

PHASE STRUCTURE AND COMPATIBILITY OF LADDERLIKE POLYPHENYLSILSESQUIOXANE (PPSQ) / POLYCARBONATE (PC) BLENDS PREPARED BY SOLUTION CASTING*

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Abstract Blends of PC and PPSQ (A) with high M_w and good ladderlike regularity or PPSQ(B) with low M_w and more defective Si-atoms in its structure have been prepared by solution casting. The dispersed spheres (PPSQ(A)-rich) are unevenly dispersed in the continuous PC-rich phase and there is no phase-inversion as PPSQ(A) content increases when the percentage of PPSQ(A) is not more than 70%. PPSQ(B)-rich spheres are evenly dispersed in the continuous phase (PC-rich) and phase-inversion occurs when PPSQ(B) percentage is up to 70%. T_g of PPSQ(A)/PC or PPSQ(B)/PC at some compositions are lower than that of pure PC due to the enlarged free-volume of PC-rich phase because some spheres of rigid PPSQ chains are included in the PC-rich phase. PC and PPSQ(A) or PPSQ(B) are partially compatible. The compatibility of PC and PPSQ(B) is better than that of PC and PPSQ(A) with high M_w and good ladderlike regularity. Heat history has some influence on the T_g s and compatibility of PPSQ(A)/PC and PPSQ(B)/PC blends.

Key words Ladderlike PPSQ/PC, Compatibility, Phase structure, Glass transition temperature

INTRODUCTION

Polyphenylsilsesquioxane (PPSQ), a ladderlike polymer, is composed of two Si—O main chains bridged by oxygen. Its good thermal stability is similar to that of some crosslinked polymers because of its special ladderlike structure and phenyl side groups. But PPSQ is very easily dissolved in some common solvents, i.e., acetone, trichloromethane, tetrahydrofuran and benzene. PPSQ with appropriate molecular weight and ladderlike regularity has been synthesized by choice of polymerization conditions^[1, 2]. Some studies on PPSQ blend with the other linear polymers have been done, such as transesterification in PPSQ/PET blends^[3], miscibility and mechanical properties of PPSQ/PS *in situ* blends^[4-6]. Until now, PPSQ/PC blends have not been studied. In this paper, PPSQ (PPSQ(A) and PPSQ(B)) with different molecular weight and PC blends at certain weight ratios were prepared by solution casting. The phase structure of PPSQ(A)/PC and PPSQ(B)/PC blends was studied by TEM. The compatibility and the effect of heat history on the compatibility of the blends were also investigated.

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EXPERIMENTAL

Preparation of Specimens

We synthesized the samples of PPSQ with different molecular weights and ladderlike regularity ourselves. The weight average molecular weight (M_w) of PPSQ(A) and PPSQ(B) are 2.51×10^4 and 1.24×10^4 , respectively. The percentages of defective Si-atoms in the PPSQ(A) and PPSQ(B) ladderlike structures are 0% and 23.6%. PPSQ(A) has high M_w and good ladderlike regularity while PPSQ(B) has low M_w with some unreacted OH groups attached to defective Si-atoms. PC (T-1230) was obtained from the Shanghai Zhong Lian Chemical Factory. PPSQ(A)/PC and PPSQ(B)/PC with different compositions (100/0, 70/30, 50/50, 30/70 and 0/100) were dissolved in trichloromethane with 5% (w/w) concentration. All solutions are transparent. Specimens used for TEM measurement were prepared by dropping some solution on the copper net and then vaporizing off all the solvent. Glass fiber braid was dipped into PPSQ(A)/PC or PPSQ(B)/PC blend solution several times. Then the braids coated by these blends for torsional braid analysis (TBA) were placed in the oven for some time in order to remove all the solvent.

Measurements

The phase structures of the PPSQ(A)/PC and PPSQ(B)/PC (30/70, 50/50 and 70/30) blends were observed using a JEM-100-C-XII transmission electron microscope (TEM).

The mechanical loss over temperature changes of the PPSQ(A)/PC or PPSQ(B)/PC blends were measured by using of GDP-3 TBA apparatus. These experiments were carried out at temperatures ranging from room temperature to 470 K at a rate of 2 K/min. The heater was automatically started and the data were recorded on a computer.

RESULTS AND DISCUSSION

Phase Structure of PPSQ/PC Blends

TEM micrographs of PC and PPSQ(A) with high M_w and good ladderlike regularity at different blend weight ratios are shown in Fig.1. When PPSQ(A) content is 30%, the black spheres (PPSQ(A)-rich) are dispersed in the white continuous phase (PC-rich). The sizes of the spheres are uneven, with maximum diameter of about $2\mu\text{m}$ (Fig.1(a) and (b)). When the percentage of PPSQ(A) is up to 50%, the maximum diameter of the dispersed particles increases to $5\mu\text{m}$ and there is more of the black phase in the form of dispersed big particles (Fig.1(c) and (d)). When the content of PPSQ(A) in the blend increases to 70%, the PPSQ(A)-rich phase is still distributed within the PC-rich continuous phase and some

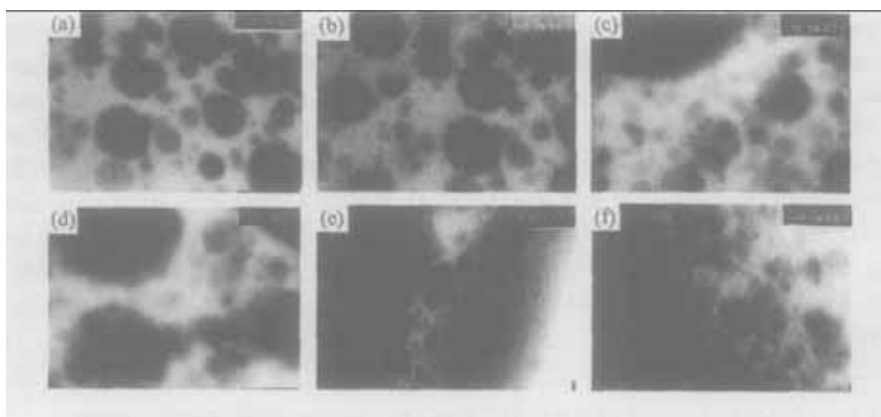


Fig.1 TEM micrographs of PPSQ(A)/PC blends (at 1000X magnification)
1. 30/70 ((a) and (b)), 2. 50/50 ((c) and (d)) and 3. 70/30 ((e) and (f))

particles are connected and their interface disappears (Fig.1(e) and (f)). No phase-inversion occurs in the PPSQ(A)/PC blends with an increase in the percentage of PPSQ(A), when the percentage of PPSQ(A) is not more than to 70%. TEM micrographs of PC and PPSQ(B) with low M_w and some defective Si-atoms blends are given in Fig.2. Black spheres (PPSQ(B)-rich) are evenly dispersed in the white continuous (PC-rich) phase (Fig.2(a) and (b)) and the maximum diameter of the spheres is $1.2\ \mu\text{m}$ when PPSQ(B) content is 30%. When the percentage of PPSQ(B) reaches 50%, the maximum diameter of the dispersed spheres increases to $3\ \mu\text{m}$ (Fig.2(c) and (d)). These values are much less than those of PPSQ(A)/PC blends in some compositions. When the amount of PPSQ(B) increases to 70%, phase-inversion occurs and the dispersed black spheres (PPSQ(B)-rich) becomes the continuous phase while the continuous (PC-rich) phase now appears as dispersed particles with the maximum diameter of $1.8\ \mu\text{m}$ (Fig.2(e) and (f)).

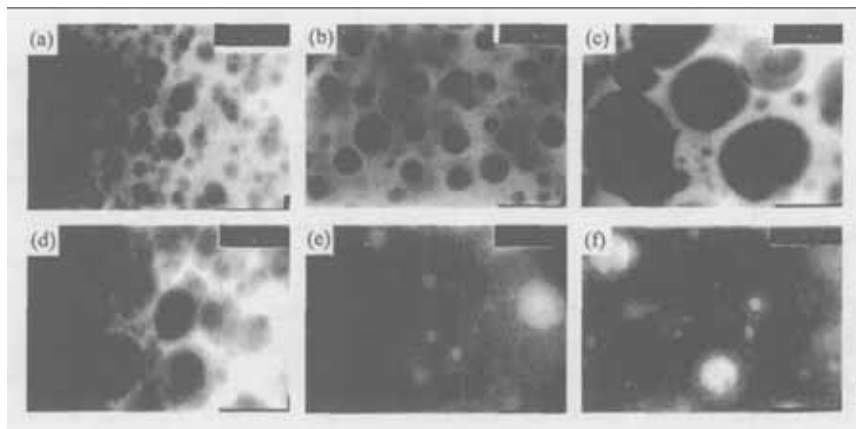


Fig.2 TEM micrographs of PPSQ(B)/PC blends (at 1000X magnification)
(1) 30/70 ((a) and (b), (2) 50/50 ((c) and (d)) and (3) 70/30 ((e) and (f))

Compatibility of PPSQ/PC Blends

Mechanical loss versus temperature curves of PPSQ(A)/PC blends are shown in Fig.3. The temperature at each peak can be defined as the glass transition temperature (T_g). No distinct loss peak of PPSQ(A) is observed over the whole experimental temperature range due to its double chain and big side groups and therefore, no glass transition is observed. T_g of PC is 420K. There is only one loss peak in each TBA graph of the PPSQ(A)/PC blends. Their T_g s are 415K (PPSQ(A)/PC 30/70), 412K (PPSQ(A)/PC 50/50) and 423K (PPSQ(A)/PC 70/30), respectively. The T_g s of PPSQ(A)/PC (30/70 and 50/50) are lower than that of pure PC because of the enlarged free-volume of the PC-rich phase, in which some spheres composed of rigid PPSQ(A) molecules are included. The mechanical loss versus temperature curves of PPSQ(B)/PC are given in Fig.4. The phenomenon of no loss peak observed in the TBA curves of PPSQ(B) is the same as that of PPSQ(A). The T_g s of the PPSQ(B)/PC (30/70, 50/50 and 70/30) blends are 418K, 407K and 411K, respectively. All T_g s values of the PPSQ(B)/PC blends are less than that of PC due to the enlarged free-volume of the PC-rich phase as the PC-rich phase contains some rigid PPSQ(B) molecules or some phase composed by PPSQ(B).

From the above analysis, PPSQ and PC are partially compatible. The compatibility of PPSQ(B) with low M_w and poor ladderlike regularity and PC is better than that of PPSQ(A) and PC because PPSQ(B) has lower M_w and there are some -OH attached to defective Si-atoms in PPSQ(B).

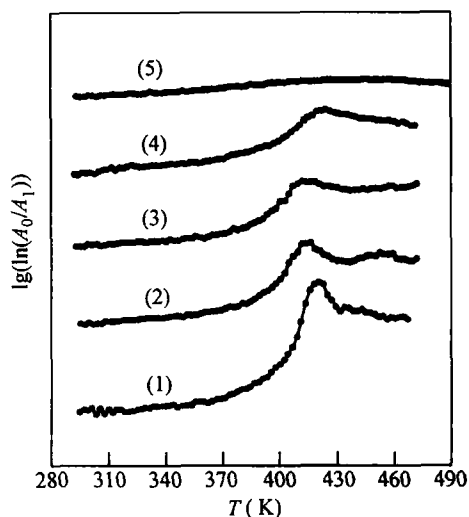


Fig.3 Loss versus temperature of PPSQ(A)/PC blends with different compositions (1) 0/100, (2) 30/70, (3) 50/50, (4) 70/30 and (5) 100/0

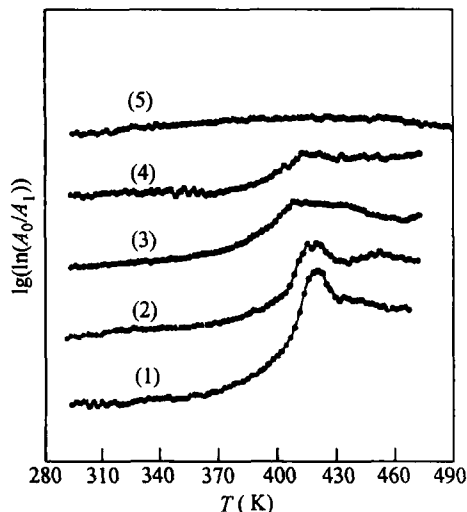


Fig.4 Loss versus temperature of PPSQ(B)/PC blends with different compositions (1) 0/100, (2) 30/70, (3) 50/50, (4) 70/30 and (5) 100/0

Effect of Heat History on Compatibility of PPSQ/PC Blends

The mechanical loss versus temperature curves of PPSQ(A)/PC (30/70, 50/50 and 70/30) at the first heating and at the second heating are shown in Fig.5. The T_g s of PPSQ(A)/PC (30/70, 50/50 and 70/30) blends at the first heating are 415 K, 412 K and 423 K, respectively. The mechanical loss peaks of the PPSQ(A)/PC blends become narrow at the second heating and their T_g s are 418 K, 419 K and 420 K, which are similar to that of pure PC. This result indicates that phase-separation occurs in PPSQ(A)/PC blends after the first heating. TBA curves of PPSQ(B)/PC blends at the first heating and at the second heating are

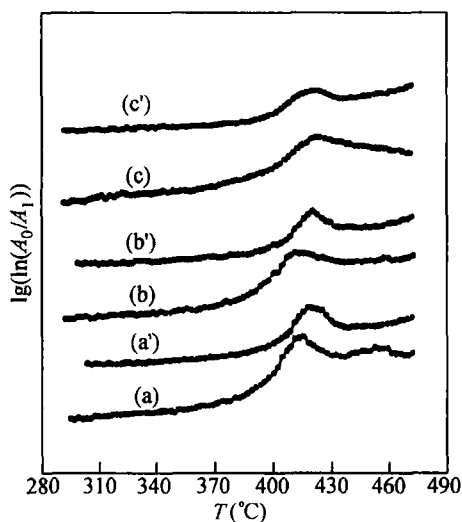


Fig. 5 Loss versus temperature of PPSQ(A)/PC (30/70, 50/50 and 70/30) blends at the first heating (a, b and c) and at the second heating (a', b', and c')

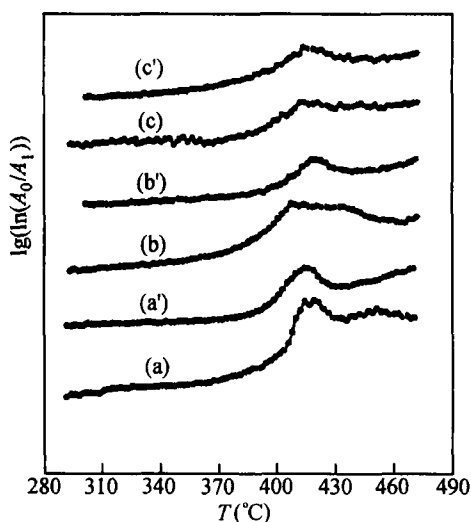


Fig. 6 Loss versus temperature of PPSQ(B)/PC (30/70, 50/50 and 70/30) blends at the first heating (a, b and c) and at the second heating (a', b', and c')

shown in Fig.6. T_g s of PPSQ(B)/PC (30/70, 50/50 and 70/30) blends are 418 K, 407 K and 411 K at the first heating and change into 414 K, 418 K and 413 K respectively at the second heating. The loss peaks of PPSQ(B)/PC blends become narrow at the second heating and their T_g s are lower than that of pure PC. So, phase-separation in PPSQ(A)/PC blends is serious compared with that of PPSQ(B)/PC blends after the first heating. The heating history has much more influence on the compatibility of PPSQ(A)/PC blends than that of PPSQ(B)/PC blends.

CONCLUSIONS

PPSQ(A)-rich spheres are dispersed in PC-rich continuous phase in different compositions of PPSQ(A)/PC blends and there is no phase-inversion as PPSQ(A) content increases when the percentage of PPSQ(A) is not more than 70%. Phase-inversion occurs in PPSQ(B)/PC blends when the percentage of PPSQ(B) is up to 70%. PC and PPSQ(A) or PPSQ(B) are partially compatible. Compatibility of PC and PPSQ(B) with low M_w and poor ladderlike regularity is better than that of PC/PPSQ(A) blends. T_g s of PPSQ(A)/PC (30/70 and 50/50) and PPSQ(B)/PC (30/70, 50/50 and 70/30) are lower than that of PC because of the enlarged free-volume in PC-rich phase. Heat history has some effect on the T_g and compatibility of PPSQ(A)/PC and PPSQ(B)/PC blends.

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