Polymer Bulletin 40, 477–484 (1998)

Polymer Bulletin

Polymer compatibility enhancement via ion-ion and ion-dipole interactions: Ternary blends of polyurethane, poly(vinyl chloride) and poly(styrene-*co*-maleic anhydride)

Hasan A. Al-Salah

Polymer Science and Technology Research Laboratory, Chemistry Department,
Mu'tah University, Mu'tah, Jordan

Received: 14 December 1997/Accepted: 3 February 1998

Summary

Ternary polymer blends (TPB) based on polyurethane (PU) containing tertiary amine, poly(vinyl chloride) (PVC), and poly(styrene-co-maleic anhydride) (SMA) containing 6.25% maleic acid were prepared via solution technique. The blends were investigated by using differential scanning calorimetry (DSC), dynamic mechanical (DMA), stress-strain testing, and density. DSC, DMA and density results showed extensive molecular mixing of the three polymer components through ion pair-ion pair, ion pair-dipole and dipole-dipole interactions. The glass transition temperatures (Tg) of TPBs gradually merged from two distinct transitions to one transition temperature. The mechanical properties of TPBs exhibited synergistic behavior with respect to tensile strength and the stress-strain behavior similar to reinforced elastomers at low PVC or SMA contents and well-developed yield points, stress whitening and necking at high PVC or SMA contents.

INTRODUCTION

Ionic polymer systems have been considerable academic and technological interest in recent years. The incorporation of ionic functionality into the polymers provides a very useful and versatile technique for major modifications and produces some interesting blends with certain polymers.[1-14] The incorporation of ionic groups into the hard segment units of PU block copolymers improves the driving force for phase separation by increasing the polarity difference between the soft and hard units. [15,16] The increased phase separation and domain cohesion are responsible for the improvement of mechanical properties that typically accompanies ionic incorporation.

Recently, the ionic interactions have been utilized as miscibility enhancers in polymer blends.[17-19] The blending of PU ionomers with poly(vinyl alcohol) (PVA) [20] exhibits a positive synergistic effect with respect to the tensile strength. The amorphous phase of PVA is at least partially compatible with both the disordered hard and the soft domains of the ionomers. It has shown that poly(ethylene oxide) could be mixed with poly(styrene-lithium methacrylate) to achieve one phase blends.[21] Blends of poly(vinyl chloride) (PVC) with various types of PUs have gained considerable technological values. [22-27] This polyblend has additional interest since chlorine containing polymers are reported to interact with oxygen containing polymers like PU through specific forces. [28] Piglowski at al[29] reported on the properties of PVC modified with thermoplastic PU elastomers and on the thermal stability of PVC-PU blends. Hourston et al [30] discussed the compatibility of the ternary blends of PVC, PU, and Hytrel.

The purpose of this investigation is to study the effect of ion-ion interactions and ion-dipole interactions in enhancing the miscibility of ternary polymer blends based on polyurethane, PVC, and poly(styrene-co-maleic anhydride) (SMA). In this work, isocyanate-terminated PU prepolymer extended by N-methyldiethanol amine (MDEA) and quaternized with SMA containing 6.25% maleic acid to impart attractions between tertiary amine and carboxylic groups in the polymer blends.

EXPERIMENTAL

Materials

Poly(tetramethylene oxide) (PTMO, supplied by DuPont) of 1000 molecular weight was dried under vacuum at 70°C overnight before being applied. Toluene diisocyanate (TDI, Merck) which is an 80/20 mixture of 2,4- and 2,6- isomers was used as received from the supplier. The commercial poly(vinyl chloride) (PVC) was additive free, supplied by Merck, purified by a twofold precipitation from tetrahydrofuran into methanol, and dried under vacuum to a constant weight. Molecular weights (Mn = 45,000, Mw = 78,000) were determined in tetrahydrofuran at 25°C by gel permeation chromatography (GPC). Poly(styrene-co-maleic anhydride) (SMA, styrene content 75 wt% supplied by Aldrich) of a molar mass of 1900 and acid number 275 was used as received. N-Methyldiethanol amine (MDEA, Aldrich), tetrahydrofuran (THF, Fluka) and N,N-dimethylformamide were purified by standard procedures.

Synthesis of Polyurethene containing Tertiary Amine

The isocyanate-terminated PU prepolymer was prepared by reacting two equivalents of TDI and one equivalent of PTMO in a 500 ml resin kettle. The reaction was carried out under a dry nitrogen and allowed to proceed until the isocyanate content (NCO%) reached the theoretical value of 6.34 as determined by di-n-butylamine titration. MDEA solution of the chain extender was added to a 50% NCO-terminated PU prepolymer solution in DMF. The reaction was continued until the NCO content reached zero as evidenced by the disappearance of the NCO peak.

Synthesis of Poly(styrene-co-maleic anhydride-co-maleic acid (SMA-H)

Poly(styrene-co-maleic anhydride) (25 g) was added to a solution containing 1.72 g (30.64 mmole) KOH in aqueous ethanol. The mixture was refluxed for 24 h, cooled and the ethanol removed. The solution was neutralized with HCl. The precipitate was collected by filtration and dried under vacuum. The resulting copolymer contains 6.25% maleic acid.

Synthesis of Ternary Polymer Blends.

The ternary polymer blends were prepared by solution blending. The SMA-H was dissolved DMF, while PU was weighed separately and dissolved in the DMF solvent to obtain approximately 15% wtw. The SMA-H solution was added dropwise to the vigorously stirred PU solution. The PVC solution in the THF (20% w/w) was added to the stirred solution of (PU-SMA-H). The ternary solution was stirred for 1h at ambient temperature and subsequently the solution was degassed to remove air bubbles. The films were prepared by casting the degassed solution on an aluminum mold coated with teflon. The sample films were dried in an oven at 60 °C for 5h and at 70°C under vacuum for 24h. The compositions of TPB series are designated by three numbers such as T-811 refers to the weight percent of PU:PVC:SMA components.

Characterization

Thermal transition temperatures of all specimens were determined by using a differential scanning calorimeter (DSC) (DuPont 2000) under a nitrogen atmosphere, at a heating rate of 10°C min^{-1}. Dynamic mechanical analysis (DMA) measurements were conducted with a DMA 983 of DuPont instrument with a frequency of 10 Hz in the extension mode and a heating rate of 2°C min^{-1}. The results have been measured in a temperature range from -100 °C to 160 °C. The mechanical properties were measured at room temperature on an Instron tensile tester, Model 1026. ASTM D-638 procedure was followed, employing a crosshead speed of 5 cm min^{-1} and 1 cm min^{-1} for brittle samples have elongation at break less than 10%. The density was calculated from specific gravity measured at 25°C with the ASTM D-792.

RESULTS AND DISCUSSION

Thermal Analysis

Fig. 1 shows the DSC thermograms of TPB series materials and the results are summarized in Table 1.

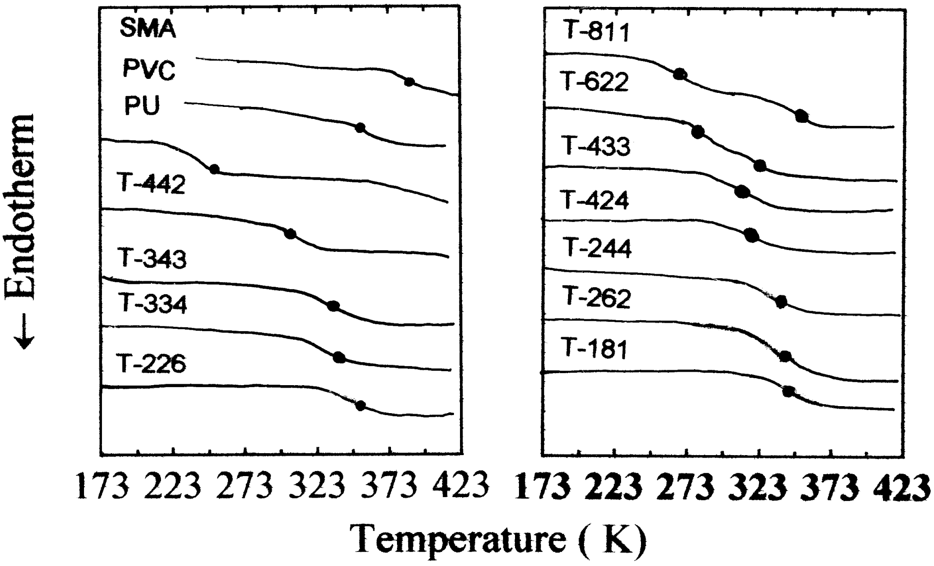

Fig. 1. DSC thermograms of PU, PVC, SMA and TPB series materials.

The thermograms of all these materials exhibit only one glass transition temperature except T-811 and T-622 which show two glass transition temperatures (Tg). The most The most noticeable aspect of these results is the lack of high temperature endotherms related to hard segment ordering. The lack of discernible hard segment ordering is related to the structure of TDI and the methyl side group of MDEA which do not allow compact of the hard segments [16,32]. . The amorphous character of the hard segments containing the isomeric TDI and MDEA units may result in considerable intermixing of this phase with the soft segment (PTMO). [32]

TABLE 1. Glass Transition temperature (Tg) and density (ρ) of TPBs.

	$Tg_{(exp)}$ (K)	$Tg_{(calc)}$ (K)	$\rho_{(exp)}$ $g.cm^3$	$\rho_{(callc)}$ $g.cm^3$
T-811	264 (348)	269	1.183	1.190
T-622	280 (323)	288	1.214	1.226
T-433	308	311	1.268	1.251
T-244	335	338	1.295	1.284
T-181	345	341	1.338	1.326
T-262	336	331	1.315	1.298
T-343	328	323	1.280	1.271
T-424	317	314	1.258	1.245
T-118	372	367	1.286	1.277
T-226	351	345	1.281	1.270
T-334	330	326	1.275	1.264
T-442	305	309	1.258	1.213
PVC	351	-	1.356	-
SMA	391	-	1.283	-
PU	250		1.162	

The results show that the Tgs of PVC and SMA shift towards lower temperatures whereas the soft segment glass transition temperature shifts toward higher temperatures with increasing SMA and PVC contents in the blends. In the present case, as the SMA-H is added, proton transfers from SMA-H to the tertiary nitrogen in PU to form PU ionomer. This would lead to strong coulombic interactions between the carboxylate anion (-COO^-) on the SMA chain and the quaternary ammonium cation on the hard segment of the PU and acidic hydrogen of PVC (ion-dipole interaction), which would result in very intimate mixing of the SMA copolymer with the hard segment of PU and PVC. The increase in Tg of soft segment suggests that the dipole-dipole interactions between PVC and soft segment ether oxygen[28] and hard segment-soft segment interactions decreases the phase separation between soft and hard segments. These interactions can produce restrictions on the mobility of the PTMO soft segments and increase the Tg of the PU. [32] It is worth pointing out that the mixing of PVC molecules in the presence of SMA with PTMO soft segment prevents the segregation of the hard segments, but even more, in the TPBs of high PVC or SMA content, the hard segments become more dissolved in the soft segment matrix diluted by PVC or SMA molecules. Eisenberg et al.[7] found that the process of quaternization and ionomer blends in PU enhanced the phase separation between hard and soft segments. The Tg values of the TPB series in the last column in Table 1 are calculated from the DSC data using the Fox copolymer equation:

$$1/Tg = w_1/Tg_1 + w_2/Tg_2 + w_3/Tg_3$$

where w_1, w_2, and w_3 are the weight fraction of the components in TPBs and Tg_1 = 252 K, TG_2 = 348 K, Tg_3 = 391 K are the glass transition temperatures for PU, PVC, and SMA, respectively. It is seen that the observed values of Tg are substantially very close to the calculated values. It is evident that the TPBs were at least significantly compatible as they exhibited only one major Tg whose position on the temperature scale changes with composition.

The temperature dependences of the dynamic storage modulus, E', and the mechanical loss, tanδ, for some of these TPB series materials and PU are shown in Fig. 2.

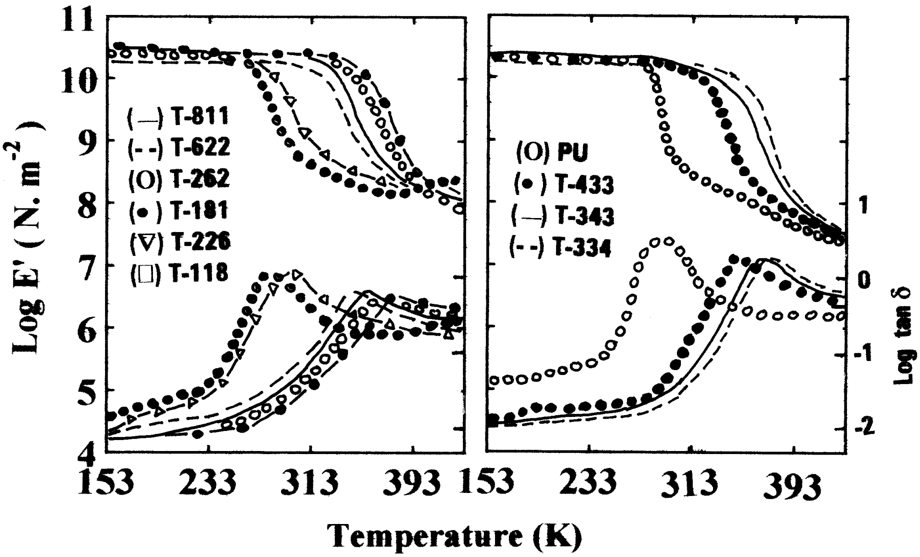

Fig. 2. Dynamic storage modulus (E') and (tan δ) curves for the TPB series.

The PU itself exhibited a broad glass-rubber transition in the tanδ vs temperature plot with a maximum at -10°C, which was taken to be the Tg of this PU. The curves in Fig. 2 reflect the shift in Tg and relative peak broadening associated with the Tg is increased by increasing PVC and SMA concentrations. The analysis of the glass transition temperatures for these TPB series materials suggests that the development of a microphase separation within PU block copolymer has occurred to minor degree, if present at all. This indicate good phase mixing of PVC and SMA with the soft segment of PU, which is consistent with the DSC results. From the dynamic storage modulus curves, it is seen that the increase in PVC and SMA concentrations in the TPBs shift the sharp modulus decrease associated with the Tg to higher temperatures and increases the magnitude of the rubbery plateau modulus.

Stress-Strain Properties

Table 2 lists the mechanical properties of the investigated ternary polymer blend series materials of different composition and Fig. 3 shows the stress-strain behavior of the TPB blends materials. Obviously, a synergism was observed for tensile strength of the TPB series materials (T-343, T-442, T-224).

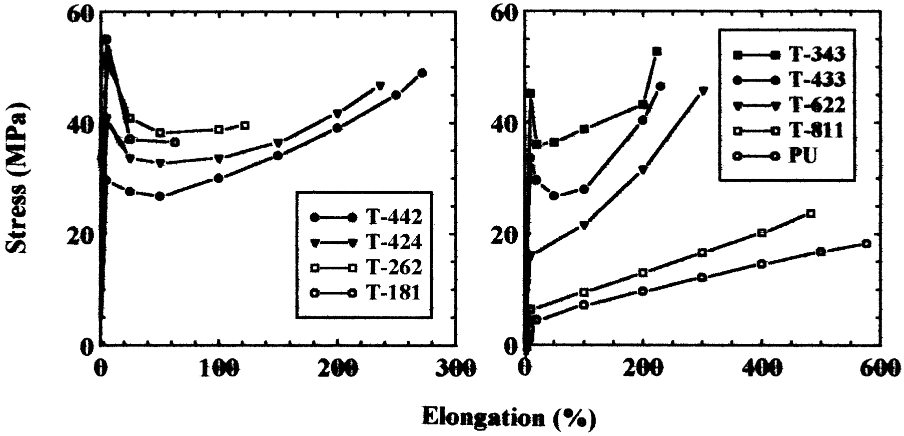

Fig. 3. Stress - strain curves for the TPB series.

These blends possess tensile strength even higher than that of either individual components. Since both the PU ionomer and SMA are physically crosslinked through ion-ion interactions and ion-dipole and dipole-dipole interactions between PUI-SMA and PVC. This provides a necessary condition for the three polymers physical interpenetrating to enhance the miscibility of these components. This results in a better adhesion of interphase between phases and efficient transfer of stress between phases. The TPBs display a systematic variation of stress-strain behavior as a function of composition. They behave as toughened plastic at PVC and SMA-rich compositions. All specimens except T-811, T-442, and to a less degree T-622 exhibit yield point. The yield point at around 2-5% strain and stress whitening along before failure suggests a possible mechanism of failure by crazing. In some of these specimens, stress remains constant with further elongation up to about 80% strain. This is a typical plastic-like behavior. For the samples PVC-rich composition, necking and stress whitening suddenly appears at a localized region in the sample when the applied stress exceeds the yield point, which subsequently grows continuously until the whole specimen is covered. This behavior is not observed in the samples SMA-rich composition.

subsequently grows continuously until the whole specimen is covered. This behavior is not observed in the samples SMA-rich composition.

For all the SMA-rich composition series, an increase in the SMA content greatly increased the Young's modulus. The overall nature of the curves of these series differ from other series. The variation of tensile strength at yield point and modulus of the PVC-rich series show a similar trend where tensile strength and Young's modulus gradually increase with increasing PVC content. It can also be seen that the addition of PU reduces the tensile strength and Young's modulus and increases the elongation at break of the samples. The behavior is more pronounced in systems containing higher proportions of PU. This indicates that low PVC or SMA content behave as reinforced elastomers

TABLE 2. Mechanical properties of ternary polymer blends

Sample	Tensile strength (MPa)		Young's modulus (MPa)	Elongation (%)
	At yield	At break		
T-811	-	24.6	62	483
T-622	19.5	45.7	138	302
T-433	34.8	46.5	290	230
T-244	52.2	34.0	506	7
T-181	55.0	33.2	568	63
T-262	50.5	39.5	467	122
T-343	46.5	52.8	422	224
T-424	40.5	46.5	375	236
T-118	57.0	45.5	605	5
T-226	55.5	48.0	566	7
T-334	54.0	36.5	545	10
T-442	29.0	52.0	284	272
PVC	56.4	42.5	705	6
SMA	61.2	47.4	874	4
PU	-	18.0	23	577

Density

The actual densities and the calculated ones based on the volume additivity of the components are listed in Table 1. The results show significantly increased density in most of the blends and slightly exceeds the maximum experimental error range of 0.004, compared to the theoretical densities calculated based on volume additivity. This behavior agrees with the DSC and DMA results, since it indicates greater molecular mixing and strong interchain interpolymer interactions among the polymer blend components. Recently, in a study on compatible polystyrene-poly(vinylmethyl ether) linear blends, Kwei et al.[31] observed densities higher than the theoretical densities based on volume additivity of the two-component polymers. The results were attributed to the mixing of polymer components.

REFERENCES

1. Eisenberg, A. & Bailey, F. F., Coulombic Interactions in Macromolecular Systems. ACS Symp. Ser., No. 302, 1986
2. Visser, S. A. & Cooper, S. L., *Mocromolecules,* **24** (1991) 2576
3. Chen, S. A., & Hsu, J. S., *Polymer,* **34** (1993) 2769
4. Lam, P. K. H., George, M. H., & Barrie, J. A*., Polymer,* **30** (1989) 2320
5. Al-Salah, H. A., Xiao, H. X., McLean, J. & Frisch, K. C., *J. Polym. Schi., Polym. Chem. Ed.,* **26** (1988) 1609
6. Al-Salah, H. A., & Al-Raheil, I. M., *J. Appl. Polym. Sci.,* **45** (1992) 1661
7. Rutkowska, M., & Eisenberg, A., *Macromolecules,* **17** (1984) 821
8. Weiss, R. A., Agarwal, P. K., & Lundberg, R. D., *J. Appl. Polym. Sci.,* **29** (1984)2719
9. Al-Salah, H. A., Xiao, H. X., McLean, J. A., & Frisch, K. C., *Polym. Intern.,* **28** (1992) 323
10. Hsieh, K. H., Chou, L.M., & Chiang, Y. C., *Polym. J.*, **21** (1989)1
11. Hourston, D. J., & SchÄfer, F. U., *Polymer,* **37** (16) (1996) 3521.
12. Campbell, J. R., Conroy, P. M., & Florence, R. A*., Polym. Prepr.* Am. Chem. Soc., **27**(1) (1986) 331.
13. Xie, H. Q., Xu, J., & Zhou, S., *Polym.*, **32** (1991) 95
14. Xie, H. Q., & Ma, B. Y., Contemporary Topics in Polymer Science. Vol. 6, ed. Culbertson, M. B., Plenum, New York, 1989, p 601
15. Yang, C. Z., Li, C., Cooper, S. L., *J. Polym. Sci., Polym. Chem. Ed.,* **29** (1991) 75
16. Speckhard, T. A., Hwang, K. K. S., Yang, C. Z., Laupan, W. R., & Cooper, S. L., *J. Macromol. Sci-Phys.,* **B23** (1984) 175
17. Rutkowska, M., & Eisenberg, A., *J. Appl. Polym. Sci.,* **30** (1985) 3317
18. Alice NG, C. W., & MacKnight, W, J., *Mocromelecules,* **22** (1996) 2412.
19. Murali, R., Eisenberg, A., Gupta, R. K., & Harris, F. W., *Polym. Prepr. Am. Chem. Soc.,* **27** (1) (1986) 343
20. Hsu, J. S., Su, F. H., & Chen, S. A., *Makromol. Chem.,* **193** (1992) 833
21. Hara, M., & Eisenberg, A., *Mocromolecules,* **17** (1984) 1335
22. Wang, C. B., & Cooper, S. L., *J. Appl. Polym. Sci.,* **26** (1981) 2989
23. McGrath, J. E., & Matzner, M.,U.S. Patent 3 798 289 (1974), Union Carbide Corp.
24. Bandyopadhyay, P. K., & Shaw, M. T., *J. Appl. Polym. Sci.,* **27** (1982) 4323
25. Matsuda, O., Okamoto, J., Suzuki, N., Ito, M., & Tabata, Y., *J. Macromol. Sci, Chem.,* **A8** (1974) 775.
26. Kalfloglou, N. K., *J. Appl. Polym. Sci.,* **26** (3) (1981) 823.
27. Xiao, F., Shi, L., & Xu, M., *Chinese. J. Polym. Sci.,* **9** (1991) 55.
28. Paul, D. R., Polymer Blends, ed. Paul, D. R., & Newman, N., Academic Press, New York, 1978, Chap. 7.
29. Piglowski, J., Skowronski, T., & Maiulanis, B., *Angew. Makromol. Chem.,* **85** (1980) 129.
30. Hourston, D. J., & Hughes, I. D., *J.* Appl. *Polym. Sci.,* **29** (1981) 3467.
31. Kwei, T. K., Nishi, T., & Roberts, R. F., *Macromolecules,* **7** (1974) 5.
32. Seefried, C. G., Koleske, J. V., & Critchfield, F. E., *J. Appl. Polym. Sci.,*