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Polystyrene/bisphenol A polycarbonate molecular composite by in situ polymerization. I. Preparation and characterization

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Abstract

Polystyrene (PS) and bisphenol A polycarbonate(PC) molecular composites prepared by in situ polymerization techniques have been investigated by FT-IR, ^{1}H NMR, scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermogravimetry analysis (TGA) and mechanical testing. The homogeneous PC–styrene monomer mixture (solution) polymerized in situ yielded a partially miscible composite. Partial miscibility was established by a comparison of the experimentally determined glass transition temperatures (T_g) with those estimated by an equation formulated from a completely miscible amorphous polymer system. The partial miscibility was also confirmed by images obtained from the SEM and optical micrographs, size exclusion chromatograms and dissolution behaviors in common organic solvents. SEM of the fracture surfaces revealed that the dispersed PC domains sized 1–2 μm in diameter emerged from the continuous PS phase over time. Etching experiments confirmed that the PC domain contains subinclusions of PC/PS microdomains. Both the thermal and tensile properties of the composite were found to be enhanced than pure PS. The entropic gains by mixing the flexible component polymers and the possible formation of n–π complex between carbonate–benzene mixture are proposed for the partial miscibility. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: In situ polymerization; Molecular composite; Polystyrene

1. Introduction

It is well known that polymer composites are being used in steadily increasing quantities in diverse fields, such as in aerospace, microelectronics, automotive, medical and even in the recreation industries, as a result of improved material performance and manufacturing flexibility. In particular, molecular composites [1–3] currently being investigated to produce molecularly dispersed blending products have received considerable attention owing to the potential for the development of new polymeric materials having enhanced performance and strength, along with other advantages [4].

In a so-called idealized molecular composite by in situ polymerization, rod-like chain molecules would be molecularly dispersed in a matrix comprising a flexible coil-like chain [3]. Various attempts, therefore, have been made to prepare a molecular composite having homogeneous phase morphology, but most of them are found to be unsuccessful. Undoubtedly, the unfavorable entropic interactions between the two component polymers assuming different conformations accentuated the tendency for immiscibility [5–10]. Meanwhile, blendings of bisphenol A polycarbonate (PC) with numerous polymers have been the subject of some interest in recent years. Enhancements of optical property, rheological behaviors and property–price ratio were the main objectives [11–16]. However, neither the use of various compatibilizers nor blending strategies has ever led to the miscible materials having high modulus, enhanced strength and ease of processing. Furthermore, no research paper concerning the preparation of bisphenol A polycarbonate–polystyrene (PC–PS) composite by in situ technique can be found in literature. Thus, it is intended to prepare a composite by dispersing a PC which is less flexible ($[\langle R_g \rangle_o^2/M]_{PC} = 2.20 \times 10^{-3}$ nm^2 mol/g) than PS ($[\langle R_g \rangle_o^2/M]_{PS} = 0.83 \times 10^{-3}$ nm^2 mol/g) in a PS matrix, polymerized in situ. This is because a homogeneous blending can be anticipated due both to the increased entropy of mixing and the possibility of the n–π complex formation [17] between the aromatic ring of PS and the ester group of PC. Additionally, one of the most essential requirements to achieve a successful in situ polymerization, i.e. that the guest polymer be completely soluble in the monomer, was satisfied by this PC–styrene monomer pair. The experimental confirmation of the complete dissolution of PC in styrene

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monomer at around 90°C leads us to perform this study. Besides, an expectation on the unique set of optical transparency, thermal stability and mechanical properties which might result from the composites, being highlighted recently as a material for the compact disc, is the particular interest of this study because of its availability on a commercial basis.

This article describes the synthetic method of PC–PS molecular composite by in situ polymerization of styrene monomer in the presence of PC, and their structural and material characteristics. In particular, efforts have been to establish the miscibility of this system by employing various characterization techniques.

2. Experimental

2.1. Materials

An additive-free bisphenol A polycarbonate ($M_w = 52\,000$, $M_w/M_n = 2.60$) was obtained from Samyang Co. (Korea) and purified by dissolution in chloroform and precipitation by methanol. Polymers separated were dried under reduced pressure. Chemical grade styrene monomer was obtained from Aldrich and purified by distillation under reduced pressure. Purification of other solvents was carried out by fractional distillation before use. The polystyrene homopolymer ($M_w = 361\,000$, $M_w/M_n = 2.41$) used for the solvent-cast blending, was provided by the Miwon Co. (Korea) and purified by the precipitation method.

2.2. In situ polymerization

Mixtures of styrene monomer and PC were prepared on a weight percent basis. The initial PC content was controlled so as not to exceed over 40 wt%, owing to the experimental infeasibility caused by the high viscosity of the reaction mixture at higher PC concentration. In situ polymerization was carried out by bulk method with neither addition of initiator nor of other additives. The initial heterogeneous mixture containing PC was heated gently up to 80–90°C when PC dissolved completely. The homogeneous reaction mixture was polymerized at 90°C for 4 h under vigorous stirring until stirring was infeasible due to the high viscosity of reaction mixture. The polymerization was then terminated by cooling the reaction mixture to room temperature. The product was then dissolved in chloroform followed by addition of the solution into large amounts of methanol. The precipitated polymers were separated and purified by several cycles of dissolution and reprecipitation from the chloroform/methanol system, which yielded white fibrous state of final products (PCS series). Separately, a part of the final product was exposed to hot toluene extraction for two days (EPCS series). For comparison purpose, a solvent-cast blend (PCSB series) was prepared. Chloroform was employed as the common solvent.

2.3. Measurements and characterizations

The ^{1}H NMR spectrum was recorded on a Bruker AC 250 spectrometer operating at 250 MHz. Chloroform-d containing 0.03% of tetramethylsilane was used as the solvent. The integrated intensity of an absorption in the proton NMR spectrum depends only upon the molar concentration of the substance times the number of nuclei per molecule responsible for the peak. On this theoretical basis, the content of component polymer in a composite is estimated by the following equations derived from the values of arithmetic mean of the integrated intensities of characteristic proton absorptions per mole of component polymers,

$$I_{PS} = \frac{1}{4}\left[\frac{I_1}{n_1} + \frac{I_2}{n_2} + \left(\frac{I_{3,m}}{n_{3,m}} + \frac{(I_{3,o} + I_{3,p})}{(n_{3,o} + n_{3,p})}\right)\right] \quad (1)$$

$$I_{PC} = \frac{1}{3}\left[\frac{I_4}{n_6} + \frac{I_{5,o}}{n_{5,o}} + \frac{I_{5,m}}{n_{5,m}}\right] \quad (2)$$

where I is the integrated intensity of the characteristic peak, n, the number of nuclei responsible for the peak, and o, m, p denote the *ortho*, *meta* and *para* positions of the aromatic proton, respectively. Thus, the wt% of the component polymers can be written as:

$$w_{PS} = \frac{I_{PS}M_{PS}}{I_{PS}M_{PS} + I_{PC}M_{PC}} \times 100 \quad (3)$$

$$w_{PC} = \frac{I_{PC}M_{PC}}{I_{PS}M_{PS} + I_{PC}M_{PC}} \times 100 \quad (4)$$

where w is the wt% of component polymer and M denotes the molecular mass of the repeating unit.

The FT-IR spectrum was recorded on a Nicolet spectrophotometer in the range 4000–400 cm^{-1}. The KBr pellet method was used for the measurements. A Nikon Optiphot 2-pol system equipped with a hot stage was used for optical microscopic studies. Sample was heated from 30 to 270°C at a heating rate of 20°C/min. The morphology of the fracture surfaces of composites was observed by scanning electron microscopy (SEM, JEOL JSM-5200). The accelerating voltage was 20 kV. Differential scanning calorimetry (DSC) data were obtained on a Perkin–Elmer DSC 7 calorimeter. Values were taken after one complete cycle of heating to 250°C and cooling at a heating rate of 20°C/min under a nitrogen atmosphere. Thermogravimetric analysis (TGA) of the products were carried out by employing a Dupont 9900 thermogravimetric analyzer. A 20 mg sample was heated to 600°C at a heating rate of 20°C/min under nitrogen atmosphere. The stress–strain behavior of the composite was observed by tensile testing. An Instron (Instron Co. Series IX Automated Material Testing System 1.16) operated with a chart speed of 5 pts/s and a cross-head speed of 1.3 mm/min was used. Specimen was prepared by the dumbbell molder (Model CS-183, Custom Scientific Instruments, Inc.) set at 230 ± 5°C. Tests were carried out at 25°C

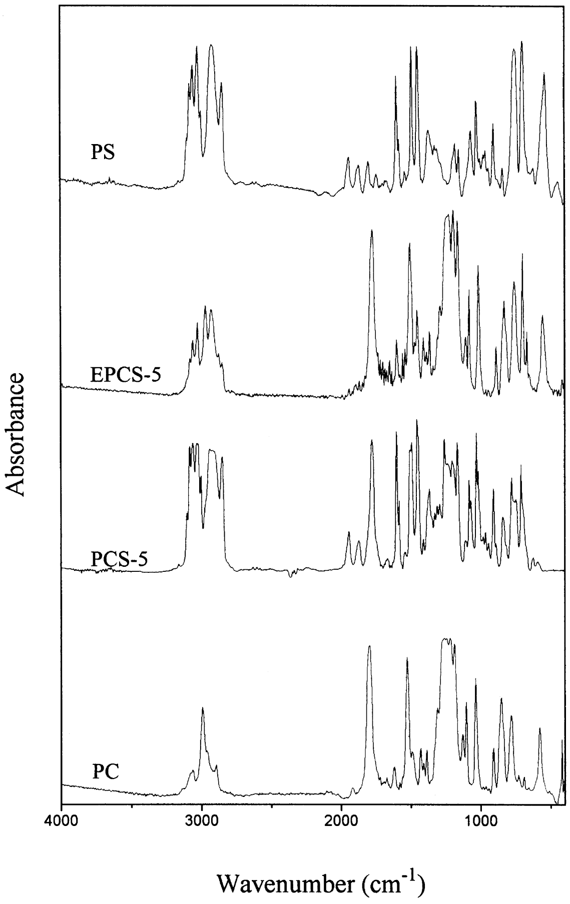


Fig. 1. IR spectra of pure PS, PC and PC–PS molecular composite (PCS-5).

and at 60% relative humidity. Average molecular masses and polydispersity indices of the products were measured by size exclusion chromatography (SEC) equipped with Waters 510 pump, RI and UV detectors, Rheodyne injector, and 4 linear columns packed with μ-Styragel. The flow rate of THF was 1.0 ml/min and the columns were calibrated with polystyrene standards.

3. Results and discussion

3.1. Structural characterization

The FT-IR spectrum of the PCS-5 is compared with those of homopolymers PS and PC in Fig. 1. As is evident from the figure, the composite exhibits characteristic aromatic stretching bands at 3100 and 1500 cm^{-1}, and a carbonyl stretching at 1760 cm^{-1}, indicating the possible formation of a molecular composite. Surprisingly, the spectrum obtained from a purified composite (EPCS-5), which was extracted with hot toluene for two days, showed medium intensities for the aromatic stretching bands. This is a strong indication that a considerable amount of matrix polymer molecules (PS) still coexist with dispersed phase (PC). This effect might possibly stem from the molecular coiling between the component polymer chains, due mainly to the increased entropy of mixing.

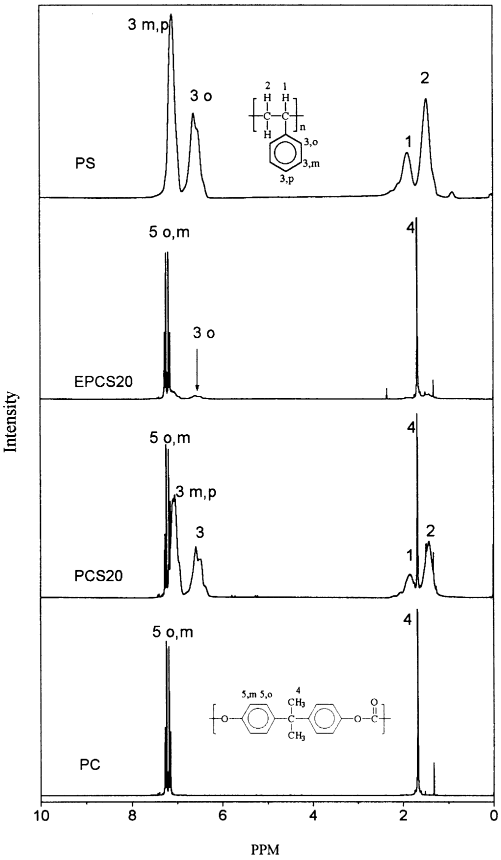


Fig. 2. ^{1}H NMR spectra of pure PS, PC and PC–PS molecular composite (PCS-20).

The ^{1}H NMR spectra obtained from the PCS-10 and EPCS-10 samples are shown along with those of PC and PS homopolymers in Fig. 2. Clearly, all the characteristic proton absorptions corresponding to benzyl proton (1), methylene proton (2), aromatic proton (3) of PS and methyl proton (4), aromatic proton (5) of PC can be observed from

Table 1
The feed ratio of styrene monomer/polycarbonate (PC) and the contents of polymers in the composite

Sample code	Feed ratio	Polymer content[b]
	SM[a]/PC (g/g)	PS/PC (g/g)
PCS-5	95/5	91/9
PCS-10	90/10	84/16
PCS-20	80/20	76/24
PCS-30	70/30	67/33
EPCS-5		12/88
EPCS-10		13/87
EPCS-20		15/85
EPCS-30		17/83

[a] Styrene monomer.

[b] Estimated from the ^{1}H NMR spectrum.

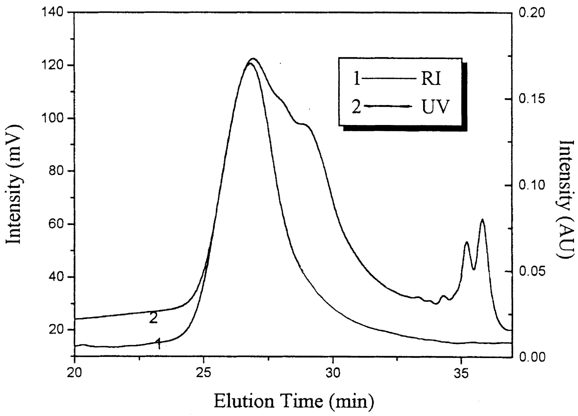


Fig. 3. SEC chromatogram of PC–PS molecular composite (PCS-10).

the spectrum of PCS-10. In particular, it is of interest to note that the spectrum of EPCS-10 shows absorption due to the aromatic proton of PS, suggesting the substantial occurrence of partial molecular mixing.

Interestingly, on the other hand, the peak of the benzyl proton (1) of styrene in the composite (PCS-10) is found to be slightly shifted toward higher magnetic field. This effect can be considered to be a result of n–π complex formation between the unshared pair of electrons of the carbonate groups in PC and the π electrons of the aromatic rings of PS [17]. This result may be due to the fact that the intimate mixing of the component polymer chains has forced the benzene rings of PS, being oriented perpendicular to the main chain, to approach closer to the carbonate groups so that an intermediary interaction can occur. Possibly, this n–π complex formation contributes to the miscibility of ester–benzene mixtures [18]. It is, therefore, reasonable to suggest that the entropic gain by mixing two flexible component polymer chains has led to intimate molecular entanglement, which in turn contributes to the formation of n–π complex between the different polymer chains. This effect is considered to be responsible for the partial miscibility of the composite.

The feed ratios of styrene monomer against PC and the contents of component polymers in the products estimated from Eqs. (3) and (4), are summarized in Table 1. A trend is immediately obvious from the data, i.e. the variations of PS content in the products show a decreasing trend throughout when compared with the quantity of styrene monomer added initially. This is due, among others, to the higher viscosity of the reaction mixture at the early stage of polymerization, which leads to a relatively low conversion, and hence a considerable amount of monomers might be either unreacted or is only oligomerized.

Table 2
The molecular masses and polydispersity indices of PC and PC–PS molecular composites by size exclusion chromatography

Sample code	$\overline{M}_n \times 10^{-5}$	$\overline{M}_w \times 10^{-5}$	$\overline{M}_w/\overline{M}_n$
PC[a]	0.20	0.52	2.60
PCS-5	1.01	2.60	2.58
PCS-10	0.79	2.29	2.89
PCS-20	0.70	3.16	4.52
PCS-30	0.56	2.78	4.98

[a] Measured in chloroform solution.

In the polymer content data for EPCS series a considerable amount of PS is still found remaining in the composite, corresponding with the results observed in ^{1}H NMR and IR spectra. This residual PS can be regarded as a component polymer that has been perfectly solubilized in the PC chains, due possibly to the intensive coiling and n–π complexation. This is substantial evidence showing the degree of miscibility of the given system.

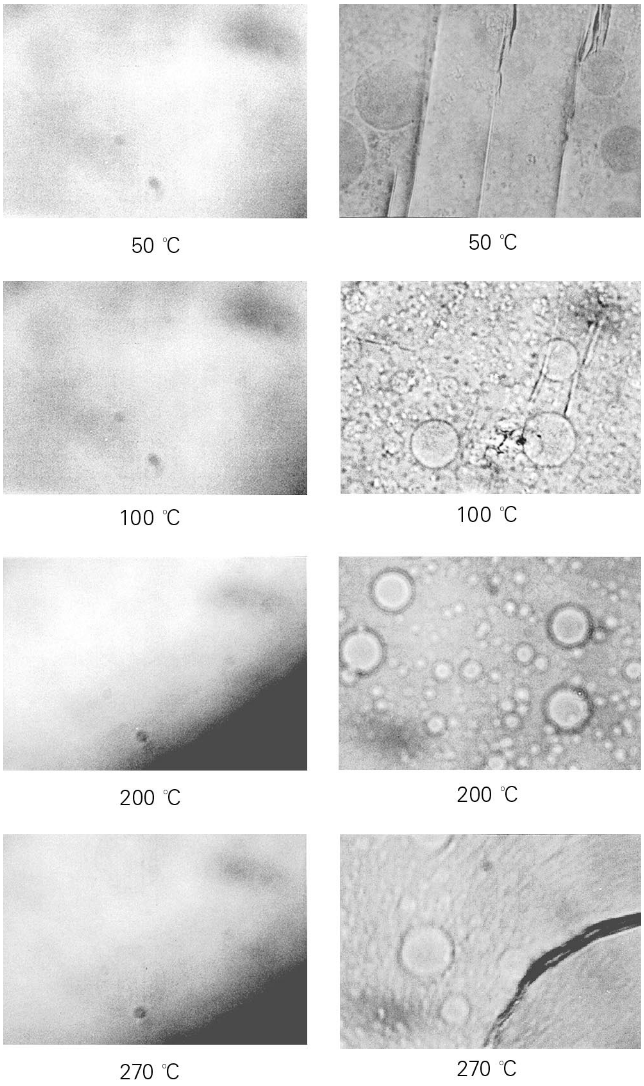
3.2. Size exclusion chromatography

The complete dissolution of PCS series in THF at room temperature not only gives a strong evidence of the occurrence of molecular mixing but also allows measurements of molecular masses and polydispersity indices of the products by SEC. In Fig. 3 are illustrated representative chromatogram which have been drawn by both the RI and UV (254 nm wavelength) detectors for the PCS-10 sample. Clearly, two distinctive chromatograms in overall shape can be seen from Fig. 3, especially different in the range of elution time at around 28–30 min. The indication of a shoulder in the UV chromatogram in this range can be attributed to the aromatic chromophores ($\lambda_{\max} = 255$ nm) of bisphenol A group in PC. The UV chromatogram, thus, confirms that PCS-10 is constituted of different component polymers, while the chromatogram by RI detector indicates that the molecules of different polymers act as a homopolymer, leading to a conclusion that the molecules of PC and PS are mixed at a molecular level.

Table 2 summarizes the data obtained from the SEC measurements for the PCS series and PC. In all compositions studied, PCS series exhibits higher molecular masses than that of PC homopolymer indicative of the formation of high molecular mass PS. In addition, the table also shows that the M_n values, which are known to be highly sensitive to the presence of low molecular mass polymer, are inversely proportional to the input quantity of PC. This trend is attributed primarily to the initial high viscosity of reaction mixture with increasing content of PC, because of which the conversion to high molecular weight polystyrene becomes difficult. This result is well reflected by the variations in the polydispersity index.

3.3. Morphological characteristics

Fig. 4 shows the representative optical micrographs taken with temperature variation from 50 to 270°C for the PCS-10 and PCS-10B samples. The time required for the temperature cycling was about 60 min and the micrographs taken were during the second cycling of temperature. In all optical micrographs of the composite PCS-10, neither a distinctive



(a) PCS-10 (b) PCS-10B

Fig. 4. Optical micrographs of PC–PS molecular composite (PCS-10) and blend (PCS-10B) (× 400).

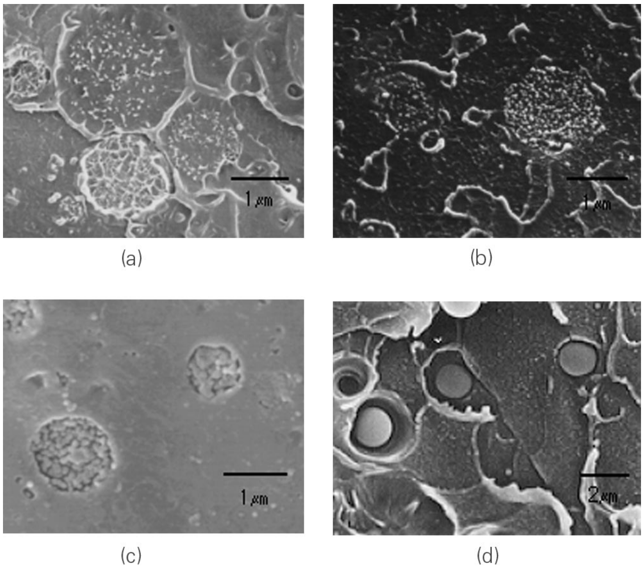


Fig. 5. SEM micrographs of fracture surfaces of molecular composite (PCS-10) and blend (PCS-10B). (a) Macrodomain emerging from the continuous phase; (b) details of macrodomain containing subinclusion of PC/PS micro-domain; (c) etched by NaOH solution; and (d) micrograph of PC/PS blend.

domain nor signs of phase separation can be found, regardless of the temperature. Whereas, the solvent-cast blend product demonstrates PC domains sized about 10 μm, and the numbers of domains and their sizes show an increasing trend with temperature, indicating phase separation. It is, therefore, noticeable that the phase stability revealed by the composite against temperature up to 270°C is significant for processability without phase separation.

The SEM micrograph of fracture surfaces of the PCS-10 composite is shown in Fig. 5, which reveals an interesting fracture morphology. It can be seen from Fig. 5(a) that macrodomains begin to emerge from the continuous phase in which PS is the major component and PC is the minor one. Over time, SEM appears to show macrodomains sized 1–2 μm, as illustrated in Fig. 5(b). An etching experiment with NaOH solution to remove the PC selectively from the composite yielded an SEM image shown in Fig. 5(c), which gives the details of the structure of the macrodomain. Clearly, the etched image demonstrates that the dispersed phase domain contains subinclusions of PC and PS micro-domains sizes of the order of tens of nanometers, which

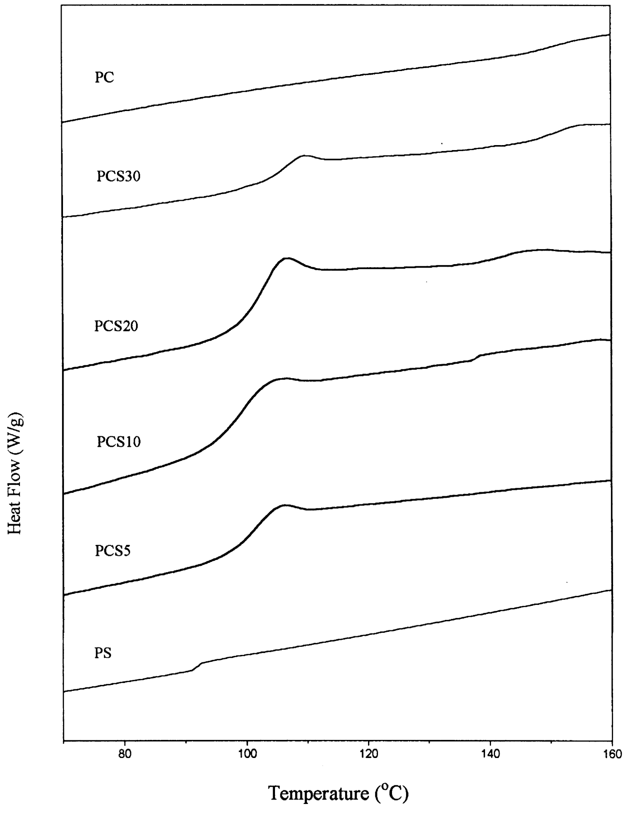


Fig. 6. DSC thermograms of various composites as a function of temperature.

Table 3
Glass transition temperatures of composites and apparent weight fraction (W_1) of PC in the PS-rich phase from DSC measurements

Sample code	T_g		T_g(p)	W_1
	PS	PC	Linear equation[a]	PS-rich
PS	92	—		
PCS-5	94	—	97	0.03
PCS-10	98	138	102	0.13
PCS-20	102	143	107	0.16
PCS-30	105	150	112	0.26
PC		153		

[a] Data estimated by a linear equation established from a completely miscible amorphous polymer system.

implies that the adhesion between the continuous and the dispersed phase has taken place. On the contrary, SEM micrograph of the solvent-cast blend product, shown in Fig. 5(d), reveals a different morphology from those of the composites. This blending product shows large spherical dispersed phase and pock marks does not show adhesiveness with the continuous phase, due likely to the high immiscibility. This fracture morphology is considered to be a typical feature of brittle fracture with spherical holes due to poor adhesion of the dispersed phase.

3.4. Glass transition temperature

The glass transition temperatures (T_g) of the composites were measured by DSC. Fig. 6 shows the DSC traces of the various composites as a function of temperature. The T_g of PC does not appear until the PC concentration is 0.16 weight fraction and then gradually increases with increasing PC content in the composite. The PS T_g is observable over the entire composition range and also increases with increasing PC content. In all compositions studied, however, the composites containing PC contents greater than 0.16 weight fraction exhibit two T_gs. As the composition of composite changes from pure PS to 0.67 weight fraction, the T_g value of PS is elevated toward higher temperature by about 13°C, while for PC content less than 0.33 weight fraction, the T_g is lowered by as much as 15°C from the T_g value of pure PC, indicating the partial miscibility of the given system [19,20].

The various T_gs found for the composites and the apparent weight fractions of PC in the PS-rich phase, predicted by the equation derived by Stoelting et al. [21] are listed in Table 3. The values of predicted single T_g(p) between the component polymers are estimated by the following simple linear equation under an assumption that the polymers are completely miscible:

$$T_{gAB} = T_{gA}w_a + T_{gB}(1 - w_a) \tag{5}$$

where T_{gAB} is the glass transition temperature of the miscible composite, T_{gA} and T_{gB} are the experimentally determined T_g values of the pure components PC and PS, respectively, and ws are the weight fractions of the component polymers in the composite. Clearly, the T_g(p) values come close to that of PS, which implies that an overwhelming fraction of PS is mixed molecularly with the PC chains within the limit of composition range studied. Likewise, the apparent weight fractions of PC (W_1) in the PS-rich phase are found to be smaller than the actual phase concentrations, but shows an approaching trend to the actual phase concentration when the PC content is increased. This would imply, though not decisively, that the miscibility of PS with PC may be increased with increments in PC contents.

3.5. Material characterization

In order to evaluate the miscibility effect on the thermal stability of the composites, TGA was performed. The

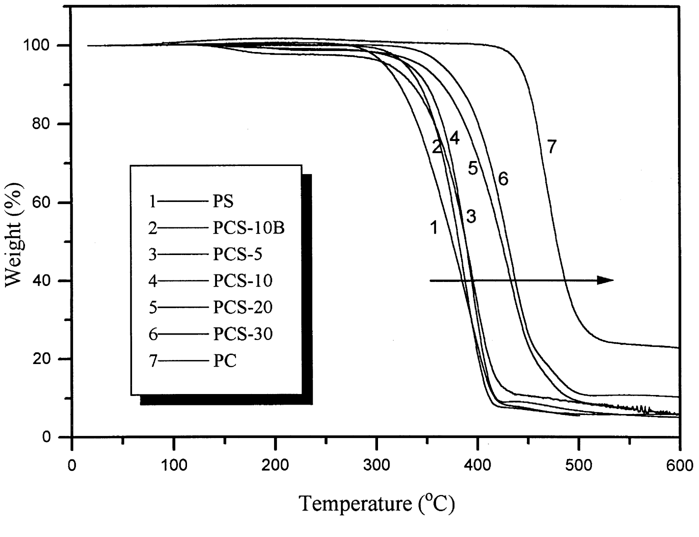


Fig. 7. TGA thermograms of pure PS, PC, PC–PS molecular composites and blend (PCS-10B).

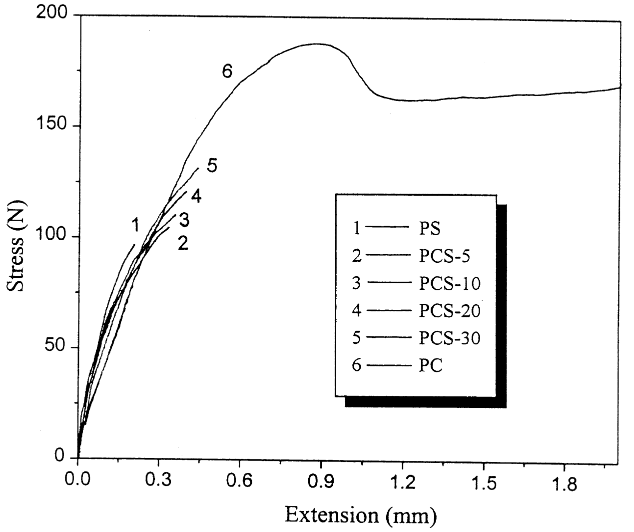


Fig. 8. Stress–strain behaviors of pure PS, PC and PC–PS molecular composites.

measurements of the weight loss as a function of temperature for three different samples (pure PS, PCS-10 and PCS-10B) are shown in the TGA thermograms in Fig. 7. In all the composites, the first sign of 1% of the initial weight loss was observed at approximately 330–350°C, but in contrast the pure PS and blend product have onset temperatures of decomposition at approximately 270–275°C and 285–290°C, respectively. This elevation of thermal decomposition temperature of composites can be attributed to the enhanced miscibility of PS with PC. Accordingly, this thermal stability behavior of the composites gives another evidence of elevated miscibility of the given system.

The tensile stress–strain behaviors of the composites are presented in Fig. 8 and the corresponding data are summarized in Table 4. From this table, it can be seen that the composites exhibit higher values of tensile strength at break than pure styrene. Also, a trend is obvious that the tensile strength increases gradually with increments in PC concentration. Because the morphology of the composite changes over time, as has been observed before, it can be inferred that the origin of the increase in tensile strength lies in the composite structure. After the initial stages of compression molding, the macrodomain containing PC/PS microdomain is dispersed in a PS matrix. This distribution of phases possibly contributes to the enhancement of the tensile strength. Also, Table 4 shows the fracture elongations of the composite system, which are higher than that of the pure PS. This effect is likely to be due to the ductile property of PC which yields before fracturing. The tensile modulus of the composite, on the other hand, is found to be slightly lower than pure PS, except for the case of PCS-30. These relatively low values of moduli are, in the main, a consequence of the effect exerted by the ductile PC.

Table 4
Stress–strain data of PC–PS molecular composites

Sample code	Tensile strength (MPa)	Elongation (%)	Modulus (GPa)
PS[a]	40.3	3.34	1.21
PCS-5	49.2	4.72	1.04
PCS-10	54.0	5.11	1.05
PCS-20	58.4	5.05	1.16
PCS-30	63.4	4.42	1.43

[a] Miwon Petrochemical Corp.

4. Conclusions

The homogeneous solution of styrene monomer and bisphenol A PC polymerized in situ yielded a partially miscible molecular composite. The two T_g values observed over the composition range of composite changed significantly with composition, giving substantial evidence of partial miscibility. The fracture morphology observed by SEM micrograph revealed the subinclusion of PC/PS microdomain in a macrodomain, indicative of the good adhesion between PS matrix and PC dispersion phase. ^{1}H NMR spectrum obtained from the composite showed a chemical shift of the benzyl proton of PS to higher magnetic field.

All the experimental results so far obtained lead us to conclude that the system is partially miscible. This miscibility can be considered to be a result of entropic gain by mixing two flexible component polymer chains, and in turn this contributes to the formation of a n–π complex between the unshared pair of electrons in the carbonate groups and the aromatic rings of PS.

Acknowledgements

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