) of blocked PU (40 wt %)–VE (60 wt %) IPNs.

and PU were 168.3 and −46.9°C, respectively. From Figure 14(b), (c), and (d), it is found that the two T_gs were shifted inward and apparently have one broad damping peak for each of the compositions. The literature[20,21] indicated that when the two polymers were mixed, the dynamic mechanical behavior showed two distinct transitions, indicating the incompatibility between the two polymers. As the compatibility increased, the two T_gs shifted toward each other and formed a broad transition at intermediate temperatures between the T_g of the individual components. This means that there is excellent compatibility between the blocked PU and VE matrices. It is also apparent that the damping peak of IPNs was shifted to a higher temperature as the VE content increased; and as the blocked PU content increased, the peak intensity of the tan δ of VE domain gradually decreased, and the peak intensity of the tan δ of the blocked PU domain gradually increased. This can be explained by the existence of VE hard segments and in the way that the VE is dissolved in the blocked PU matrix. Figure 15 shows the dynamic storage modulus (E') versus temperature for 0.5 phr initiator blocked PU–VE IPNs. From the figure, it is evident that the storage modulus increased with increasing VE content in the using temperature range of −30–150°C. This means that the greater the VE content, the more rigid the blocked PU–VE IPNs.

Figure 16 showed the dynamic damping curve (tan δ) versus temperature for unfilled and 10 phr filled (kaolin) of blocked PU (40 wt %)–VE (60 wt %) IPNs. It was found that the dynamic peak of IPNs became broad with increasing 10 phr filler content; meanwhile, the glass transition temperature (T_g) of IPNs was shifted to a higher temperature when the IPNs with filler content. Figure 17 showed the dynamic storage modulus (E')

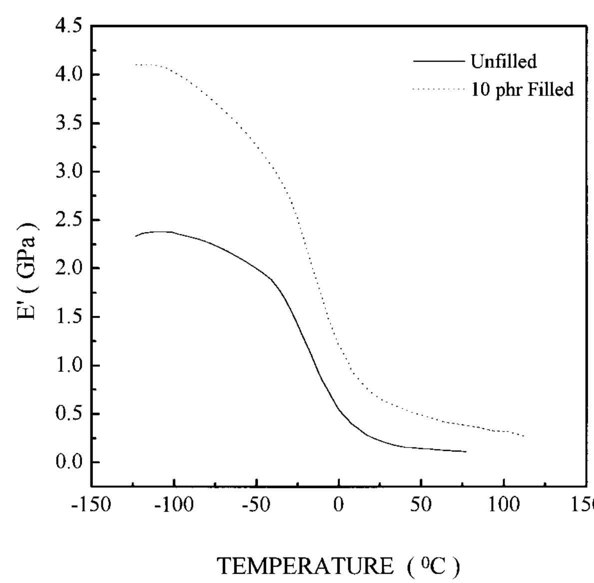


Figure 17 Dynamic storage modulus (E') versus temperature for unfilled (——) and 10 phr filled (kaolin) (· · ·) of blocked PU (40 wt %)–VE (60 wt %) IPNs.

versus temperature for unfilled and 10 phr filled (kaolin) of blocked PU (40 wt %)–VE (60 wt %) IPNs. From the figure, it is seen that the dynamic storage modulus (E') of IPNs with filler was higher than that unfilled. The glass transition temperature was shifted to a higher temperature, and dynamic storage modulus increased with filler because the IPNs structure became more tightly constrained when the filler is added.

CONCLUSIONS

In this study, full-IPN preparations based on a blocked PU and VE network using the SINs method. The static and dynamic properties of IPNs have been discussed.

The effect of parameters on static mechanical properties included blocked PU content, filler (kaolin) content, and initiator content of VE. Results show that the tensile strength and flexural strength of IPNs increased with blocked PU content to a maximum value and then decreased. The maximum tensile strength and flexural strength occurred at 7.5 wt % blocked PU content. The tensile modulus, flexural modulus, and shore D hardness of IPNs all decreased with increasing blocked PU content. The IPNs exhibited a higher impact strength when the blocked PU content increased. The tensile strength and flexural strength of IPNs increased with filler content to a maximum value and then decreased. The maximum tensile and flexural strength occurred at 20 phr filler content. The tensile modulus and flexural modulus of IPNs also increased with filler content to a maximum value and then decreased. The maximum tensile and flexural modulus occurred at 25 phr filler content. The shore D hardness of IPNs exhibited a higher hardness when the filler content increased. The notched Izod impact strength of IPNs decreased with increasing filler content. The tensile strength, tensile modulus, flexural strength, flexural modulus, and shore D hardness of IPNs all increased with increasing VE initiator content.

The glass transition temperature (T_g) was measured from the peak temperature of tan δ by DMA. The glass transition temperatures were shifted inward and apparently have one broad damping peak compared with pure component blocked PU and VE. This means that there is excellent compatibility between the blocked PU and VE matrices. The dynamic storage modulus (E') increased with increasing VE content in the using temperature range of -30–150°C. It was found that the dynamic peak of IPNs became broad with increasing filler content; meanwhile, the glass transition temperature (T_g) of IPNs was shifted to a higher temperature when the IPNs with filler content. The dynamic storage modulus (E') of IPNs with filler was higher than that unfilled.

This research was funded by the National Science Council, Taiwan, Republic of China, under Contract No. NSC 85-2216-E034-001.

REFERENCES

1. Akay, M.; Rollins, S. N.; Riordan, E. Polymer 1988, 29, 37.
2. Frisch, H. L.; Xhou, P. J Polym Sci, Part A: Polym Chem 1992, 13, 2749.
3. Byun, J.; Lee, Y. M.; Cho, C. S. J Appl Polym Sci 1996, 61, 697.
4. Shiomi, T.; Okada, K.; Teezuka, Y.; Kazama, H.; Imai, K. Makromol Chem 1993, 194, 3405.
5. Lipatov, Y. S.; Karabanova, L. V.; Gorbach, L. A.; Lutsyk, E. D.; Sergeeva, L. M. Polym Int 1992, 28, 99.
6. Hourston, D. J.; Schafer, F. U. Polymer 1996, 37, 3521.
7. Mishra, V.; Du Prez, F. E.; Goethals, E. J.; Sperling, L. H. J Appl Polym Sci 1995, 58, 347.
8. Li, Y.; Mao, S. J Appl Polym Sci 1996, 61, 2059.
9. Rong, M.; Zeng, H. Polymer 1996, 37, 2525.
10. Sperling, L. Polym Eng Sci 1985, 25, 517.
11. Jones, J. J.; Burford, R. P. Polym Int 1991, 26, 163.
12. Hepburn, C. Polyurethane Elastomer; Applied Science Publishers: New York, 1982; pp 1–2.
13. Schildknecht, C. E. Polymerization Processes; John Wiley: New York, 1978.
14. Chen, C. H.; Ma, C. C. M. Comp Sci and Technol 1994, 52, 427.
15. Peterm, M. Mod Plastics 1990, 70, 40.
16. Kim, S.; Klempner, D.; Frisch, K.; Frisch, H. Macromolecules 1976, 9, 258.
17. Kim, S.; Klempner, D.; Frisch, K.; Frisch, H. Macromolecules 1977, 10, 1187.
18. Hermant, I.; Meyer, G. Eur Polym J 1984, 20, 85.
19. Ma, C. C. M.; Goang, D. Y.; Han, J. L.; Hsieh, K. H. Die Angew Makromol Chem 1994, 214, 39.
20. Akay, M.; Rollins, S. N. Polymer 1993, 34, 967.
21. Chen, C. H.; Ma, C. C. M. Comp Part A: Appl Sci Manufact 1997, 28A, 65.