

Charge Distributions in PC/SAN/PCL Polymer Blends

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ABSTRACT

The formation of space charge in polycarbonate (PC)/poly (styrene-co-acrylonitrile) (SAN) blends containing poly (ϵ -caprolactone) (PCL) as a compatibilizer for improving the miscibility, has been studied by measuring spatial charge distributions. It is found that the miscibility of PC/SAN blends is improved as the PCL content increases. The amount of charge accumulated in the blends decreases when the PCL content increases to 15% by weight and then increases when the PCL content is > 15% wt. The decrease of charge at the PCL content < 15% wt was attributed to the combined effects of changes in conductivities and the molecular interactions at the domain interfaces. The increase of charge at the PCL content > 15% wt was attributed to the trapping of charge at the amorphous and crystalline phases of PC and PCL.

1. INTRODUCTION

POLYMER blends frequently are used in the field of polymer engineering to overcome drawbacks of an individual polymer. In the blend systems, interfaces play an important role in the determination of physical properties including the electrical ones. Better physical properties are expected when some level of chemical interaction exists at domain interfaces.

Many techniques, including the thermal and mechanical ones, are proposed to study the compatibility of polymer blends [1]. Here, an electrical method was proposed for the study of the compatibility of polymer blends. This technique measures spatial charge distributions in polymer blends with which the behavior of electrons at do-

main interfaces is speculated by considering the capability of electrons to transport through domain interfaces.

Subjected to dc stresses, the polymers are charged by various mechanisms such as dipolar orientation and charge injection from the electrodes [2]. The injected charge is trapped and becomes immobile if there are trapping sites in the polymers. In semicrystalline polymers, the interfaces between the amorphous and crystalline phases are well known trapping sites [3]. In this situation, we can see a large amount of negative charge in the dielectrics. However, the charges will be dissipated and return very easily to the electrodes where they came from if there are hopping sites through which the charge can migrate. It is expected that sharply defined

domain interfaces in immiscible polymer blends do not dissipate the space charge developed during the voltage application because they block charge transport. The polar molecules at laminate interfaces provide the bridge for the charge to be dissipated efficiently crossing the domain interfaces [4]. This implies that polymer miscibility may govern the dissipation of charge in the blends.

In order to prove this idea, the effects of miscibility on the formation of space charge in the blend system have been studied. For the study, blends of polycarbonate (PC), poly (styrene-co-acrylonitrile) (SAN) and poly (ϵ -caprolactone) (PCL) have been selected because (1) PC and SAN are amorphous polymers, so that charge trapping at the amorphous/crystalline interfaces can be excluded and (2) the polymer miscibility is governed by the PCL content. Details of this blend system are described as below.

Blends of PC/SAN have been reported to be partially miscible by many researchers [5, 6]. Mechanical properties such as elongation at break and impact strength of the blend fall off rapidly at $> 10\%$ wt of SAN because of limited miscibility. It is of interest to note that blends of PC/PCL and SAN/PCL are miscible according to previous studies [7, 8]. It is therefore expected that PCL may be a compatibilizer for improving the miscibility of the PC/SAN blend. Paul and his coworkers studied blends of PC/SAN/PCL and reported that the ternary blend became miscible as the content of PCL was increased, based on the glass transition temperatures of the system [9].

2. EXPERIMENTAL DETAILS

2.1. SAMPLE PREPARATION

Three commercial polymers were used in this study. These are polycarbonate (PC) (General Electric, Lexan 141), poly (styrene-co-acrylonitrile) (SAN) (Hannam Chemical, Hanasan 300) and poly (ϵ -caprolactone) (PCL) (Union Carbide, Tone 700), (Table 1). The acrylonitrile content of the SAN used is known to be 25% wt.

Table 1.

Volume conductivity σ and relative permittivity ϵ of PC, SAN and PCL

Property	PC	SAN	PCL
$\sigma, \Omega\text{m}$	10^{-17}	10^{-16}	10^{-13}
$\epsilon(10^6 \text{ Hz})$	2.9	2.8	4.4

According to the previous studies by Paul and his coworkers, the amount of PCL required to solubilize the blend of 50/50 PC/SAN is larger than that required to solubilize the blend of 25/75 PC/SAN or the blend of 75/25 PC/SAN [9]. Thus we chose the blend of 50%

PC/50% SAN as a control blend in order to study the effects of PCL on the properties of PC/SAN blend. Ternary blends of PC/SAN/PCL were prepared using a twin screw extruder (TEX-30, Japan Steel Workers Ltd.). The contents of PCL were 5, 10, 15, 20 and 33% wt in the blends in which the ratio of PC/SAN were fixed 50/50% wt.

2.2. MEASUREMENT OF PROPERTIES

The blends were injection molded for tests of tensile strength, elongation at break and notched Izod impact strength according to ASTM D638 and D256. Light transmittance of injection molded specimen of thickness 3.2 mm was measured using a direct reading hazemeter (Toyoseiki Seisakusho). Thermal properties of the blends were studied employing differential scanning calorimeter (DSC Du Pont 910).

2.3. MEASUREMENT OF CHARGE DISTRIBUTIONS

Charge distributions were measured by a pulsed electroacoustic (PEA) method. The details of measurement principles of this technique have been described elsewhere [10, 11]. It consists of electric pulse generator (pulse width 30 ns, pulse height -1 kV), 30 kV HV power supply, test cell with a piezoelectric detector and data acquisition system. The piezoelectric detector was made of a 28 μm thick PVDF film because of its excellent wideband characteristics in the frequency domain. The data acquisition system consisted of wideband preamplifier, digitizing oscilloscope and a personal computer.

This technique uses the electric pulse as a probe to scan the sample. When an electric pulse is applied to the specimen containing the charge inside, an electroacoustic pressure wave is generated at the site where the charge exists, following $F = qE$ where F is an electric force, q is the charge and E is the electric field. This signal propagates throughout the sample and the component that reaches the electrode where the piezoelectric detector exists is converted to an electric signal by a piezoelectric transducer. This output signal is transmitted to a personal computer through a general purpose interface board (GPIB) and then calibrated to provide the charge density distributions in the sample.

Voltages to 23 kV dc were applied for 30 min. The spatial charge distributions were measured within 5 min after the discharge. Sample thickness was $\sim 1 \text{ mm}$. The semiconductive film of $\sim 200 \mu\text{m}$ thickness was used as an electrode in order to improve the acoustic impedance match. This film was prepared by compression molding of semiconductive compound made of olefinic polymer, conductive carbon black and processing aids such as wax and stearate at 180°C for 20 min. Measurements

of charge distributions were made both during the voltage application and after the discharge. The charge remaining after the discharge is the residual charge which indicates the trapped charge. The sound velocity v of the sample can be calculated from the sample thickness and the time interval between the charge peaks induced at the electrodes in an oscilloscope.

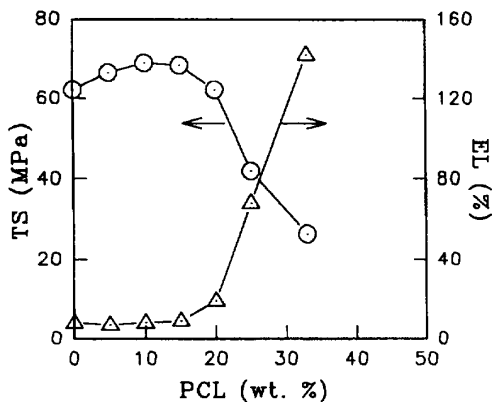


Figure 1.

Tensile strength (TS) and elongation at break (EL) vs. PCL content for the PC/SAN (50/50) blends.

3. EXPERIMENTAL RESULTS

3.1. MISCIBILITY OF PC/SAN/PCL BLENDS

In Figure 1, the tensile strength and the elongation at break of the PC/SAN blends containing PCL as a compatibilizer are shown. It is seen that the tensile strength of the blend shows a maximum and the elongation at break increases as the content of PCL is increased. It is of interest to note that the tensile strength of the blend increases with the PCL content in the blend to 15%, even though the tensile strength of PCL is lower than those of PC and SAN. MacKnight *et al.* pointed out that the miscible blends show a small maximum in tensile strength over certain blend compositions [12]. It is speculated that the synergism in tensile strength observed similar to miscible blends is attributable to improved miscibility of PC and SAN and better molecular packing by virtue of PCL in the blends.

In Figure 2, the notched impact strength for blends of different PCL content is given. It is seen that the impact strength increases very much when the content of PCL in the blends is $> 20\%$. The beneficial effects of PCL on impact strength also may be attributed to the improved miscibility between PC and SAN in the blend.

In Figure 3, the light transmittance of the injection molded tensile test specimen of the blends is shown. It is observed that this light transmittance shows a maximum

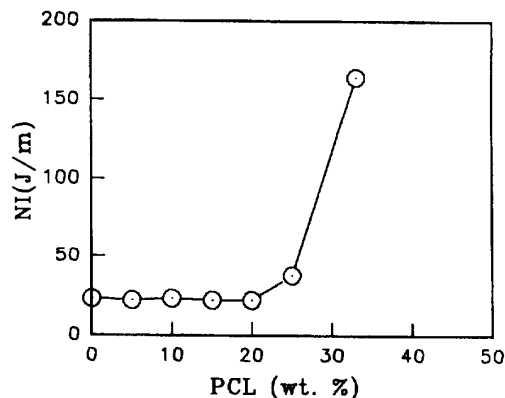


Figure 2.

Notched Izod impact strength (NI) vs. PCL content for the PC/SAN (50/50) blends.

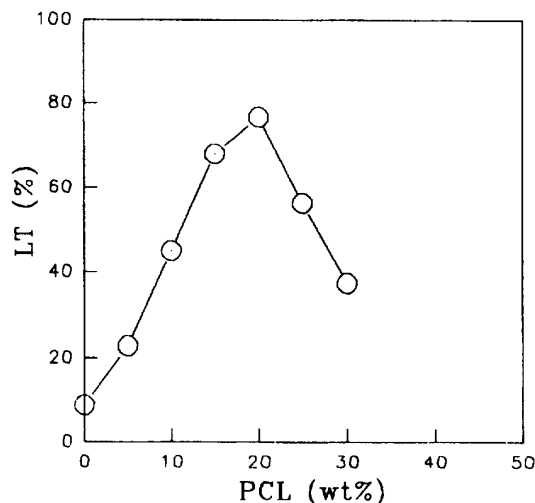


Figure 3.

Light transmittance (LT) vs. PCL content for the PC/SAN (50/50) blends.

with increasing PCL content in the blends. Transparency of a heterogeneous blend depends on the domain size and the difference in refractive indices of the constituents. The critical domain size of transparency of heterogeneous blend is known to be $\sim 0.1 \mu\text{m}$ [12]. According to Bohn, the critical difference between refractive indices should be < 0.01 for transparency [13]. The domain size of the PC/SAN blend was as large as $\sim 1 \mu\text{m}$. The refractive indices of PC and SAN are 1.585 and 1.570, respectively, and this difference is not small enough for transparency of the blend. The PCL is an opaque semicrystalline polymer and its refractive index can not be measured. However, the PCL in the blends is miscible with SAN and PC and thus the crystallization may be depressed. It is speculated that the difference between refractive in-

dices of PC rich phase and SAN rich phase in the blends decreases and consequently the light transmittance of the blends increases as the PCL content increases to 20% in the blends.

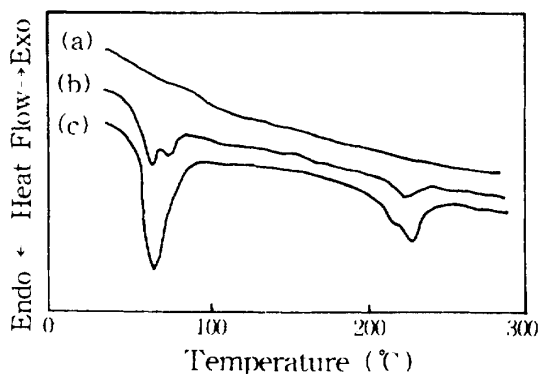


Figure 4.

DSC thermogram of PC/SAN (50/50) blends containing various amount of PCL (% wt) (a) 20, (b) 25, (c) 33.

It is of interest to note that light transmittance of the blends decreases at a PCL content > 20%. This phenomena is attributable to crystallization of PC induced by PCL and PCL itself. The presence of crystallinity in the blend was confirmed by DSC as shown in Figure 4. The crystallinity was seen by endothermic melting peaks at 65 and 225°C due to PCL and PC, respectively. It is suggested that the transparency of the blends can change depending on crystallinity.

3.2. CHARGE DISTRIBUTIONS IN PC/SAN/PCL BLENDS

Spatial charge distributions of a control blend sample, PC/SAN (50/50%), are shown in Figure 5. In this Figure, the charge distribution obtained during the voltage application (Figure 5(a)) is compared to the one obtained after the discharge (Figure 5(b)). All data were obtained at 120 ns/div in a digitizing oscilloscope.

In Figure 5, three bulk charge peaks are discernible in the blend. One is the charge overlapped with the negative induced charge peak, the polarity of which remains unchanged after the discharge. This peak may be due to the electrons injected from the cathode and subsequently got trapped in the blend sample. Upon removing the applied voltage, this negative charge remains in the sample and the induced charge at the cathode becomes positive. Two more peaks are found in the center region of the sample. Interestingly, the polarity of these peaks reverses after the discharge. In general, the lifetime of trapped electrons is longer than that of heterocharge and even the heterocharge usually does not change polarity in such a

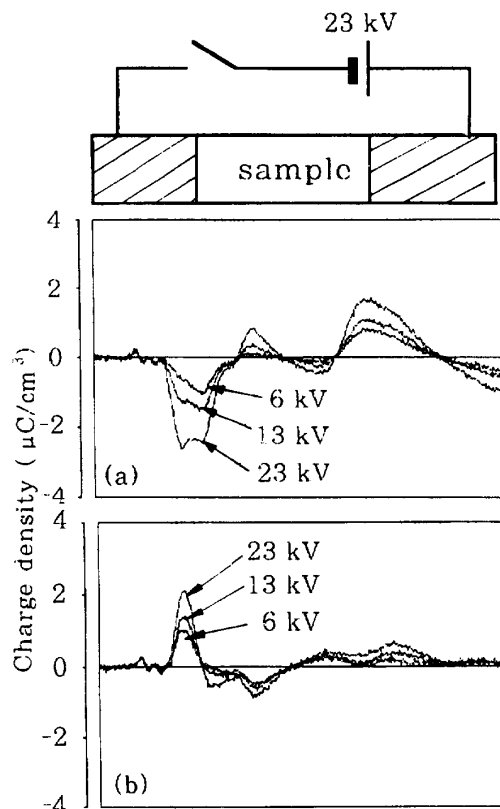


Figure 5.

Spatial charge distributions of PC/SAN (50/50) blend at various voltages. (a) during voltage application; (b) after the discharge.

short time. These charges could be related to the charges such as from dipoles which have very fast mobility and short lifetime. At the present time, however, the exact origins for these charges are not known.

Spatial charge distributions of parent polymers, PC, SAN and PCL, are shown in Figure 6. The PC shows a negligible amount of charge both during the voltage application and after the discharge. The polarity of induced charge peaks shown in Figure 6(b) suggests that the negative charge remains in the PC after the discharge, the amount of which should be very small. The SAN shows a bimodal induced charge peak at the cathode during the voltage application, indicating that the first peak is the induced charge peak at the cathode and the second one is the injected charge peak. Upon discharging, however, the SAN has a negligible amount of residual charge. The PCL shows some negative charge during voltage application, whereas almost no charge is observed after the discharge. In all samples, the residual charge after the discharge is negligible. A major difference between par-

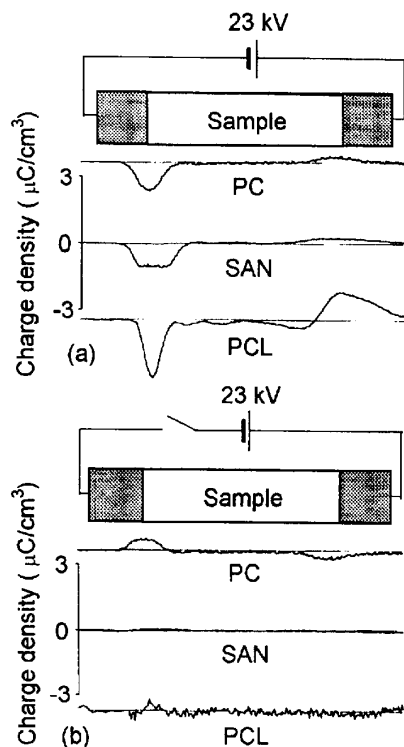


Figure 6.

Spatial charge distributions of parent polymers. (a) PC, (b) SAN, (c) PCL.

ent polymers and their blend is the existence of domain interfaces in the blend. It is speculated that the negative bulk charge in PC/SAN (50/50) blend (Figure 5(b)) developed because the injected electrons were trapped at domain interfaces.

In Figure 6, the charge distributions for both PC and SAN were obtained at 60 ns/div and the charge distributions for PCL were obtained at 120 ns/div. In this Figure, the intervals between the signals due to charges induced on the cathode and the anode are almost the same, although sample thicknesses are almost the same (1.0 mm). This is because the sound velocities of these samples are different, which will be discussed in the following Section.

Charge distributions at 23 kV of blends are shown in Figure 7. The amount of charge found in the bulk of specimen decreases as the content of PCL increases to 15%. At 15% PCL, almost no charge remains after the discharge. Negative charge increases again when the content of PCL is > 15% wt.

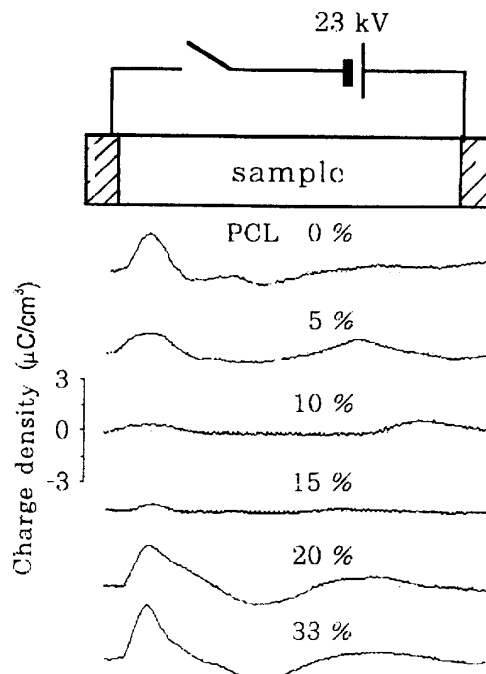


Figure 7.

Spatial charge distributions after the discharge of PC/SAN (50/50) blends containing various amount of PCL (% wt). PCL content from the top: 0, 5, 10, 15, 20, 33%.

3.3. SOUND VELOCITY OF PC/SAN/PCL BLENDS

Sound velocities of all samples were calculated from measured charge distributions, the results of which are summarized in Table 2 and plotted as a function of PCL content in Figure 8. The sound velocity of PC/SAN (50/50%) is 2700 m/s, which is quite low compared to that in PC (4200 m/s) and SAN. The sound velocity of PC/SAN/PCL blends decreases as the PCL content increases to 33% wt. The change of sound velocity of PC/SAN/PCL does not follow the additive rule. At PCL content > 33% wt, the sound velocity of PC/SAN/PCL blends is expected to increase to the value of PCL. The reason for the decrease of v with the PCL content is not clear at this moment. Further work is needed on the relationship between the sound velocity vs. compatibility and crystallization in these blends.

4. DISCUSSION AND SUMMARY

IT was observed in the study that the miscibility is improved by the addition of PCL. At higher PCL content, the crystallization of PC and PCL was observed, which led to a decrease of light transmittance. The amount of charge accumulated in the blends decreased when the

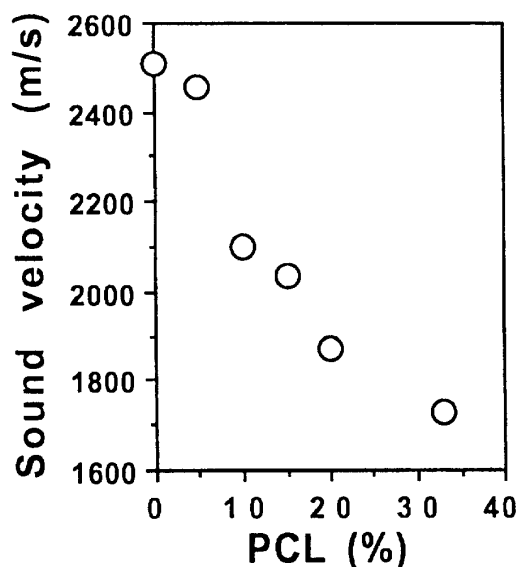


Figure 8.

Sound velocities of the blend as a function of PCL content.

Table 2.

Sound velocity v (m/s) of PC, SAN, PCL and their blends

Polymer	Comp. (%)	v
PC		4210
SAN		4570
PCL		2470
PC/SAN	50/50	
PCL	0	2510
	5	2454
	10	2100
	15	2037
	20	1870
	33	1730

PCL content increased to 15% wt, while it increases when the PCL content is > 15% wt.

Some level of molecular interaction, hydrogen bonding in this particular case, is expected in the PC/SAN blend. There may be the additional molecular interactions, *i.e.*, hydrogen bonding, at the PC/PCL interfaces and the PCL/SAN interfaces, resulting in an improved miscibility in PC/PCL/SAN blends.

Since both PC and SAN are amorphous polymers and contain polar groups which can act as hopping sites for the charge transport, the residual charge should be very small. This was confirmed by the observation of a negligible amount of residual charge in these polymers, as shown in Figure 6. The accumulation of negative charge was found in a control blend, PC/SAN (50/50%), although

the permittivity and conductivity are very similar. Since both PC and SAN show a negligible amount of residual charge, the residual negative charge in a control blend may be considered to originate from trapping of injected electrons at the domain interfaces, which suggests that all the charges developed in a PC phase and/or in a SAN phase are not dissipated after the discharge and some of them get trapped at the domain interfaces. There may be the structural defects such as voids at the domain interfaces between PC and SAN because they are not fully miscible, although this is not confirmed by experimental evidence. The charges may be trapped at these voids.

The addition of PCL to this blend reduces the accumulation of electrons. This decrease of trapped electrons may be explained by a combined effect of the changes in conductivity and the nature of domain interfaces by the addition of PCL.

The PCL may exist as a separate phase and as a layer between PC and SAN phases. The latter may be the case for the blends at relatively low PCL content. Since the conductivity of PCL is much higher, by 3 to 4 orders of magnitude than those of both PC and SAN, the PCL between PC and SAN may provide the passage for the charge transport such that the charge is dissipated along the PCL layer. It may be possible that the conductivities of both PC and SAN change by the addition of PCL. The molecular interaction at domain interfaces via the PCL layer may provide the bridges for the charge transport, resulting in a more efficient dissipation of charge crossing the domain interfaces. However, when the PCL content is relatively high, crystallization of PC and PCL occurs. In this situation, the trapping of charge at the interfaces between the amorphous and crystalline phases is quite possible, resulting in an increase of negative charge.

Considering all these facts, it can be concluded that the decrease of residual charge by the addition of PCL may be attributed to a combined effect of changes in conductivities and the molecular interactions by the addition of PCL into the PC/SAN (50/50) blend. At high PCL content, however, the crystallization of PC and PCL may enhance the trapping of charge at the interfaces between the amorphous and crystalline phases, resulting in an increase of negative charge.

This work has been confined to the blend of two amorphous polymers containing a semicrystalline compatibilizer. More work is needed to prove whether a similar concept can be extended to other blends.

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