

Morphological, Mechanical and Rheological Properties of Poly(acrylonitrile-butadiene-styrene)/Polycarbonate/Poly(ϵ -caprolactone) Ternary Blends

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Abstract: The effects of poly(ϵ -caprolactone) (PCL) on poly(acrylonitrile-butadiene-styrene) (ABS) and polycarbonate (PC) blends were studied. Blends of ABS/PC (70/30, wt%) with PCL as a compatibilizer were prepared by a twin screw extruder. From the glass transition temperature (T_g) results of the ABS/PC blends with PCL, the T_g (PC) of the ABS/PC (70/30) blends decreased with increasing PCL content. From the results of the morphology of the ABS/PC (70/30) blends with PCL, the phase separation between the ABS and PC phases became less significant after adding PCL in the ABS/PC blends. In addition, the morphological studies of the ABS/PC blends etched by NaOH indicated that the shape of the droplet was changed from regular round to irregular round by adding PCL in the ABS/PC blends. These results for the mechanical properties of the ABS/PC blends with PCL indicated that the tensile, flexural and impact strengths of the ABS/PC (70/30) blends peaked at a PCL content of 0.5 phr. From the results for the rheological properties of the ABS/PC (70/30) blends with PCL content, the storage modulus, loss modulus and complex viscosity increased at PCL content up to 5 phr. From the above results of the T_g , mechanical properties, morphology and complex viscosity of the ABS/PC blends with PCL, it was concluded that the compatibility was increased with PCL addition in the ABS/PC (70/30, wt%) blends and that the optimum concentration of PCL as a compatibilizer is 0.5 phr.

Keywords: polymer blends, compatibilizer, mechanical properties, morphology, rheology.

Introduction

The blending of poly(acrylonitrile-butadiene-styrene) (ABS) with various polymers has been a subject of recent years.¹⁻¹⁴ ABS and polycarbonate (PC) are known to be incompatible.¹⁻⁴ In partially miscible polymers, phase separation occurs, but at the same time a certain number of molecules of one phase penetrate the other phase and vice versa.¹⁻⁴ The interface between the two phases becomes diffuse and good mechanical properties may result by the introduction of secondary intermolecular interactions. For example, Wilders *et al.*⁵ have shown that the improvement of the properties has been obtained by the addition of amine-functionalized styrene-acrylonitrile copolymer as a compatibilizer in the blends of ABS with polycarbonate (PC). Tan *et al.*⁸ have studied the mechanical and morphological properties of the ABS and PC blends with the rubber content in the ABS.

Other polymer blends of poly(ϵ -caprolactone) (PCL) that have been reported have contained PC,¹⁵⁻²² poly(styrene-co-acrylonitrile) (SAN),²³⁻²⁷ poly(vinyl chloride)^{28,29} and polyethylene.^{30,31} Most of these blends with PCL have been found to be miscible. For

the blending of PC with PCL, Herrera *et al.*¹⁷ have studied the crystallization behavior of PCL in the blends and shown the single glass transition of the PC and PCL blends. Also, for the blends of PC and PCL, Chun *et al.*¹⁸ have studied the thermal properties of the blends and reported the polymer-polymer interaction parameter from the glass transition temperatures of the PC and PCL blends. PCL is known to have some unique properties such as a relatively low molecular weight and a carbonyl group in the repeating unit. The carbonyl oxygen in the PCL could be used for the formation of hydrogen bonding with hydrogen in the other polymer. Hydrogen bonding is known to be one of the specific interactions useful in forming miscible polymer blends.

Recently, ternary polymer blends have been studied by many investigators.³²⁻³⁸ Ternary blends that have contained PCL include blends of PC/PCL/polyhydroxy ether of bisphenol-A and blends of PC/PCL/polyamide-6 that have been studied by Christiansen *et al.*³² and Kim *et al.*,³⁴ respectively. Shah *et al.*³³ have studied the blends of PC/PCL/SAN, and reported the thermal behavior of the blends. In these ternary polymer blends, PCL was used as a compatibilizing agent to increase the miscibility of the blends. Choi *et al.* have studied the rheological, morphological, mechanical and thermal

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properties of the PC/ABS blends with a flame retardant.^{37,38}

In our present study, mechanical, rheological, and morphological properties of the ABS/PC (70/30, wt%) blends with PCL are reported by the universal testing machine (UTM), Izod impact tester, advanced rheometric expansion system (ARES) and scanning electron microscopy (SEM). In particular, compatibilization effects by the addition of the polymeric compatibilizer such as PCL in the ABS/PC blends are investigated.

Experimental

Materials. The polymers used in this study were obtained from commercial sources. The ABS was provided by LG Chem. Ltd. The PC was provided by LG-DOW Chem. Ltd. The PCL as a compatibilizer was supplied by Aldrich. The characteristics of the ABS, PC, and PCL are summarized in Table I.

Blend Preparations. Blends of ABS and PC were prepared using a 11 mm diameter twin screw extruder with a screw ratio of 40 : 1 length to diameter. For the ABS/PC (70/30, wt%) blend, the ABS with the weight fraction of 0.7 was mixed with the 0.3 weight fraction PC using the extruder. Also, concentrations of the PCL, ranged from 0.0 to 5.0 phr were added in the ABS/PC blends. The temperatures of the extruder were set at 180 to 240 °C in feeding and barrel zones, respectively. The screw speed of the extruder was set at 90 rpm. Samples were compression molded using a hot press at 240 °C for 5 min. Before preparation of the samples, all the samples were dried under vacuum (< 1 mmHg) at 80 °C for 24 h.

Dynamic Mechanical Thermal Analysis (DMTA). DMTA measurements of the ABS/PC/PCL blends were carried out on advanced rheometric expansion system (ARES) in oscillatory torsional mode at 0.1% strain and 1 Hz frequency. The measurement was scanned 40 to 200 °C at a rate of 5 °C/min.

Scanning Electron Microscopy. The morphology of the ABS/PC/PCL blends was obtained by scanning electron microscopy (model: Hitachi S-4300) after gold coating. The samples were fractured with the cryogenic condition.

Rheology. Dynamic measurements of the ABS/PC/PCL blends were carried out using advanced rheometric expansion system (ARES) in oscillatory shear at 5% strain in the parallel-plate arrangement with 25 mm plate. The frequency sweep from 0.1 to 100 rad/s was performed at 240 °C under the dry nitrogen condition. For the ARES measurements,

Table I. Characteristics of the Polymer used in this Study

Samples	\bar{M}_w	T_g (°C)
ABS ^a	160,000	110.6
PC ^b	28,000	152.7
PCL ^c	65,000	-64.0

^aSupplied by LG Chemical Ltd.(acrylonitrile: 22, butadiene:15, styrene: 63 wt%). ^bSupplied by LG-DOW Co. ^cSupplied by Aldrich.

samples were tested within the linear viscoelastic strain range.

Mechanical Properties. The mechanical properties of the ABS/PC/PCL blends were investigated using an universal testing machine (Instron 4467). Tensile test was performed according to the ASTM D-638. The speed of cross-head movement for tensile test was 5.0 mm/min. Flexural test was performed according to the ASTM D-790. The span length and the speed of cross-head movement were set at 40 mm and 2.8 mm/min, respectively. For flexural and tensile tests, 7 specimens were measured and averaged. The impact strength of the ABS/PC/PCL blends was measured by notched izod impact strength method (McVan Instruments: ITR-2000). The impact tester was performed according to the ASTM D-256 and 7 specimens were measured and averaged.

Results and Discussion

Poly(acrylonitrile-butadiene-styrene) (ABS) and polycarbonate (PC) are known to be incompatible and two glass transition temperatures (T_g s) are observed, T_g (ABS), associated with ABS-rich regions, and T_g (PC), associated with PC-rich regions. Figure 1 shows the T_g (ABS) and T_g (PC) from the measurement of dynamic mechanical thermal analysis (DMTA), which are 115.9 and 158.9 °C, respectively. From Figure 2 and Table II, the T_g (PC) of the ABS/PC/PCL (70/30/0.5 phr) blend shows 135.3 °C which is about 23.6 degrees lower compared with the T_g (PC) of the pure PC, which suggests partial miscibility between the ABS and PC. From Figure 2, when the PCL was added in the amount of 3 and 5 phr in the ABS/PC (70/30) blends, a single T_g peak was observed because the T_g s of the blends were overlapped by

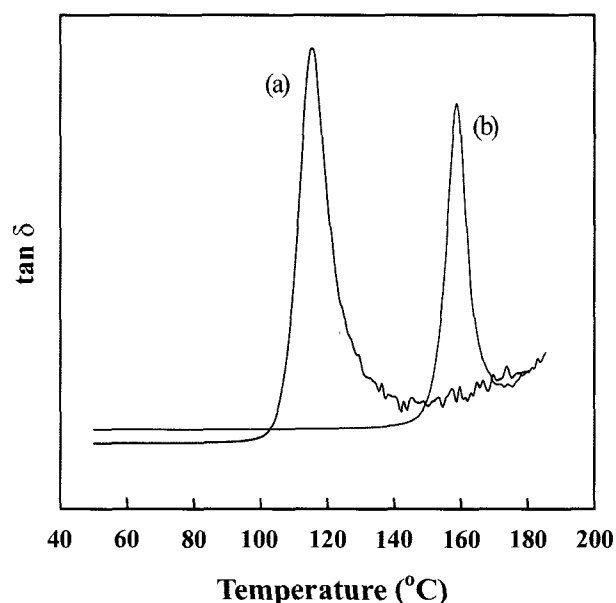


Figure 1. Tan δ vs temperature of the (a) ABS and (b) PC.

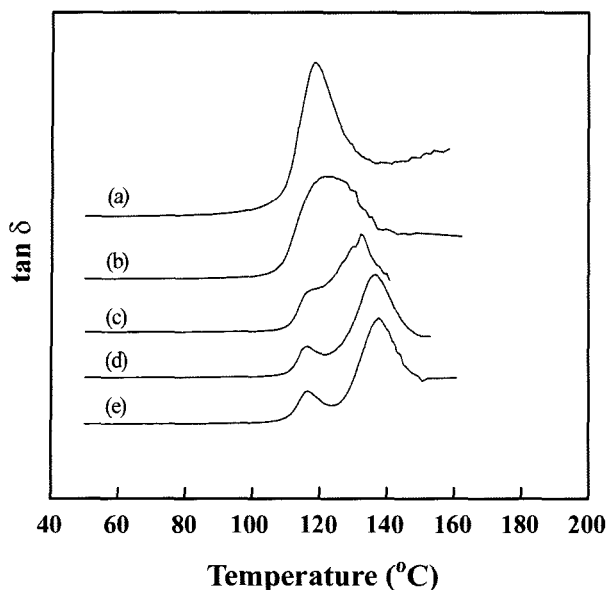


Figure 2. $\tan \delta$ vs temperature of the ABS/PC (70/30) blends with PCL: (a) 5 phr, (b) 3 phr, (c) 1 phr, (d) 0.5 phr, and (e) 0 phr.

the DMTA measurement. But the ABS/PC (70/30) blends showed still incompatible by the microscopic measurement when the PCL was added 3 and 5 phr in the blends.

To see the compatibilization effects of the PCL on the ABS/PC (70/30) blend, morphological studies using the SEM were performed. Figures 3 (a)-(e) show the SEM images of the cryogenically fractured surfaces of the ABS/PC (70/30) blends with the PCL in the amount of 0, 0.5, 1, 1,

Table II. Glass Transition Temperatures of the ABS, PC, and ABS/PC (70/30) Blends by Dynamic Mechanical Thermal Analyzer

ABS/PC (70/30) Blends	T_g (ABS) (°C)	T_g (PC) (°C)
ABS	115.9	-
ABS/PC	116.4	137.5
ABS/PC/0.5 phr PCL	116.7	135.3
ABS/PC/1.0 phr PCL	117.2	132.2
PC	-	158.9

3, and 5 phr, respectively. The droplet size of the PC in the ABS/PC (70/30) blend with the PCL is appeared to be small and has been found to be from 1.0 to 1.5 μm . The droplet size of the PC did not change significantly with the amount added PCL in the ABS/PC blend, however, the phase separation between the ABS and PC phases became less significant after adding the PCL in the ABS/PC blends.

Figures 4(a)-4(e) show the SEM images of the cryogenically fractured cross-sectional surfaces of the ABS/PC/PCL blends with the PCL of 0, 0.5, 1, 3, and 5 phr, respectively. The PC phase was etched selectively by using NaOH. In Figure 4, the droplet size of the PC in the ABS/PC/PCL blends does not change significantly with the PCL and has been found to be from 1.0 to 1.5 μm when the PCL is added up to 5 phr. From Figure 4, however, it is observed that the shape of the droplet is changed from regular round shape to irregular round shape by adding PCL in the ABS/PC blends. This is maybe because that the PCL is known to be miscible with the PC and SAN, therefore the PCL is dissolving into the PC phase as well as the SAN of the ABS phase. Then, the PC

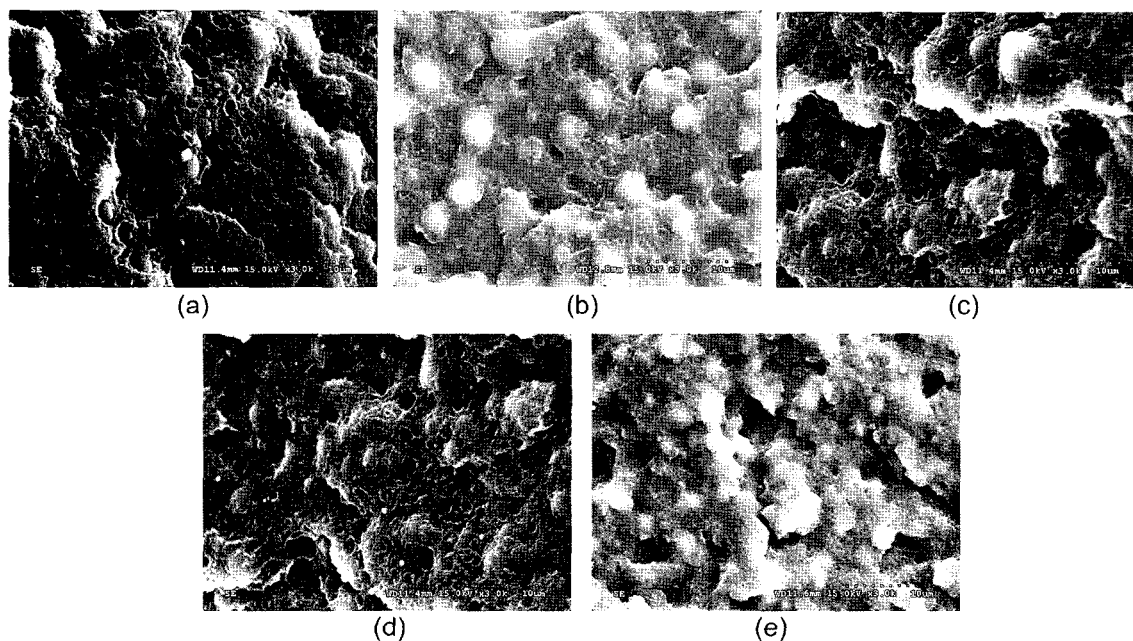


Figure 3. Scanning electron micrographs of the ABS/PC (70/30) blends with PCL: (a) 0 phr, (b) 0.5 phr, (c) 1 phr, (d) 3 phr, and (e) 5 phr.

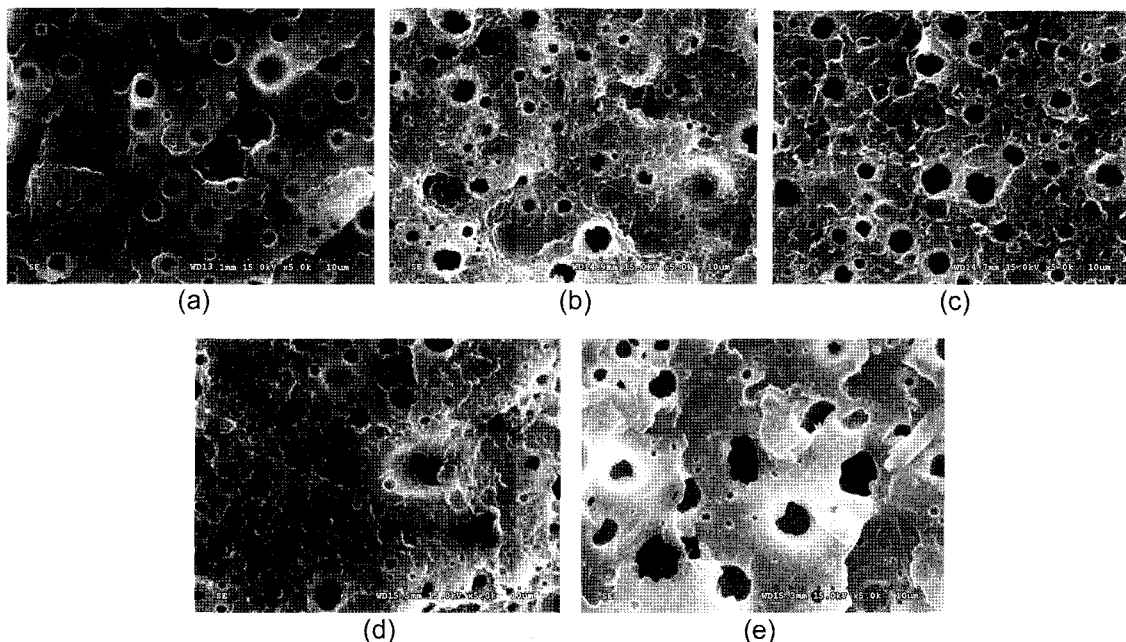


Figure 4. Scanning electron micrographs of the ABS/PC (70/30) blends with PCL: (a) 0 phr, (b) 0.5 phr, (c) 1 phr, (d) 3 phr, and (e) 5 phr: etched by an aqueous NaOH solution.

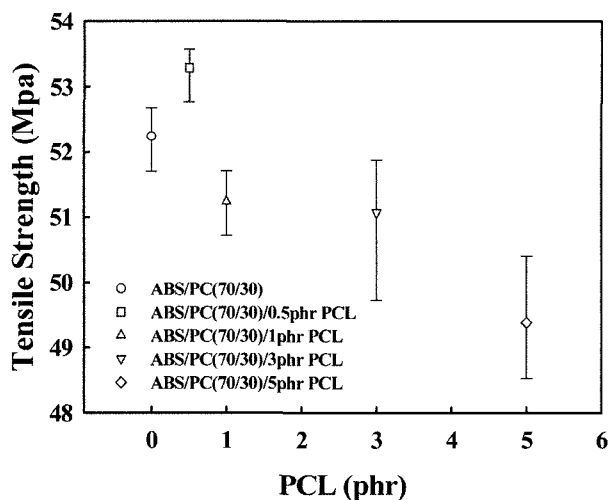


Figure 5. Tensile strength of the ABS/PC (70/30) blends with PCL content.

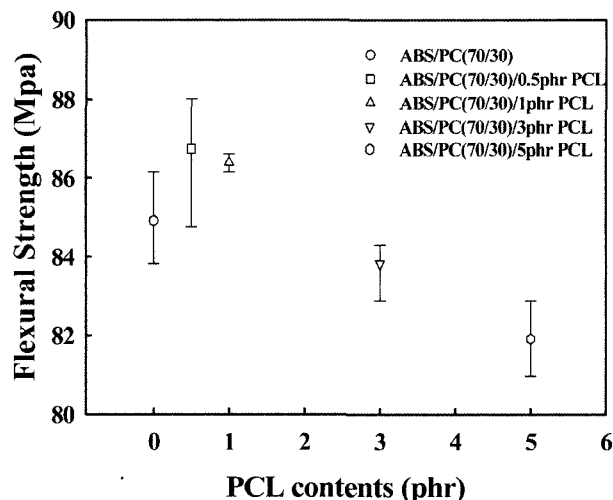


Figure 6. Flexural strength of the ABS/PC (70/30) blends with PCL content.

phase with the dissolved PCL was etched by NaOH, therefore, irregular round shape of the PC domain was observed in Figure 4. From the results of T_g and morphology of the ABS/PC (70/30) blends shown in Figures 1-4, it is suggested that partially miscibility is achieved by adding the PCL in the ABS/PC (70/30) blends.

Figures 5 and 6 show the tensile and flexural strength of the ABS/PC (70/30) blends with the PCL content (0.5, 1, 3, and 5 phr). From Figures 5 and 6, it is observed that the tensile and flexural strength of the ABS/PC (70/30) blends show maximum values of about 53.5 and 84.5 MPa at the PCL of

0.5 phr, respectively. Tensile and flexural strength, then, decrease with the increases of the PCL. The decreases of the tensile and flexural strength of the blends are maybe due to the solubilizing effect of the PCL since the tensile and flexural strength of the PCL are not as high as those of the ABS and PC. Figure 7 shows the flexural strength of the ABS/PC (80/20) blends with the PCL content (0.5, 1, 3, and 5 phr). From Figure 7, it is observed that the flexural strength of the ABS/PC (80/20) blends show maximum value of about 78.4 MPa at the PCL of 0.5 phr, which is similar behavior with that of the ABS/PC (70/30) blends.

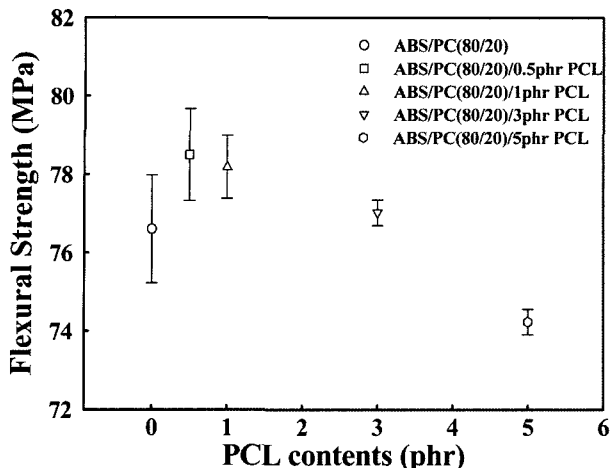


Figure 7. Flexural strength of the ABS/PC (80/20) blends with PCL content.

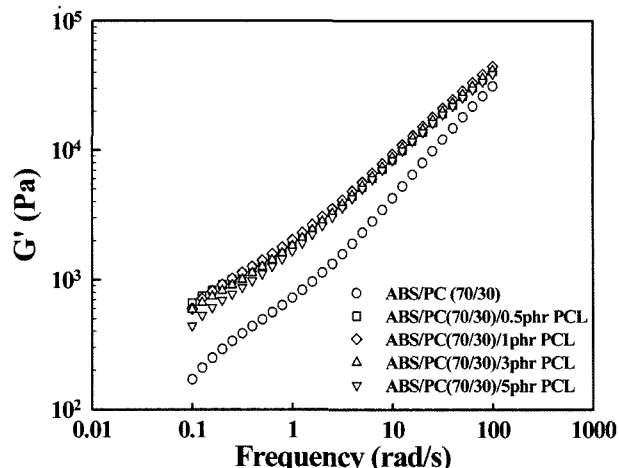


Figure 9. Storage modulus of the ABS/PC (70/30) blends with 0.5, 1, 3, and 5 phr PCL.

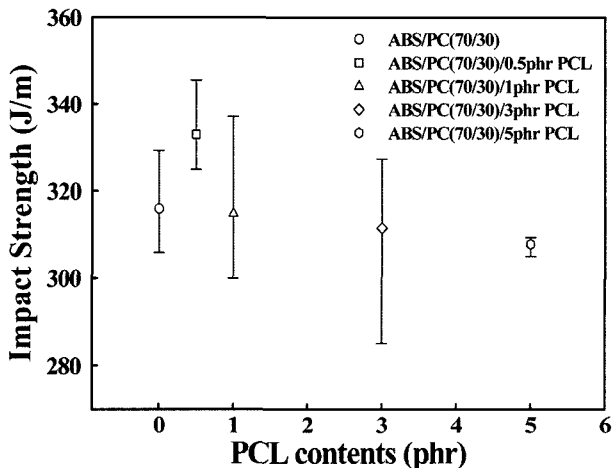


Figure 8. Impact strength of the ABS/PC (70/30) blends with PCL content.

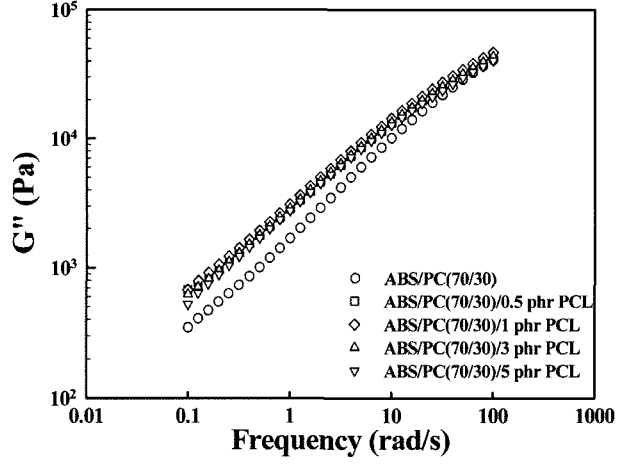


Figure 10. Loss modulus of the ABS/PC (70/30) blends with 0.5, 1, 3, and 5 phr PCL.

Figure 8 shows the impact strength of the ABS/PC (70/30) blends with the PCL content (0.5, 1, 3, and 5 phr). From Figure 8, it is observed that the impact strength of the ABS/PC (70/30) blends shows maximum value of about 330 J/m at the PCL of 0.5 phr. Then, the value of the impact strength of the blends decreases with the increases of the PCL. From the results of the tensile, flexural and impact strength of the ABS/PC (70/30) blends with the PCL, it is suggested that the PCL is an effective compatibilizer of the blends and the compatibility is increased by adding the PCL of 0.5 phr into the ABS/PC (70/30) blends.

Figures 9-11 show the storage modulus, loss modulus and complex viscosity of the ABS/PC (70/30) blends with the frequency at different PCL content, respectively. From Figures 9-11, the increases of the storage modulus, loss modulus and complex viscosity of the ABS/PC (70/30) blends are observed by adding the PCL (0.5, 1, 3, and 5 phr). From

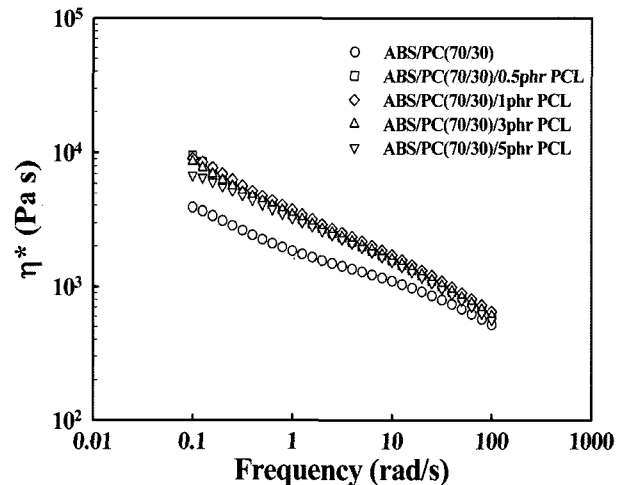


Figure 11. Complex viscosity of the ABS/PC (70/30) blends with 0.5, 1, 3, and 5 phr PCL.

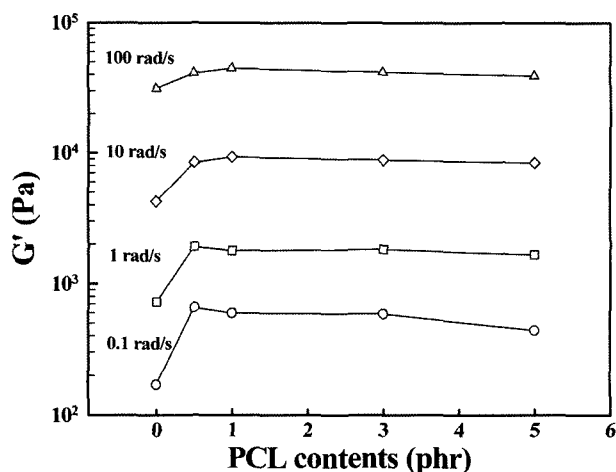


Figure 12. Storage modulus versus PCL content at different frequencies; ABS/PC (70/30) blends with 0.5, 1, 3, and 5 phr PCL.

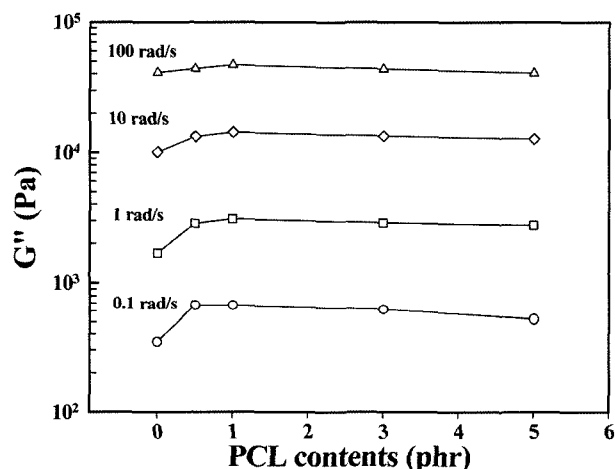


Figure 13. Loss modulus versus PCL content at different frequencies; ABS/PC (70/30) blends with 0.5, 1, 3, and 5 phr PCL.

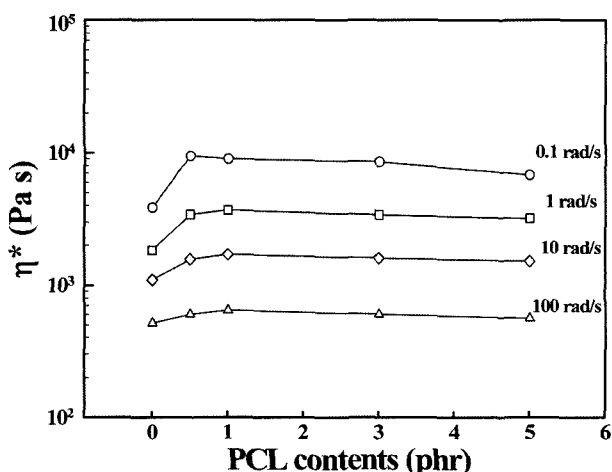


Figure 14. Complex viscosity versus PCL content at different frequencies; ABS/PC (70/30) blends with 0.5, 1, 3, and 5 phr PCL.

Figures 9-11, it is observed that the storage modulus, loss modulus and complex viscosity show the higher values when the PCL is added in the amount of 0.5 and 1 phr compared when the PCL is added in the amount of 3 and 5 phr. The increase of the complex viscosity in the ABS/PC (70/30) blend with the PCL may be due to the compatibilizing effect of the PCL. The increase of the complex viscosity is consistent with the results of the mechanical properties, which is that the tensile, flexural and impact strength of the ABS/PC (70/30) blends are increased when the PCL is added in the amount of 0.5 phr.

Figures 12-14 show the storage modulus, loss modulus and complex viscosity of the ABS/PC (70/30) blends with the PCL content at different frequencies, respectively. From Figures 12-14, it is observed that the storage modulus, loss modulus and complex viscosity at the frequency of 0.1 rad/s show the highest value when the PCL is added in the amount of 0.5 phr. From Figure 14, the increase of the complex viscosity is more significant at low frequency (0.1 rad/s). This is because that the rheological properties of the complex viscosity at long time relaxation region (low frequency) reflects the interfacial properties of the polymer blends.¹⁷ When the concentration of the PCL is 3 and 5 phr in Figure 14, the decrease of the complex viscosity, compared that of the 0.5 and 1 phr, is observed and this is maybe due to the solubilizing effect of the PCL because that the PCL has lower complex viscosity than those of the ABS and PC.

From the above results of the glass transition temperature, mechanical properties, morphology and complex viscosity of the ABS/PC blends with the PCL, it is suggested that compatibility is increased when the PCL is added in the ABS/PC (70/30) blends and the optimum concentration of the PCL as a compatibilizer is 0.5 phr.

Conclusions

In this study, the effects of PCL on the ABS/PC blends were investigated. From the results of dynamic mechanical thermal analysis of the ABS/PC blends with PCL, the T_g (PC) of the ABS/PC (70/30) blends decreased with the increase of PCL content, which suggested partial miscibility between the ABS and PC. In the study of the morphology of the ABS/PC (70/30) blends with PCL, the droplet size of the PC did not change significantly with the amount added PCL in the ABS/PC blend, however, the phase separation between the ABS and PC phases became less significant after adding the PCL in the ABS/PC blends. From the morphological studies of the ABS/PC blends etched by the NaOH, it is observed that the shape of the droplet has been changed from regular round shape to irregular round shape by adding PCL in the ABS/PC blends. From the results of T_g and morphological studies of the ABS/PC (70/30) blends with PCL, it is suggested that miscibility is increased between the ABS and PC phases by adding the PCL in the ABS/PC (70/30) blends.

In the study of the mechanical properties of the ABS/PC blends with PCL, it was observed that the tensile, flexural and impact strength of the ABS/PC (70/30) blends showed maximum values when the PCL was added in the amount of 0.5 phr. From the results of the tensile, flexural and impact strength of the blends with PCL, it is suggested that the PCL is an effective compatibilizer in the ABS/PC (70/30) blends and the compatibility is increased by adding the PCL in the amount of 0.5 phr in the ABS/PC (70/30) blends.

From the results of rheological properties of the ABS/PC (70/30) blends with the PCL content at different frequency, it was observed that the storage modulus, loss modulus and complex viscosity showed the higher values when the PCL was added up to 5 phr. The increase of the complex viscosity is consistent with the results of the mechanical properties, which is that the tensile, flexural and impact strength of the ABS/PC (70/30) blends are increased when the PCL is added in the amount of 0.5 phr.

From the above results of the glass transition temperature, mechanical properties, morphology and complex viscosity of the ABS/PC blends with PCL, it is concluded that compatibility is increased when the PCL is added in the ABS/PC (70/30) blends and the optimum concentration of the PCL as a compatibilizer is 0.5 phr.

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