PII: S0032-3861(97)00170-5

Polymer Vol. 38 No. 24, pp. 6071–6078, 1997

0032-3861/97/\$17.00 + 0.00

Blends of polycaprolactone-poly(dimethylsiloxane)-polycaprolactone triblock copolymer with poly(vinyl chloride): preparation and characterization

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(Revised 30 January 1997)

Miscibility, thermal, mechanical, gas permeation, morphological and surface properties of poly(vinyl chloride) (PVC) blends containing 1–10% triblock polycaprolactone–poly(dimethylsiloxane)–polycaprolactone (PCL-PDMS-PCL) copolymer were investigated by using several techniques. Fourier transform infra-red analysis of blends reveal the existence of specific interactions via hydrogen bonding between the α-hydrogen of PVC and the carbonyl group of PCL in the triblock copolymer. This PCL-PDMS-PCL/PVC blend system exhibited a single glass transition according to differential scanning calorimetry and dynamic mechanical thermal analysis results. Stress–strain results showed that PCL-PDMS-PCL triblock copolymer is a very effective plasticizer for PVC. Gas permeability of the blends increased with the copolymer content. Morphological and surface properties of the blend system were examined by scanning electron microscopy and contact angle measurements. © 1997 Elsevier Science Ltd.

(Keywords: polycaprolactone-poly(dimethylsiloxane)-polycaprolactone; poly(vinyl chloride); miscibility)

INTRODUCTION

In recent years the blending of polymers has gained significant interest, because of their growing industrial use. The advantage of blending polymers is that properties of commercially available polymers may be modified by using an inexpensive route. Poly(vinyl chloride) (PVC) is one of the most important thermoplastics. Several polymers are currently mixed with PVC to alter its properties, such as high impact behaviour, heat resistance temperature and processability[1,2]. For example, the compatibility, morphology and mechanical properties of PVC blended with polycaprolactone (PCL) have been extensively studied[3–13]. It is well known that PCL gives miscible blends with PVC in all proportions, and it was reported to be a very effective plasticizer for PVC[3].

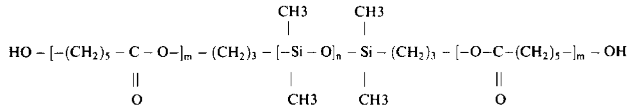
The modification of conventional polymers through the addition of small amounts of siloxane polymers have also received increasing attention in the last decade. However, siloxanes, especially poly(dimethylsiloxanes) (PDMS), are totally immiscible with most other materials, although it possesses exceptional properties, such as good oxidative, thermal and ultraviolet stability, hydrophobicity, biocompatibility and a low glass transition temperature (T_g, −123°C), low surface energy and high chain flexibility[14]. An effective way to increase the compatibility of PDMS in blends is to form copolymers of siloxanes with carbon based polymers. A triblock polycaprolactone-poly(dimethylsiloxane)-polycaprolactone (PCL-PDMS-PCL) is a good example to combine the compatibilizing effect of PCL and the surface modifying and toughening characteristics of PDMS[15,16].

In this work, we have blended triblock PCL-PDMS-PCL copolymer with PVC homopolymer in small amounts (1–10%) to improve the mechanical and surface properties of PVC, and investigated the miscibility of these blends by several techniques (Fourier transform infra-red spectroscopy (*FT*i.r.), differential scanning calorimetry (d.s.c.), dynamic mechanical thermal analysis (d.m.t.a.), stress–strain tests, gas permeability measurements, scanning electron microscopy (SEM) and contact angle measurements).

EXPERIMENTAL

Materials

Triblock PCL-PDMS-PCL copolymer was supplied by Th.Goldschmidt A.G. of Germany, under the name Tegomer (Tegomer H-Si 6440). The molecular weight, (M_n) of Tegomer is $6500 \pm 600\,\mathrm{g\,mol^{-1}}$ with PCL end blocks, $M_n \simeq 2000\,\mathrm{g\,mol^{-1}}$. Tegomer has the following molecular structure:



$$\mathrm{HO-[-(CH_2)_5-\overset{}{\underset{\|\atop O}{C}}-O-]_m-(CH_2)_3-[-\underset{|\atop CH3}{\overset{CH3\atop |}{Si}}-O]_n-\underset{|\atop CH3}{\overset{CH3\atop |}{Si}}-(CH_2)_3-[-O-\underset{\|\atop O}{C}-(CH_2)_5-]_m-OH}$$

$n/m = 30/18$

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PVC was a commercial product of Fluka A.G. ($M_r \simeq 48\,000\,\mathrm{g\,mol^{-1}}$).

Tetrahydrofuran (THF), used as solvent in blend preparation, was a product of Merck A.G.

Preparation of polymer blends

Polymer blends were prepared by solvent casting from THF with a total polymer concentration 3% (w/v). Solutions were poured into teflon-coated aluminium moulds, and THF was slowly evaporated under ambient conditions in a vacuum desiccator to provide low humidity. The resulting films were dried to a constant weight in a vacuum oven for 2 weeks at 50°C. The films produced were optically clear, and they were kept in a desiccator at room temperature until being used for further investigations.

Characterization

The infrared spectra of polymers and polymeric blends were obtained using a Nicolet 510 P *FT*i.r. spectrometer, at room temperature.

Thermal characterization of the polymers and blends were performed using a Schimadzu DSC-41 model apparatus. The samples were scanned from −140 to +140°C, with a heating rate of $10^\circ\mathrm{C\,min^{-1}}$. D.s.c. samples were first heated under nitrogen atmosphere to +140°C, then quenched to −140°C using liquid nitrogen. This heating/cooling cycle was repeated twice. Reported thermograms were always taken from the last scan. The T_g was taken at the onset of the corresponding heat-capacity jump.

A Polymer Laboratories d.m.t.a. was used. Measurements were made at a frequency of 1 Hz. The rate of heating was $5^\circ\mathrm{C\,min^{-1}}$. Mechanical properties of the blended samples were determined by standard tensile stress–strain tests to measure the modulus (E), ultimate strength (σ), and elongation and break (ϵ). Standard tensile stress–strain experiments were performed at room temperature on a Tensilon, Toyo Measuring Instruments Co. Ltd. (UTM II) tester, using a crosshead speed of $10\,\mathrm{mm\,min^{-1}}$.

The measurements of O_2 and CO_2 permeability were made on thin films of the blends (thickness about 0.03 mm) at 25°C with a gas permeability meter (GDP/E Brugger, Munich).

SEMs were taken on a JEOL-JXA 840 A SEM. The specimens were prepared for SEM by freeze-fracturing in liquid nitrogen and applying a gold coating of approximately 300 Å on an Edwards S 150 B sputter coater.

Contact angle measurements of the blend films prepared by casting from 3% (w/v) THF solutions were conducted on a Kernco Model G-III Goniometer. Contact angles were measured at room temperature using distilled, deionized water.

RESULTS AND DISCUSSION

FT*i.r. analysis*

Using *FT*i.r. spectroscopy, we have been able to show the existence of specific molecular interactions in PCL-PDMS-PCL/PVC miscible blends. *Figure 1* shows the *FT*i.r. spectrum of the PCL-PDMS-PCL/PVC (10/90) blend. The specific interactions determined by *FT*i.r. showed significant amounts of shifting in carbonyl band for PCL-PDMS-PCL/PVC system, as seen in the inset of

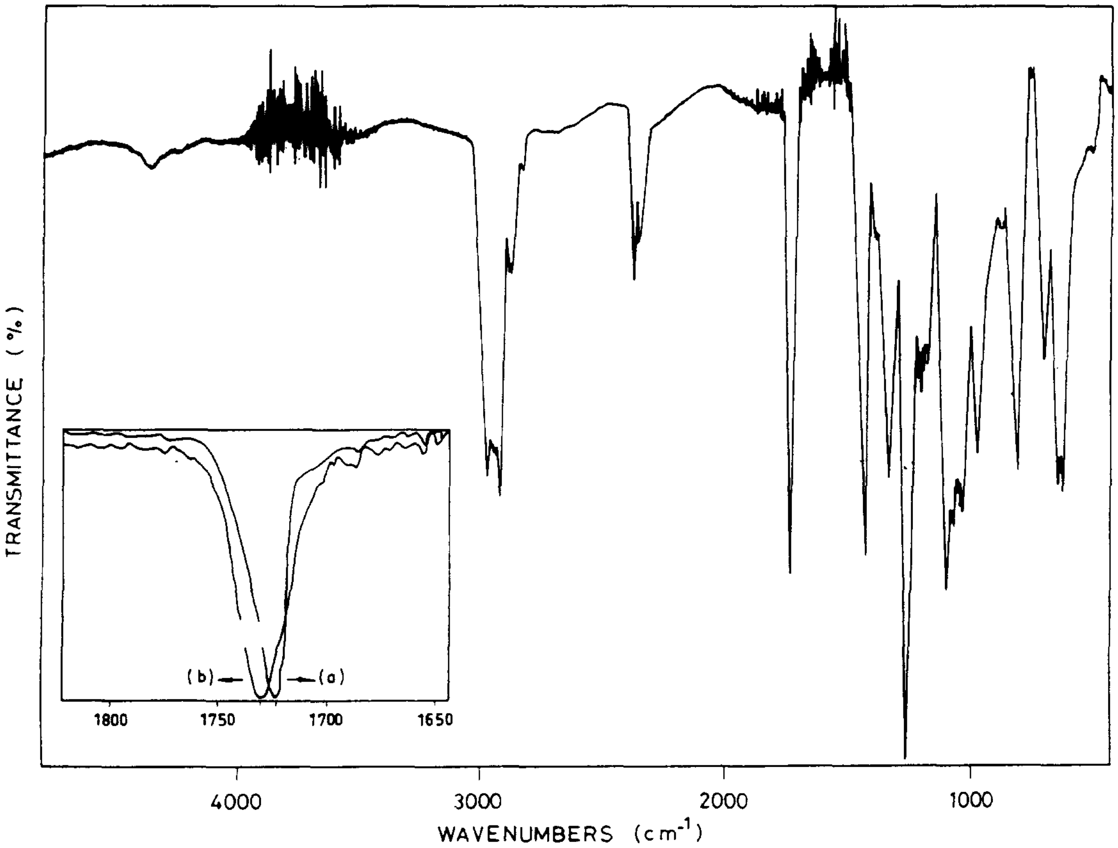


Figure 1 *FT*i.r. spectrum of PCL-PDMS-PCL/PVC blends. The shift of the carbonyl (–C=O–) band is shown in the inset. (a) PCL-PDMS-PCL triblock copolymer. (b) PCL-PDMS-PCL/PVC (10/90) blend

Figure 1. The carbonyl absorption (–C=O–) samples were observed at 1724.5 and 1730 cm^{-1} for triblock copolymer (a) and the blend (b) respectively. Approximately a 6 cm^{-1} shift in carbonyl absorption band was observed. In miscible blends a shift of the carbonyl band is observed in *FT*i.r. spectroscopy while it is not seen in immiscible blends[6]. Similar results for this type of shift were reported in earlier studies[6–8] for PCL/PVC blends. It was mentioned that the band at 1737 cm^{-1} is associated with the amorphous phase, and the band at 1724 cm^{-1} is associated with crystalline phase of PCL. At PVC concentration in excess of 2/1 molar ratio PVC/PCL, it was indicated that the blends are essentially amorphous and their miscibility in amorphous state results from a specific interaction between two polymers[8].

In this work, the carbonyl band of the PCL-PDMS-PCL triblock copolymer also showed shifting to a higher frequency (1730 cm^{-1}) to form a miscible blend with PVC. It is known that when the chlorinated polymer has α-hydrogens (e.g. PVC) extensive association will occur with the polyester, with the interaction presumably being dominated by hydrogen bonding between the carbonyl group and the α-hydrogens[6–8,17,18]. It is suggested that the miscibility behaviour of PCL-PDMS-PCL/PVC blend is due to a hydrogen bonding interaction, $C{=}O \cdots H{-}C$, between the α-hydrogen of PVC (the α-hydrogen is that on the CHCl group) and the carbonyl groups of the PCL-PDMS-PCL triblock copolymer.

	Frequency (cm^{-1})	
Sample	C=O	C–H
PCL-PDMS-PCL triblock copolymer	1724.5	2959
PCL-PDMS-PCL/PVC blend (10/90)	1730	2963

It is also observed that the C–H stretching frequency shifts progressively to a higher frequency with increasing PCL-PDMS-PCL triblock copolymer content in the blend.

The other characteristic peaks of the PDMS component of the copolymer were observed at 1260 cm^{-1} and 800 cm^{-1} for Si–CH$_3$ deformation, at 1026 cm^{-1} for Si–O–Si asymmetric stretching vibration.

Thermal analysis

A concise arrangement of d.s.c. thermograms of PVC, PCL-PDMS-PCL triblock copolymer and the blends is shown in *Figure 2*. The glass transition of pure PVC was observed at 79°C (*Figure 2a*). PCL-PDMS-PCL/PVC blends exhibit single T_gs, which change with blend composition (*Figures 2b–2g*). The T_gs of the blends at the range of composition we worked (1–10%) decreased with the amount of triblock copolymer in the blend. The T_g seen for the 10/90 blend was 35°C, the lowest T_g observed for the PCL-PDMS-PCL/PVC system. D.s.c. analysis of pure PCL-PDMS-PCL triblock copolymer clearly indicated the formation of two-phase morphology with the siloxane T_g around -125°C and polycaprolactone melting points around $+55$°C, as shown in *Figure 2h*. These transitions could not be observed in the d.s.c. thermograms of the blends, probably due to the small amounts of copolymer addition (1–10 wt%).

The d.s.c. data obtained for each sample are also shown in *Figure 3* in a plot of T_g vs copolymer composition. According to the T_g criterion[4], since these blends show single T_gs, it can be said that there is extensive interaction between the segments of the two polymers and they are then miscible. This result is confirmed by a decrease in T_g with the addition of copolymer to PVC, as shown in *Figure 3*.

Dynamic mechanical analysis

Figure 4 shows the dynamic storage modulus (E') and the dynamic loss modulus (E'') vs temperature plot for the PVC homopolymer and PCL-PDMS-PCL/PVC (10/90) blend. The T_g of PVC that corresponds to a sharp decrease in E' (*Figure 4a*) is observed at 50°C, whereas the T_g of the 10/90 blend is at 37°C. The d.m.t.a. spectrum of the blend is consistent with the single T_g behaviour observed in the d.s.c. results. The dynamic mechanical testing results of pure PVC were compared with previous studies[3,19–21]. At this temperature range (20–100°C), the peaks of E' and E'' seem to move to lower temperatures upon blending, as was previously reported for PCL/PVC[3] blends. The value of E' (at 20°C) for PVC is relatively higher (1.65 GPa) than blend (1.20 GPa) at the same temperature. This decrease in E' in the blend (10/90) may be attributed to the plasticizing effect of triblock copolymer on PVC. PCL-PDMS-PCL/PVC blend (10/90) exhibits a single peak in E'' vs temperature curve, however the peak seems to be broader than that of the pure PVC hompolymer.

Tensile properties

Typical stress–strain behaviour for homopolymer (PVC), and the selected blends in the range of 1–10% PCL-PDMS-PCL triblock copolymer content, are shown in *Figure 5*. The stress–strain results are summarized in *Table 1*. The data are the averages of three to four runs for ultimate strength (σ), Young's modulus (E), and the elongation at break (ϵ).

It can be seen, in *Figure 5* and *Table 1*, that the blends show an increase in flexibility with respect to the PVC homopolymer. As the copolymer concentration in the blend increases σ and E drop. The highest amount of PCL-PDMS-PCL triblock copolymer in the blend is 10%. The ultimate strength at break and Young's modulus of the blend (10/90) show a decrease by a factor of 2 compared to homopolymer PVC, however its elongation at break (ϵ) is 472%, exhibiting a dramatic increase (by a factor 59) with respect to PVC ($\epsilon = 8\%$).

The tensile properties of these blends indicate that PCL-PDMS-PCL triblock copolymer is an effective plasticizer for PVC. A similar behaviour was observed for PCL/PVC blends[3], where the modulus and ultimate strength drop rapidly until 60% PVC. The ability to elongate rises quickly with higher concentrations of PCL, up to about 50% PVC. However, when the tensile properties of PCL/PVC[3] and PCL-PDMS-PCL/PVC blends are compared, the dramatic effect of small amounts of siloxane addition on the ability of elongation of the blends can be clearly seen. The lowest PCL concentration used in the PCL/PVC blend is 25%, and it exhibits an elongation value of 148%. However, in our system, PCL-PDMS-PCL/PVC blend, the elongation at break is 472% with 10% copolymer addition to PVC.

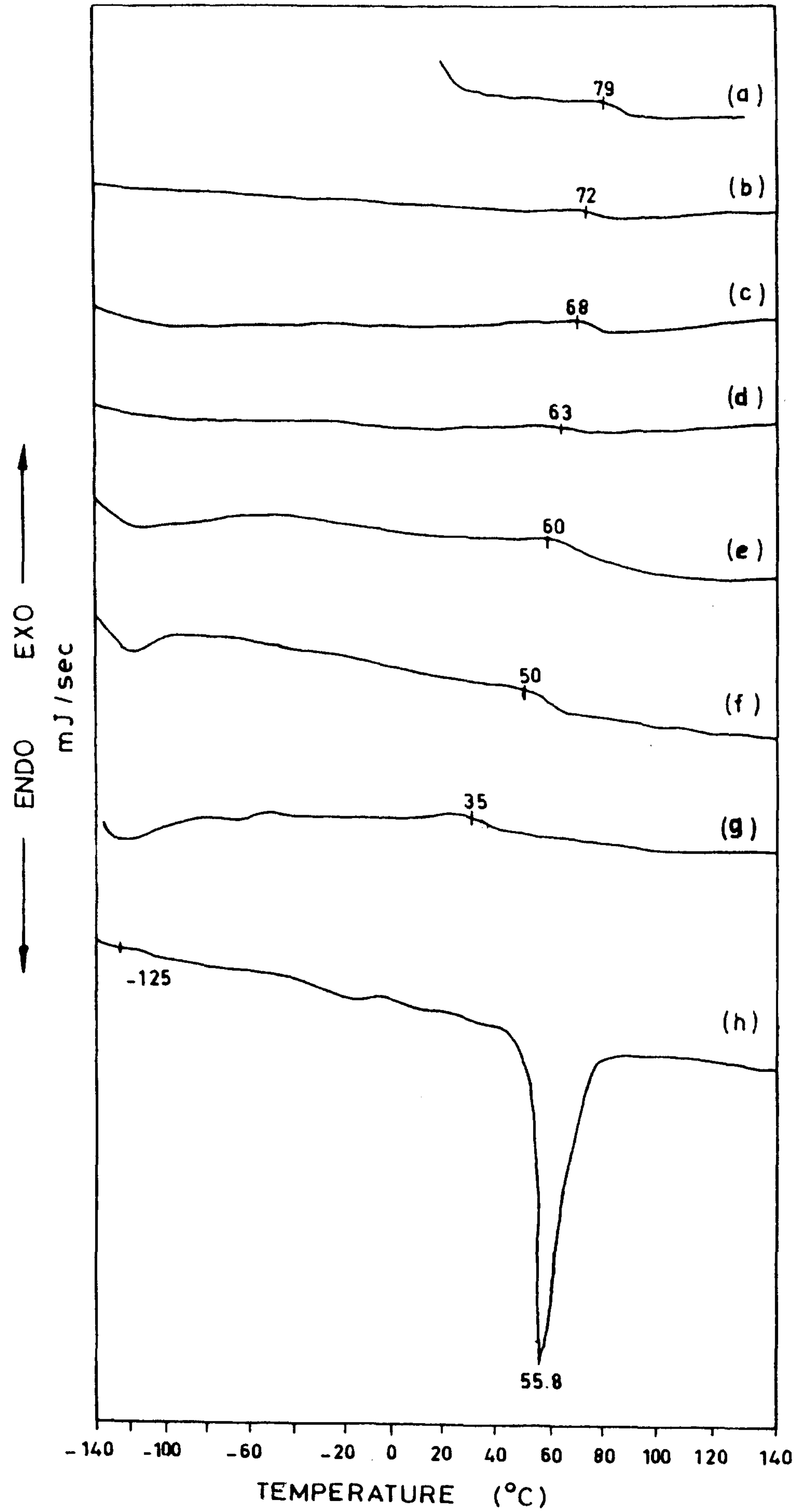


Figure 2 D.s.c. thermograms for PCL-PDMS-PCL/PVC blends of different composition: (a) pure PVC; (b) 1% copolymer; (c) 2% copolymer; (d) 4% copolymer; (e) 6% copolymer, (f) 8% copolymer; (g) 10% copolymer; (h) pure PCL-PDMS-PCL triblock copolymer

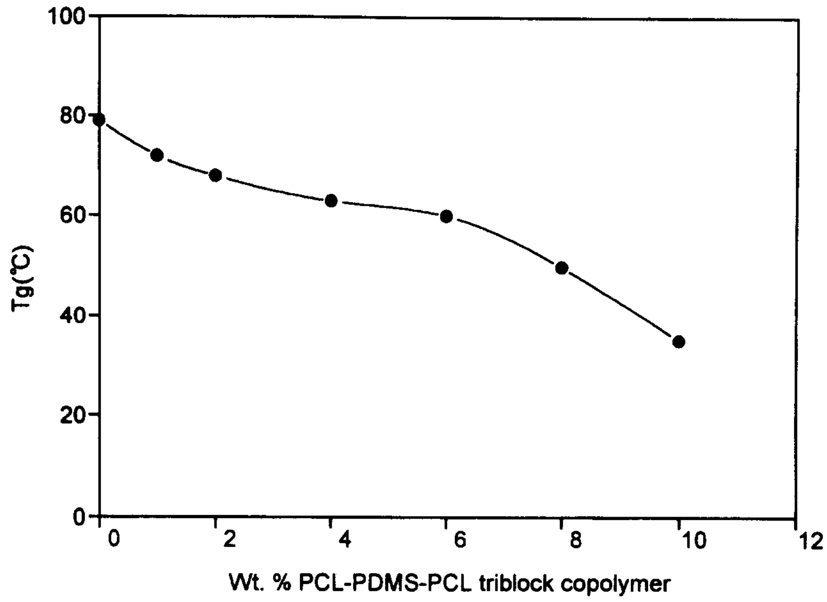


Figure 3 T_g as a function of PCL-PDMS-PCL triblock copolymer content in PCL-PDMS-PCL/PVC blends

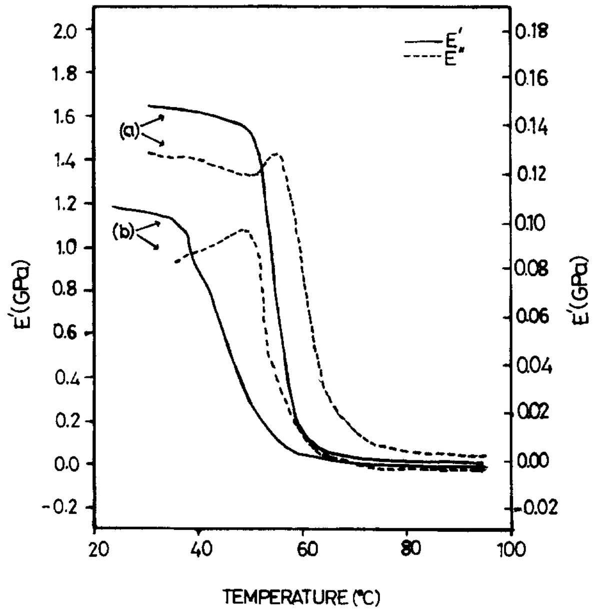


Figure 4 Plots of the dynamic storage modulus (E') and dynamic loss modulus (E'') vs temperature at 1 Hz for pure PVC (a) and for PCL-PDMS-PCL/PVC (10/90) blend (b)

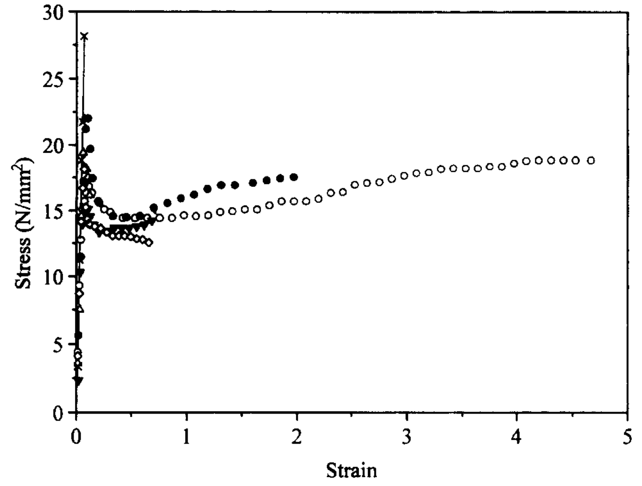


Figure 5 Stress–strain curves for PCL-PDMS-PCL/PVC blends: (x) PVC; (△) 1% copolymer; (▼) 4% copolymer; (◇) 6% copolymer; (●) 8% copolymer; (○) 10% copolymer

Table 1 Tensile properties of PCL-PDMS-PCL/PVC blends

Composition of the blends (PCL-PDMS-PCL/PVC)	Ultimate elongation (ϵ, %)	Ultimate tensile strength (σ, MPa)	Young's modulus ($E \times 10^{-2}$ MPa)
0/100	8	28	6.1
1/99	18	16	4.6
2/98	55	15	3.1
4/96	82	14	2.8
6/94	95	13	3.9
8/92	207	17	3.5
10/90	472	14	3.6

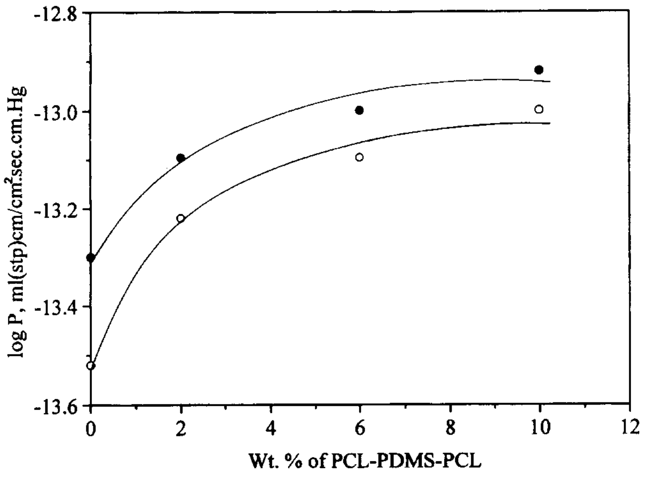


Figure 6 Permeability coefficients of (○) O_2 and (●) CO_2 vs blend composition for PCL-PDMS-PCL/PVC blends at 25°C

Table 2 Water contact angle measurements of PCL-PDMS-PCL/PVC blends

Triblock copolymer content in the PCL-PDMS-PCL/PVC blend (wt%)	Contact angle (°)
PVC	80
Tegomer[a]	88
1	90
2	92
4	94
6	94
8	90
10	91
PDMS[b]	105
PCL[a]	85

[a] Films were prepared by melting at 60°C
[b] Poly(dimethylsiloxane) network[18]

Gas permeation studies

The transport behaviour of O_2 and CO_2 in films of PCL-PDMS-PCL/PVC blends has been studied at 25°C. The results of permeability measurements for O_2 and CO_2 through the films of PCL-PDMS-PCL/PVC blends are presented in *Figure 6*. The permeability coefficient (P) values of O_2 and CO_2 tend to increase with the triblock copolymer content. From the observed relationship between logarithm of permeability coefficient and copolymer content, we could say that there is no indication of phase inversion for these blends at these compositions. According to the earlier work in the literature, Arrhenius plots of log P vs blend composition for incompatible blends have to be S-shaped, and this is interpreted as being the result of a phase inversion[13,22–25].

It is also known that plasticization increases the molecular mobility of polymer chains[5,26]. Therefore, we expect that gas permeation would be easier through polymers having increased chain mobility. Blends of PCL-PDMS-PCL/PVC have higher permeability coefficients than pure PVC homopolymer, and the increase in gas permeation is relatively greater when we compared the values with PCL/PVC blends reported earlier[13]. This might be due to the effect of PDMS segments in the copolymer. PDMS is the most commonly cited material[27], with its high gas permeability, owing to the flexibility of the Si–O–Si bonds, which impart segmental mobility to polysiloxane chains[28]. Hence, triblock PDMS copolymer with PCL seems very appropriate for optimization of gas permeation properties of PVC homopolymer, since it enhances mobility in PVC and increases permeability more effectively than pure PCL.

Morphology studies

Figures 7a–7f show the SEM images of PVC homopolymer and 10/90 PCL-PDMS-PCL/PVC blend. Secondary electron images (SEIs) were applied in SEMs.

Figures 7a–7c show the fractured surface of the homopolymer, PVC, at different magnifications. SEI of PVC at ×1200 magnification shows a brittle fracture that is consistent with mechanical properties of pure PVC polymer. At higher magnifications, a spherical structure was observed in the fractured surface of PVC. White spheres with varying sizes (500–1250 Å) form parallel lines which can be easily detected in *Figures 7b* and *7c*.

It is well known that various levels of morphology exist in suspension PVC powder[29]. Powder particles known as grains are irregular in shape and are about 100–150 μm in diameter. Each grain consists of many microparticles which are about 1–2 μm in diameter. These microparticles are made up of still smaller structures, submicroparticles[29–32]. We observed these submicroparticles as white spheres in our study, and the similar morphology of PVC is illustrated in various papers[29–34]. The parallel lines of these particles seen in the micrograph of PVC have similar characteristics with PVC samples reported very recently[33,34].

The fractured surface morphology of PCL-PDMS-PCL/PVC blend (10/90) is shown in *Figures 7d, 7e* and *7f*. *Figure 7d* shows an even and relatively smooth fractured surface of blend 10/90. This is in contrast to the uneven and rough surface of freeze-fractured PVC, as shown in *Figure 7a*. The spherical morphology found in this blend is identical to that of pure PVC. However, the particles that are deformed into dense monolayers (parallel lines) seen in pure PVC do not seem to appear in the 10/90 blend case. No two-phase morphology could be observed in these high resolution SEMs and blended PVC has a genuinely different morphology, although triblock copolymer component is not observed.

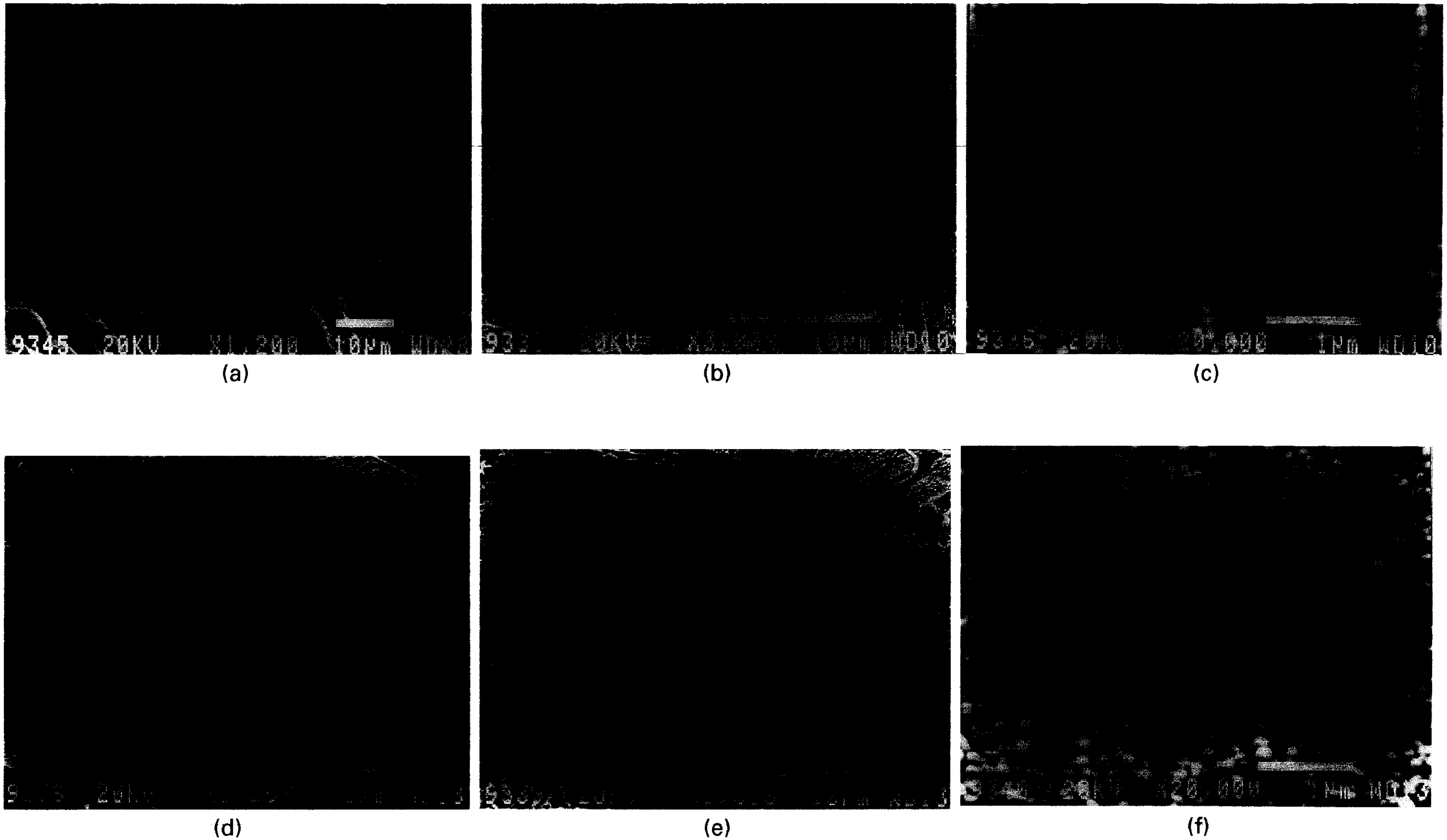
Contact angle measurements

The surface properties of the blends were investigated by contact angle measurements. Contact angles were measured at room temperature for the water droplets. The results were reproducible at ±2°C in most cases, and were given in *Table 2*.

We observed the substantial increase in water contact angles even at very low percentages of PCL-PDMS-PCL copolymer content. Usually a contact angle of 90° or more indicates silicone-like surfaces[14,35]. As a control, we measured the contact angle of poly(dimethylsiloxane) homo network which was prepared in a previous work[36], and it was found to be 105°.

It is known that siloxane containing copolymers migrate to the air polymer interface due to their low critical surface energy[37].

In this work, the increase in the water contact angles indicates that the surface accumulation of siloxane segments is not negligible in the blend, and the surface properties of PVC can be modified with the addition of small amounts of triblock PCL-PDMS-PCL copolymer.



(a) (b) (c)

(d) (e) (f)

Figure 7 SEM micrographs of homopolymer PVC (a–c) and PCL-PDMS-PCL/PVC (10/90) blend (d–f)

CONCLUSIONS

The miscibility, morphology and mechanical properties of triblock PCL-PDMS-PCL copolymer blended with PVC has been investigated by several techniques. The results of d.s.c., d.m.t.a. and *FT*i.r. showed that the binary PCL-PDMS-PCL/PVC blends are miscible for the composition range of 1–10% copolymer content. It was observed that PCL-PDMS-PCL triblock copolymer is a very effective plasticizer for PVC, and it has a synergetic effect on the properties of PVC. Even at very low percentages of copolymer content, the stress–strain behaviour of the blends changes dramatically. The extent of mechanical properties was found to be dependent on the amount of the triblock copolymer content. Elongation at break (ϵ) of the blend with 10% copolymer content ($\epsilon = 472\%$) exhibits a sharp increase with respect to homopolymer ($\epsilon = 8\%$). The O_2 and CO_2 permeability of PCL-PDMS-PCL/PVC blend system was determined and a considerable increase in permeability of the blends was observed with respect to homopolymer PVC. SEM micrographs of pure PVC and the blends show slightly different fractured surfaces, however no two-phase morphology could be observed. Contact angle measurements showed that the addition of small amounts of PCL-PDMS-PCL copolymer may change surface properties of pure PVC homopolymer dramatically.

ACKNOWLEDGEMENT

This work was partially supported by the National Science Foundation (USA) under grant NI-9507751.

REFERENCES

1. Flores, R., Perez, J., Cassagnau, P., Michel, A. and Cavaille, J. Y., *J. Appl. Polym. Sci.*, 1996, **60**, 1439.
2. Schmidt, J. J., Gardella, Jr., J. A. and Salvati, Jr., L., *Macromolecules*, 1989, **22**, 4489.
3. Hubbell, D. S. and Cooper, S. L., *J. Appl. Polym. Sci.*, 1977, **21**, 3035.
4. Olabisi, O., Robeson, L. M. and Shaw, M. T., *Polymer–Polymer Miscibility*. Academic Press, New York, 1979.
5. Paul, D. R. and Newman, S., *Polymer Blends*. Academic Press, New York, 1978.
6. Prud'homme, R. E., *Polym. Eng. Sci.*, 1982, **22**, 90.
7. Varnell, D. F., Moskala, E. J., Painter, M. C. and Coleman, M. M., *Polym. Eng. Sci.*, 1983, **23**, 658.
8. Coleman, M. M. and Zarian, J., *J. Polym. Sci. Part B*, 1979, **17**, 837.
9. Khambatta, F. B., Warner, F., Russell, T. and Stein, R. S., *J. Polym. Sci., Part B*, 1976, **14**, 1391.
10. Koleske, J. V. and Lundberg, R. D., *J. Polym. Sci., Part A-2*, 1969, **7**, 795.
11. Aubin, M., Bussieres, D., Duchesne, D. and Prud'homme, R. E., *Miscibility of Polylactone/Chlorinated Polymer Blends*, and Solc, K. *Polymer Compatibility and Incompatibility*. MMI Press Symposium Series, Michigan, 1980, **2**, 223.
12. Utracki, L. A., *Polymer Alloys and Blends: Thermodynamics and Rheology*. Hanser Publishers, New York, 1989.
13. Shur, Y. J. and Ranby, B., *J. Macromol. Sci. Phys.*, 1977, **B14**(4), 565.
14. Yılgör, I., Steckle, Jr., W. P., Yılgör, E., Freelin, R. G. and Riffle, J. S., *J. Polym. Sci., Part A*, 1989, **27**, 3673.
15. Yılgör, I. and McGrath, J. E., *Adv. Polym. Sci.*, 1988, **86**, 1.
16. Lovinger, A. J., Han, B. J., Padden, Jr. F. J. and Mirau, P. A., *J. Polym. Sci., Part B*, 1993, **31**, 115.
17. Garton, A., *J. Polym. Sci., Polym. Letts Edn*, 1983, **21**, 45.
18. Garton, A., Cousin, P. and Prud'homme, R. E., *J. Polym. Sci., Part B*, 1983, **21**, 2275.
19. Murayama, T., *Dynamic Mechanical Analysis of Polymeric Material*. Elsevier Science, New York, 1978.
20. Kim, S. J., Kim, B. K. and Jeong, H. M., *J. Appl. Polym. Sci.*, 1994, **51**, 2187.
21. Flores, R., Perez, J., Cassagnau, P., Michel, A. and Cavaille, J. Y., *J. Appl. Polym. Sci.*, 1996, **60**, 1439.
22. Shur, Y. J. and Ranby, B., *J. Appl. Polym. Sci.*, 1975, **19**, 1337.
23. Shur, Y. J. and Ranby, B., *J. Appl. Polym. Sci.*, 1975, **19**, 2143.
24. Shur, Y. J. and Ranby, B., *J. Appl. Polym. Sci.*, 1976, **20**, 3105.
25. Shur, Y. J. and Ranby, B., *J. Appl. Polym. Sci.*, 1976, **20**, 3121.
26. Pal, S. N., Ramani, A. V. and Subramanian, N., *J. Appl. Polym. Sci.*, 1992, **46**, 981.
27. Comyn, J., *Polymer Permeability*. Elsevier Science UK, 1986.
28. Mark, J. M., in *Silicone-Based Polymer Science*, eds. J. M. Zeigler and F. W. Gordon. American Chemical Society, Washington DC, 1990, **224**, 47.
29. Butters, G., *Particulate Nature of PVC-Formation, Structure, and Processing*. Applied Science, London, 1982.
30. Chen, C. H., Wesson, R. D., Collier, J. R. and Lo, Y. W., *J. Appl. Polym. Sci.*, 1995, **58**, 1087.
31. Chen, C. H., Wesson, R. D., Collier, J. R. and Lo, Y. W., *J. Appl. Polym. Sci.*, 1995, **58**, 1093.
32. Chen, C. H., Wesson, R. D., Collier, J. R. and Lo, Y. W., *J. Appl. Polym. Sci.*, 1995, **58**, 1107.
33. Yanagase, A., Masakazu, I., Yamamoto, N. and Ishikawa, M., *J. Appl. Polym. Sci.*, 1996, **60**, 87.
34. Yanagase, A., Masakazu, I., Yamamoto, N. and Ishikawa, M., *J. Appl. Polym. Sci.*, 1996, **62**, 1387.
35. McGrath, J. E., *Ring Opening Polymerization-Kinetics, Mechanisms and Synthesis*, ACS Symposium Series 286, Washington, DC, 1985.
36. Hamurcu, E. E. and Baysal, B. M., *J. Polym. Sci., Part B, Polym. Phys.*, 1994, **32**, 591.
37. Yılgör, I., Ward, R. S. and Riffle, J. S., *Polym. Prepr.*, 1987, **28**(2), 369.