

Influence of Silicone Phosphate on the Transesterification in PBT/PC Blends

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ABSTRACT: Because of the transesterification reaction between poly(butylene terephthalate) (PBT) and polycarbonate (PC), the crystallization behavior and thermal-resistant properties of the blend have been known to be decreased. Therefore it is of importance to control the transesterification degree in PBT/PC blends. In this article, the effect of silicone phosphate on the transesterification reaction between PBT and PC was studied using differential scanning calorimetry (DSC), nuclear magnetic resonance (NMR), and infrared spectroscopy (IR). It was found that the crystallization temperature of PBT/PC/silicone phosphate was 18.0°C higher than that of pure system, and the difference of the crystallization temperature between the first and secondary cooling

cycles in DSC was 15.8°C lower than that of the pure system. IR results showed that both random and block copolymer existed in the stabilized system, and both IR and NMR results proved the decrease of the copolymer content by the introduction of silicone phosphate. Compared with that of the pure system, the Vicat soft temperature of the stabilized system was increased by 17.2°C. All the results showed that silicone phosphate was an effective inhibitor for the controlling of the transesterification reaction in PBT/PC blends. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 87–95, 2009

Key words: transesterification reaction; silicone phosphate; polycarbonate; poly(butylene terephthalate)

INTRODUCTION

PBT/PC is a versatile thermoplastic alloy blend of poly(butylene terephthalate) and polycarbonate. This blend has good chemical resistance, great impact resistance even at low temperature, high heat resistance, and outstanding esthetics and flow characteristics.

It is known that in PBT/PC blends, chemical reactions^{1–3} may occur between the components in the melt. Devaux and coworkers^{4–7} in their series of papers have studied possible exchange reactions, structure of possible copolyesters, and kinetic studies of the possible reaction in PBT/PC blends. The following conclusions were reached in these studies^{4–7}: (1) the direct transesterification is the major exchange reaction between PBT and PC; (2) the rate of transesterification depends on the concentration of residual catalyst, e.g., titanium residues present in commercial PBT; (3) the reaction rate may be controlled by the use of organophosphites, and the extent of control is a function of phosphite type and its concentration. Sanket and Kale⁸ studied the rheological behavior of PBT/PC blends catalyzed by tetra-*n*-butyl *ortho*-titanate. It was found that as the transesterification reaction proceeded, the viscosity of the blend was

decreased. Wilkinson et al.^{9,10} prepared PC/PBT blends by adding alkyl titanium as transesterification catalyst. They observed that as the degree of transesterification increased, the blend changed its nature from block copolymer to random copolymer. Pompe and coworkers^{11–13} investigated the dependence of the transesterification behavior of the PBT/PC melt blend on the copolymer content. At the transition from initial homopolymers to finally random copolymers, the crystallization ability of the PBT vanished, and thus, the increase of the transesterification extent deteriorated the mechanical performance as well as solvent resistance, chemical resistance, and thermal stability.¹⁴ Hence, it is of importance to control the transesterification reaction degree in PBT/PC blends.

On the other hand, Pompe and Haubler¹¹ also reported that the formed copolymers influenced the compatibility of PBT and PC. If the formed copolymer was limited, the interphase adhesion between PBT-rich phase and PC-rich phase would be poor, leading to the brittleness of the blends. Therefore, a good balance between the interphase strength and the crystallization ability for PBT/PC blends is needed.

As concluded by Devaux and coworkers,^{4–7} the transesterification reaction can be suppressed by the addition of stabilizers. Triphenyl phosphate (TPP)^{15,16} and di-*n*-octadecyl phosphate¹⁷ have been widely used as efficient transesterification inhibitors. Devaux et al.¹⁷ analyzed the evolution of solubility in methylene chloride in the blend 50 PC/50 PBT without and

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TABLE I
Characteristics of Polymers Used in This Work

	T_g (°C)	T_c (°C)	T_m (°C)	ΔH (J/g)
PBT	41.0	180.6	228.6	45.6
PC	148.9	–	–	–

Note: T_g is the glass transition temperature; T_c and T_m are the crystallization and melting temperatures, respectively; and ΔH is the heat of fusion value.

with di-*n*-octadecyl phosphate as a stabilizer. The solubility has been observed to be constant up to times longer than 100 min in the stabilized blend. For the pure PC/PBT blend, for shorter reaction times, a sharp decrease of the solubility was observed, due to the formation of block copolymer between PC and PBT, whereas for longer times, a completely soluble product was obtained. This means for longer times, the blend changes its nature from block copolymer to random copolymer. For the stabilized blend, the solubility has been observed to be constant up to times longer than 100 min. The stabilizer shows good inhibition behavior for the formation of copolymer in PC/PBT blend. Xiong¹⁶ investigated the effect of TPP on the transesterification between PBT and PC, and it was reported that the reaction was strongly inhibited by 1% content of TPP. Yang and Zhang¹⁸ evaluated the effects of different transesterification inhibitors on the physical and thermal properties of PBT/PC blends. It was found that the addition of sodium biphosphate can raise the impact strength and thermostability of the blends. Bai et al.¹⁹ studied the effects of TPP and disodium diphosphate (DSDP) on the transesterification between PBT and PC. Both TPP and DSDP can increase the Vicat soft temperature of the blend, owing to the inhibited transesterification. In our previous article,²⁰ the effect of di-*n*-dodecyl phosphate on the transesterification between PBT and PC was studied. It was found that at the same content of di-*n*-dodecyl phosphate and TPP, the crystallization temperature of PBT/PC/di-*n*-dodecyl phosphate was higher than that of PBT/PC/TPP. Therefore, it was concluded that compared with TPP, di-*n*-dodecyl phosphate was more effective for the transesterification inhibition between PBT and PC.

However, although the aforementioned stabilizers have shown excellent transesterification inhibition behavior, the disadvantage of them is poor heat resistance. Because of their volatilization at higher processing temperature, the appearance and properties of PBT/PC final products will be poor. Therefore, it is needed to look for other inhibitors with better heat resistance. Silicone phosphate is one kind of phosphate and due to the inclusion of silicone in the molecular backbone, better heat resistance is expected.

In this article, the effect of silicone phosphate on the transesterification reaction between PBT and PC

was investigated using differential scanning calorimetry (DSC), nuclear magnetic resonance (NMR), and infrared spectroscopy (FTIR). The mechanical and thermal properties were also studied.

EXPERIMENTAL

Materials

Polymers used in this study are listed in Table I. PBT was obtained from Baling Petrochemical Company, Hunan, China. Its intrinsic viscosity in the mixed solvent of phenol/1,1,2,2-tetrachloroethane with a weight ratio of 60/40 was 1.160 dL/g. The PC used was Lexan 161 (General Electric Plastics, The Netherlands). Its weight-average molecular weight was 35,000. Prior to any experiment, PBT and PC were dried at 120°C under vacuum for at least 24 h. Silicone phosphate mainly composed of monoester was synthesized in our lab. Its molecular weight was 2000. Methylene chloride (CH₂Cl₂), 1,1,2,2-tetrachloroethane (C₂H₂Cl₄), phenol (C₆H₅OH), and methanol were all of chemical grade, purchased from Tianjin Chemical Reagent Factory, Tianjin, China.

Sample preparation

The PBT/PC blends with a weight ratio of 1 : 1 were prepared using a twin-screw extruder (L/D ratio 41) at a screw speed of 300 rpm, and silicone phosphate was added into the blend at the content of 2%. The extruded blends were dried in an air oven for 4 h at 100°C. The specimens for mechanical and thermal properties test were injection-molded in a plastic injection machine (HTB110X/1, China). The sequence of temperature was 125, 245, 245, 255, and 275°C in the five heating zones, and the mold temperature was at 50°C. The PBT/silicone phosphate blend at the silicone phosphate content of 2% was prepared at the same conditions.

The molded specimens were extracted in CH₂Cl₂ for 48 h at 55°C to make sure that no PC fraction was reserved in the nonsolute part. CH₂Cl₂ was used because it is a good solvent for PC. The insoluble fraction was further extracted in the mixed solvent of C₂H₂Cl₄ and C₆H₅OH in a 40/60 ratio by weight, which is a good solvent for PBT, at room temperature for 48 h. The solute in C₂H₂Cl₄/C₆H₅OH and in CH₂Cl₂ was precipitated using methanol, and the precipitate was dried for 24 h before further analysis.

Characterization

DSC analysis

The glass transition temperature (T_g), the melting point (T_m), and the crystallization temperature (T_c) of the injected standard samples were tested using

differential scanning calorimetry (DSC) (Perkin-Elmer DSC-7). A thin slices of materials (≈ 0.5 -mm thick) were encapsulated in a DSC pan. For the measurement of T_c and T_m , these pans were cycled in a DSC at $10^\circ\text{C}/\text{min}$ between 30 and 290°C , with a 1-min hold period at the minimum temperature and 3-min hold period at the maximum temperature. For the measurement of T_g , the pans were cycled at $20^\circ\text{C}/\text{min}$ between 30 and 200°C . T_g was obtained using the specific heat by the half-step method, similar to the method used by Pompe.¹¹ T_m was determined as the peak maximum of the melting peak. The heat of fusion (ΔH) values were calculated from the area under the endothermic peak. The temperature corresponding to the peak of the crystallization exotherm was taken as the crystallization temperature. The T_m and T_c during the first heating and cooling cycle were denoted as T_{M1} and T_{C1} , respectively. The T_m and T_c during the secondary heating and cooling cycle were denoted as T_{M2} and T_{C2} , respectively. The heat of fusion during the first heating stage was denoted as ΔH_1 , whereas that during the secondary heating stage was denoted as ΔH_2 . The sample weight was 5–7 mg.

IR analysis

The infrared spectra of silicone phosphate, pure PC, pure PBT, solute in CH_2Cl_2 , and solute in $\text{C}_2\text{H}_2\text{Cl}_4/\text{C}_6\text{H}_5\text{OH}$ were obtained using a Nicolet 510P Fourier transform infrared spectroscopy (FTIR). The scanning wavenumber was from 500 to 4000 cm^{-1} , and the spectral resolution was 20 cm^{-1} . For each sample, 150 scans were taken to produce a spectrum, from which the background spectrum was subtracted. The precipitate from the solution of CH_2Cl_2 and $\text{C}_2\text{H}_2\text{Cl}_4/\text{C}_6\text{H}_5\text{OH}$ was first compressed into a film with a diameter of 10 mm and then was used for FTIR analysis without further treatment.

Proton NMR analysis

The NMR spectra of the solute in CH_2Cl_2 were obtained by using a Bruker WP-100SY instrument working under usual conditions with tetramethylsilane as the internal standard. The solvent used was deuterated chloroform.

Testing

Tensile properties were measured according to ISO 527 with a test speed of $50\text{ mm}/\text{min}$. The flexural strength and flexural modulus were tested according to ISO 178. Impact resistance was evaluated according to ISO 180, Izod method. The Vicat soft temperature was measured based on ISO 306 at the heating rate of $50^\circ\text{C}/\text{h}$.

RESULTS AND DISCUSSION

FTIR characterization of silicone phosphate

Figure 1 gives the IR spectroscopy curve of silicone phosphate synthesized in our lab. The wide peak around 3500 cm^{-1} is assigned to the stretching vibration of $-\text{OH}$ group. The peak at 1261 cm^{-1} corresponds to the stretching vibration of $\text{P}=\text{O}$ group. The wide peak at 1000 – 1190 cm^{-1} is due to the contribution of the stretching vibration of $\text{P}-\text{O}$ in $\text{P}-\text{O}-\text{Si}$ group and $\text{Si}-\text{O}$ in $\text{Si}-\text{O}-\text{Si}$ group. The small peak around 2331 cm^{-1} attributes to the stretching vibration of $\text{O}-\text{H}$ in $\text{P}-\text{O}-\text{H}$ group. The IR results in Figure 1 prove the existence of $\text{P}-\text{O}$, $-\text{OH}$, and $\text{Si}-\text{O}-\text{Si}$ group in silicone phosphate. The $\text{Si}-\text{O}-\text{Si}$ group improves the heat resistance of silicone phosphate, and the $-\text{OH}$ group and $\text{P}-\text{O}$ group will play the role of inhibiting the transesterification by complexing the titanium catalyst residue in PBT. This point has been proved by Devaux and coworkers.^{4–7}

Effect of silicone phosphate on the crystallization and melting behavior of PBT/PC blend

Figure 2 shows the DSC curves of pure PBT/PC blend at the heating and cooling rate of $10^\circ\text{C}/\text{min}$. The crystallization temperature during the first cooling stage (T_{C1} in Fig. 2) is 174.8°C , i.e., 5.8°C lower than that of pure PBT. The value of the heat of fusion during the first heating stage (ΔH_1 in Fig. 2) is $24.4\text{ J}/\text{g}$, far lower than that of pure PBT, the value of which is $45.6\text{ J}/\text{g}$. On one hand, the introduction of PC in the PBT/PC blend leads to the fall of crystallization temperature because of its plasticizing effect. On the other hand, the occurrence of transesterification reaction results in the decrease of the crystallization capacity of PBT.^{10,21} In DSC, this is seen as a decrease of the melting peak, i.e., heat of fusion as well as a decrease in the melting peak

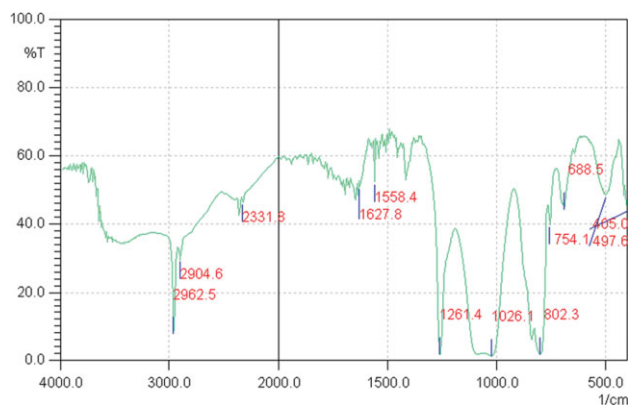


Figure 1 FTIR curve of silicone phosphate synthesized in our lab. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

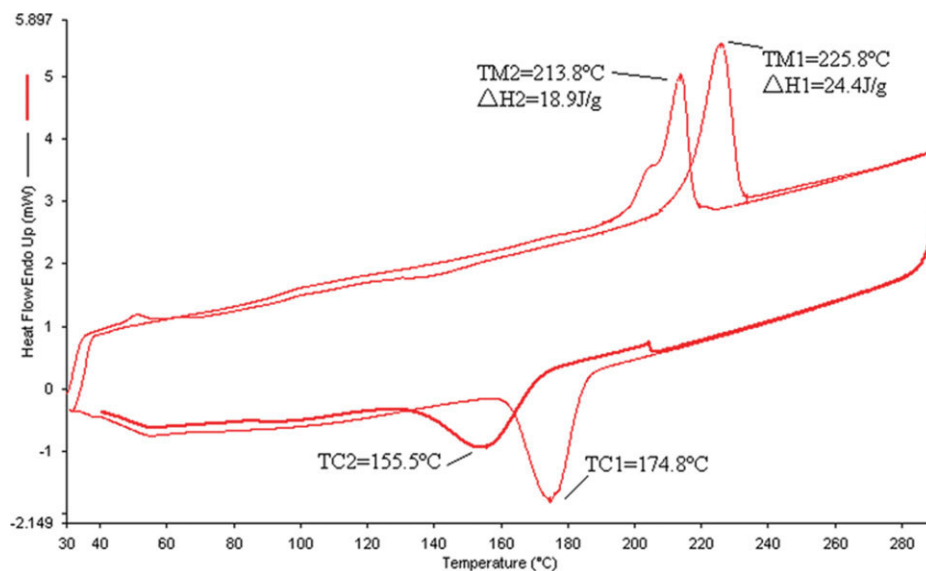


Figure 2 DSC curves of pure PBT/PC blend at a heating and cooling rate of $10^{\circ}\text{C}/\text{min}$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

temperature.²² In Figure 2, the values of the melting temperature (T_{M2} in Fig. 2) and the crystallization temperature (T_{C2} in Fig. 2) during the secondary heating and cooling cycle are lower than those during the first heating and cooling cycle (T_{M1} and T_{C1} in Fig. 2). The value of the heat of fusion during the secondary heating stage (ΔH_2 in Fig. 2) is lower than that of ΔH_1 . The peak height corresponding to the crystallization peak during the secondary cooling stage becomes shorter when compared with that during the first cooling stage. All these results imply the occurrence of transesterification reaction between PBT and PC during the heating and cooling cycles in DSC.

Figure 3 gives the DSC curves of PBT/PC blend at the silicone phosphate content of 2.0%. In contrast to those in Figure 2, apparently, the difference of the crystallization peak heights during the first and secondary cooling stage is small and the crystallization peak distance becomes short. In Figures 2 and 3, the DSC curves during the secondary heating stage show a double melting endotherm with a main peak and a smaller peak. The smaller peak is due to the melting of thin lamellae formed during the cooling stage within the first time of heating and cooling scan, as found by Hsiao et al.²³ The DSC data of PBT/PC and PBT/PC/silicone phosphate blends are tabulated in Table II. The value of the difference of

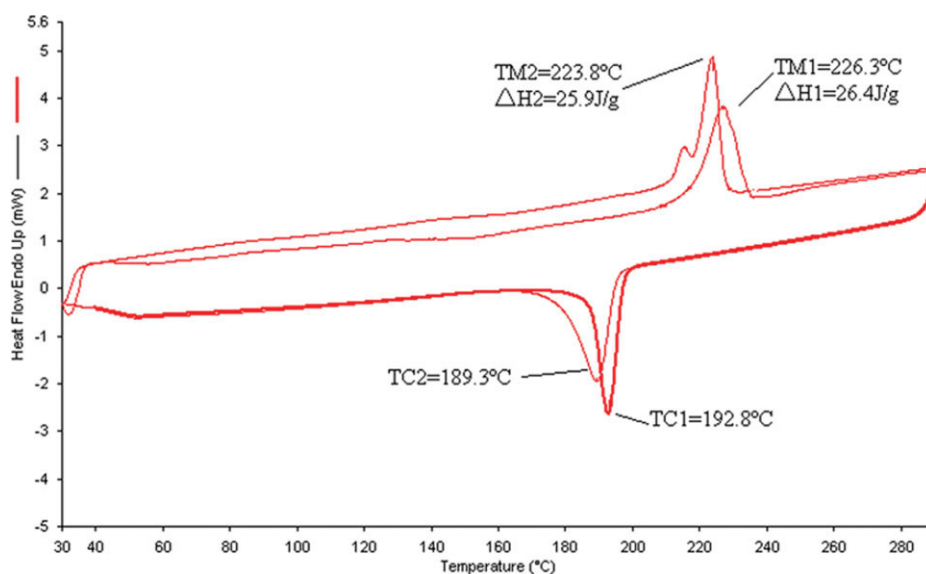


Figure 3 DSC curves of PBT/PC/silicone phosphate blend at the silicone phosphate content of 2.0% at a heating and cooling rate of $10^{\circ}\text{C}/\text{min}$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Thermal Properties of PBT/PC and PBT/PC/Silicone Phosphate Blends

Sample	T_{C1} (°C)	T_{C2} (°C)	ΔT_c (°C)	T_{M1} (°C)	T_{M2} (°C)	ΔT_m (°C)	ΔH_1 (J/g)	ΔH_2 (J/g)
Pure PBT/PC	174.8	155.5	19.3	225.8	213.8	12.0	24.4	18.9
PBT/PC/silicone phosphate	192.8	189.3	3.5	226.3	223.8	2.1	26.4	25.9
PBT/silicone phosphate	194.6			226.5				

the melting point temperature (ΔT_m) and the crystallization temperature (ΔT_c) of PBT/PC/silicone phosphate are lower than those of pure PBT/PC blend. The value of ΔH_1 and ΔH_2 of PBT/PC/silicone phosphate are higher than those of pure PBT/PC blend. The introduction of silicone phosphate improves the crystallization ability of PBT in the PBT/PC blend. This means that the transesterification reaction between PBT and PC is well controlled.

In Table II, the crystallization temperature of PBT/silicone phosphate at the content of 2.0% is listed, the value of which is 194.6°C. This means that silicone phosphate can promote the crystallization of PBT. The T_{C1} in PBT/PC/silicone phosphate is 192.8°C and lower than that of PBT/silicone phosphate. The difference between the two systems is the inclusion of PC and the existence of the transesterification reaction in the PBT/PC/silicone phosphate blend. The existence of the difference between the crystallization temperature of PBT/PC/silicone phosphate and PBT/silicone phosphate indicates that, due to its plasticizing effect, the effect of PC should not be neglected and also means that the extent of transesterification reaction between PBT and PC cannot be thoroughly inhibited.

Characterization of the solute and nonsolute in CH_2Cl_2 using DSC, NMR, and FTIR

To further investigate the inhibition behavior of silicone phosphate on the transesterification, the PBT/PC blends with and without stabilizer were extracted in CH_2Cl_2 . Wilkinson et al.^{9,10} observed that as the degree of transesterification increased, the blend changed its nature from block copolymer to random copolymer. The random copolymer and pure PC can dissolve in CH_2Cl_2 , and the nonsolute parts include pure PBT and block copolymer.¹⁸ Because of the different chemical environment of C=O in PBT and PC, the special band of C=O in PBT is at 1716 cm^{-1} , whereas that in PC is at 1770 cm^{-1} .⁷ Therefore, the kind of the copolymer in the PBT/PC blend can be ascertained by observing the situation of C=O in the IR curves. Figure 4 gives the FTIR results of the solute in CH_2Cl_2 . The spectra of pure PC are also provided for a direct comparison. From Figure 4, it can be seen that for PBT/PC blends with and without the stabilizer, the FTIR curves of the solute exhibit strong peak at

1770 cm^{-1} . For pure PBT/PC blend, there exists a small peak at 1718 cm^{-1} , which is near the C=O band of pure PBT. Devaux et al.⁴⁻⁶ attributed 1720 cm^{-1} to the aliphatic ester group in the transesterification product, 1740 cm^{-1} to the aromatic ester, and 1770 cm^{-1} to the mixed aliphatic-aromatic carbonates. Since the peak at 1770 cm^{-1} is mainly contributed by pure PC and the peak at 1740 cm^{-1} cannot be observed, the structure of the transesterification reaction product cannot be ascertained. However, the existence of the peak at 1718 cm^{-1} proves that some PBT is incorporated into the PC molecule and some quantity of random copolyester exists in the nonstabilized PBT/PC blends. For PBT/PC/silicone phosphate blend, a small peak at 1724 cm^{-1} is observed, and the maximum absorbance intensity at this peak is smaller than that at 1718 cm^{-1} for pure

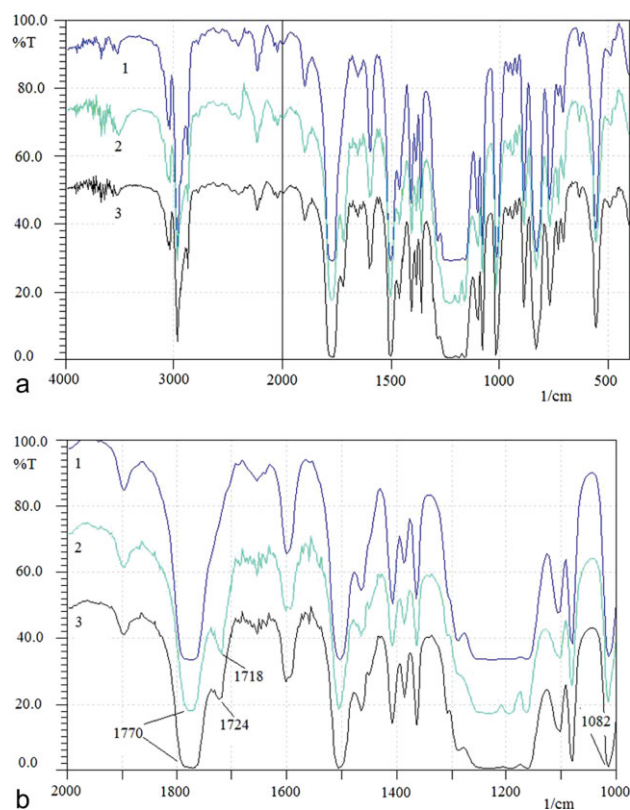


Figure 4 FTIR curves of the solute in CH_2Cl_2 of PBT/PC and PBT/PC/silicone phosphate blends: (1) Pure PC; (2) Pure PBT/PC blend; (3) PBT/PC/silicone phosphate blend. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

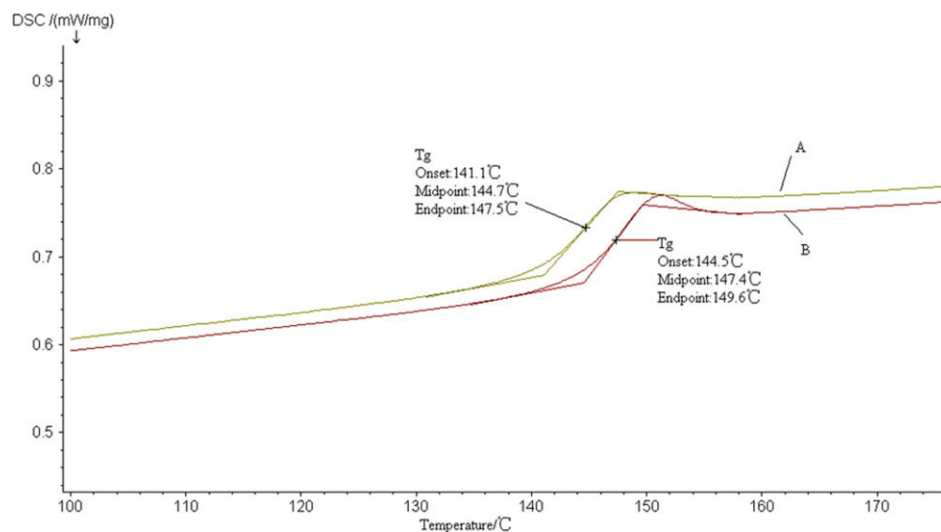


Figure 5 DSC curves of the solute in CH_2Cl_2 of PBT/PC and PBT/PC/silicone phosphate blends: (A) Pure PBT/PC blend; (B) PBT/PC/silicone phosphate blend. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

PBT/PC blend. This means for the stabilized system, the random copolymer still exists and the content of random copolymer is decreased. To prove this point, the T_g of the solute in CH_2Cl_2 of PBT/PC and PBT/PC/silicone phosphate blends were measured. The results are shown in Figure 5. The T_g of pure PBT/PC blend is 144.7°C (midpoint in Fig. 5), lower than that of pure PC, indicating the existence of random copolymer in the solute. Compared with that of pure PBT/PC blend, the T_g of PBT/PC/silicone phosphate blend moves to higher temperature, but is still lower than that of pure PC. The content of random copolymer is decreased in PBT/PC/silicone phosphate blend. The DSC results prove the existence of random copolymer in PBT/PC blends with and without the stabilizer, in agreement with the IR results in Figure 4.

Figure 6 gives the NMR results of the solute in CH_2Cl_2 for pure PBT/PC blend and PBT/PC/silicone phosphate blend. As already described by Devaux et al.,⁴ the region between 8 and 8.4 ppm in NMR curves is of special importance to analyze the structural changes during the transesterification reaction. For the terephthalic unit represented by



there occurs a chemical shift of the proton peaks, depending on the nature of R_1 and R_2 . When R_1 and R_2 are aromatic and aliphatic, respectively, there will be two peaks around 8.16 and 8.20 ppm in the

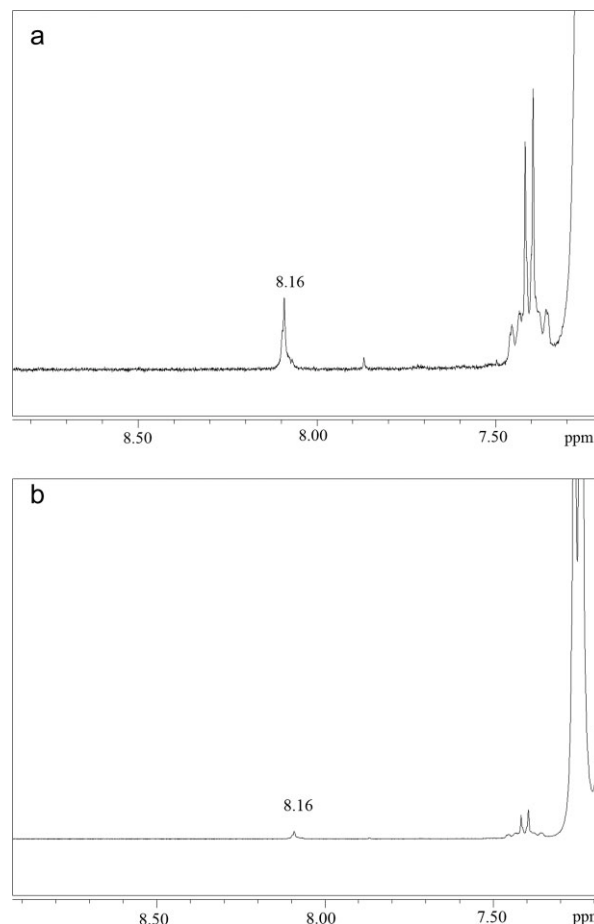


Figure 6 NMR curves of the solute in CH_2Cl_2 of PBT/PC and PBT/PC/silicone phosphate blends: (a) Pure PBT/PC blend and (b) PBT/PC/silicone phosphate.

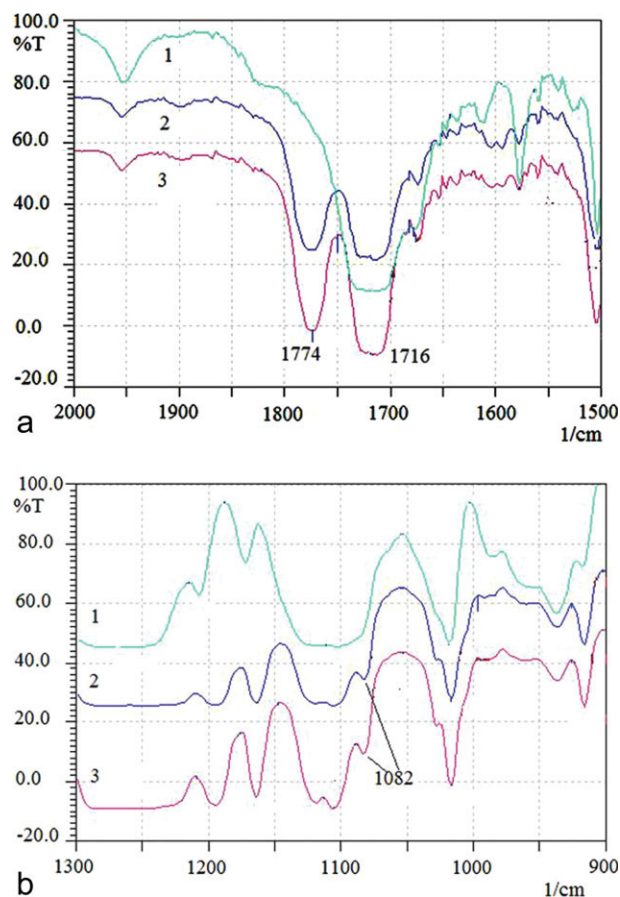
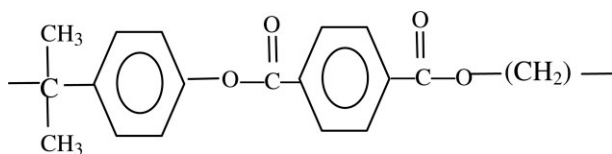


Figure 7 FTIR curves of the solute in $C_2H_2Cl_4/C_6H_5OH$ of PBT/PC and PBT/PC/silicone phosphate blends. (1) Pure PBT; (2) The solute in $C_2H_2Cl_4/C_6H_5OH$ of PBT/PC; (3) The solute in $C_2H_2Cl_4/C_6H_5OH$ of PBT/PC/ silicone phosphate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

spectra. When R_1 and R_2 are both aromatic, the peak around 8.28 will be observed, whereas when R_1 and R_2 are both aliphatic, the peak around 8.06 will be observed. By the NMR curves obtained from the solute in CH_2Cl_2 , the peak at 8.06 ppm, which is the special peak for pure PBT, cannot be observed, because pure PBT cannot be dissolved in CH_2Cl_2 . From Figure 6, apparently a peak at 8.16 ppm appears for the solute of pure PBT/PC blend, disclosing the existence of terephthalic ester units substituted by one aromatic group and proving the existence of the transesterification results as follows:



Some PBT is incorporated into the PC molecule, in agreement with the former IR results. For PBT/PC/

silicone phosphate, small peak can be observed around 8.16 ppm, indicating the controlled transesterification reaction by silicone phosphate.

The nonsolute fraction in CH_2Cl_2 was further extracted by $C_2H_2Cl_4/C_6H_5OH$, which is the best solvent for PBT and block copolymer. Figure 7 gives the FTIR curves of the solute in $C_2H_2Cl_4/C_6H_5OH$. It can be seen that the solute exhibits bands at 1716 cm^{-1} , which is the special band of C=O in PBT, and 1774 cm^{-1} , which is near the special band of C=O in PC.⁷ In Figure 7(b), the weak peak at 1082 cm^{-1} is observed for PBT/PC and PBT/PC/silicone phosphate blends, whereas no peak is found in pure PBT. The solute does not include pure PC, which has been extracted by CH_2Cl_2 . Therefore the bands at 1774 and 1082 cm^{-1} are due to the contribution of block copolymer between PBT and PC. The results indicate the existence of block copolymer in the pure PBT/PC and PBT/PC/silicone phosphate blends. The ratio value of the maximum absorbance intensity at 1774 cm^{-1} to that at 1716 cm^{-1} for pure PBT/PC is 2.18, whereas that for stabilized PBT/PC blend is 1.45. The reduction of the ratio value means the decrease of the content of block copolymer.

Table III lists the extracted solute weight fraction in CH_2Cl_2 of PBT/PC and PBT/PC/ silicone phosphate. In our experiments, the blend ratio of PBT to PC is 50 to 50 and if the transesterification does not exist, the theoretical solute fraction should be 50%. In Table III, for pure PBT/PC blend, the solute fraction is 37.5%, less than the theoretical expected value. Some PC is incorporated into the PBT-PC copolymer. This means the occurrence of transesterification in PBT/PC. The fraction of PBT/PC/ silicone phosphate blend is 42.2%, higher than that of pure system and still lower than the theoretical expected value. From the former IR results, it has been known that for PBT/PC blends with and without stabilizer, both random and block copolymer exist. Therefore, the increase of the solute fraction of PBT/PC/ silicone phosphate indicates the decrease of the content of the formed copolymer and the reduction of the content of PBT and PC involved in the transesterification reaction.

TABLE III
Extracted Solute Fraction in CH_2Cl_2 of PBT/PC and PBT/PC/Silicone Phosphate at the Silicone Phosphate Content of 2%

Sample	Solute fraction in CH_2Cl_2 (%)	Nonsolute fraction in CH_2Cl_2 (%)
Pure PBT/PC	37.5	62.5
PBT/PC/silicone phosphate	42.2	57.8

TABLE IV
Effect of Silicone Phosphate on the Mechanical and Thermal Properties
of PBT/PC Blends

Sample	Tensile strength (MPa)	Flexural modulus (MPa)	Flexural strength (MPa)	Izod impact strength (kJ/m ²)	Vicat soft temperature (°C)
Pure PBT/PC	62	2800	80	7.5	111.3
PBT/PC/silicone phosphate	60	2850	82	8.2	128.5

It has been suggested that transesterification is catalyzed by residual-trace metal polymerization catalysts, e.g., Ti, and that phosphites complex them and thus quench the catalytic effect.⁴⁻⁷ Fortunato et al.^{24,25} reported that one or more acidic OH groups in the molecule of the phosphorus additive permit the formation of adducts with Ti atoms, which can be considered inactive as catalyst, thus, inhibiting the transesterification. The IR results of silicone phosphate in Figure 1 prove the existence of P=O and =OH group in the silicone phosphate molecule. Hence, based on the analysis reported by Fortunato et al.,^{24,25} the acidic OH group will play the role of complexing Ti atoms, and therefore silicone phosphate will show the function of controlling the transesterification reaction between PBT and PC, which has been ascertained by the former DSC, NMR, and FTIR results. Besides the direct transesterification reaction between PBT and PC, the chemical reaction induced by alcoholysis is also possible between PBT and PC.² From Figure 4, it can be seen that the peak area at 3500 cm⁻¹ corresponding to —OH group in PBT/PC/silicone phosphate is smaller than that in PBT/PC blend. The content of —OH end group is decreased by silicone phosphate. From this point of view, silicone phosphate can also inhibit the transesterification induced by alcoholysis.

Effect of silicone phosphate on the mechanical and thermal properties of PBT/PC blends

Table IV gives the mechanical and thermal properties of PBT/PC blends with and without the stabilizer. The introduction of silicone phosphate does not induce significant change to tensile strength and flexural strength, but significantly improves the Vicat soft temperature. In PBT/PC blend, on one hand, due to the transesterification reaction between PBT and PC, the crystallization ability of PBT is damaged. On the other hand, also due to the transesterification reaction, the T_g of the PC phase is decreased as shown in Figure 5. The two factors result in poor heat resistance. In Table IV, the Vicat soft temperature of the stabilized system is 17.2°C higher than that of the pure system, implying that the transesterification reaction is inhibited by silicone

phosphate, in agreement with the results in Table II and Figure 5, where the stabilized system shows higher crystallization temperature and higher T_g .

CONCLUSION

Silicone phosphate is one kind of phosphate and shows better inhibition behavior for the transesterification reaction between PBT and PC. DSC results show that silicone phosphate can increase the crystallization temperature and decrease the difference of the crystallization temperature during the two times scanning in DSC. FTIR results show that both random and block copolymer exist in the PBT/PC blends with and without silicone phosphate. NMR results show that the introduction of silicone phosphate decreases the content of transesterification reaction products. The extraction results show the decrease of the copolymer content in the stabilized blend. All the results prove that silicone phosphate can effectively inhibit the transesterification reaction between PBT and PC, resulting in higher thermal resistance for PBT/PC blend.

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