Thermal, Mechanical and Rheological Properties of Eco-friendly Poly(propylene carbonate)/Poly(1,2-propylene succinate) Blends[*]

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Abstract In order to improve the flexibility of poly(propylene carbonate) (PPC), poly(1,2-propylene succinate) (PPSu) was used to plasticize PPC in a batch mixer. The effects of PPSu on the miscibility, thermal stability, mechanical and rheological properties of the blends were investigated. PPC was partially miscible with PPSu. It was demonstrated that PPSu decreased the glass transition temperature and melt viscosity of PPC, as shown in the DSC and rheological curves. With the increase in PPSu content, the PPC/PPSu blends showed decreased tensile strength, however, the elongation at break was increased to 1100% for the 70/30 PPC/PPSu blend. The introduction of PPSu provided an efficient and novel plasticization method to extend the application area of PPC.

Keywords: Biodegradable; Poly(propylene carbonate); Poly(1,2-propylene succinate); Miscibility; Blends.

INTRODUCTION

It is well known that the worldwide white pollution has become more and more serious, which mainly derived from nondegradable materials. In recent years, an increasing attention was paid to develop biodegradable materials in order to solve the environmental concerns and the shortage of petroleum resources[1–4]. Poly(propylene carbonate) (PPC) is synthetized from propylene oxide and carbon dioxide. PPC has soft chain segment, easiness to decompose, good biocompatibility, and extremely low oxygen transmittance, can be widely used in packaging materials, tissue scaffolding, *etc*[5]. PPC has attracted extensive attention not only for its high value-added fixation of CO_2, but also for its biodegradability and biocompatibility[6–11]. The wide application of PPC material may not only reduce the dependence on petroleum but also lower the massive emission of CO_2 that has been considered to be the main factor causing the greenhouse effect in the world[12]. However, as an amorphous polymeric material, PPC has many drawbacks such as poor mechanical properties and thermal resistance[13, 14]. Many efforts has been made to improve the properties of PPC by melt compounding due to a relatively simple process[15, 16]. In fact, a few blends has been prepared, using ethyl cellulose (EC), poly(lactic acid), low molecular weight urethane, poly(vinyl alcohol) or others as modifiers[17–24], to improve the physical properties of PPC and extend the application of PPC. In order to extend the application area of PPC, improving the flexibility of PPC is essential. Enhancement of the flexibility could be achieved by blending it with low

molecular weight plasticizers. In this study, a novel polyester plasticizer was used to modified PPC which can present good flexibility.

PPSu[25, 26] is a nontoxic and biodegradable polyester. The polyester plasticizer is called the "permanent plasticizer" and is now studied as replacements for traditional plasticizer[27]. It exhibits excellent performances of low toxicity, low volatility, solvents withstanding and has biodegradability. In this article, PPSu was synthesized *via* polyesterification reaction of succinic acid and 1,2-propylene glycol. It could be used to plasticize PPC. Its environment friendliness was conducive to the sustainable development of our environment and health of human body. Moreover, the study was mainly focused on the miscibility, thermal, mechanical properties and rheological behavior of PPC/PPSu blends.

EXPERIMENTAL

Materials

PPC was supplied by Inner Mongolia Mengxi High-tech Materials Co. (China). The number average molecular weight (M_n) and polydispersity index (PDI) of the purified PPC were determined by GPC as 2.61×10^5 g/mol and 1.36, respectively. Poly(1,2-propylene succinate) was synthesized *via* polyesterification reaction using 1,2-propylene glycol and succinic acid as raw materials by our laboratory (Scheme 1), PPSu has number average molecular weight (M_n) of 3320 and distribution index of 1.4. Succinic acid and 1,2-propylene glycol were purchased from Yantai Shanshui Chemical Plant and Liaoyang Petrochemical Corporation, respectively.

Sample Preparation

PPC were dried at 40 °C for 24 h in a vacuum oven. PPC/PPSu blends were prepared by melt mixing with a Haake Rheomix 600 (Karlsruhe, Germany) at a rotating speed 60 r/min at 160 °C for 5 min. The mixing compositions of the PPC/PPSu blends were 90/10, 80/20, and 70/30 *W/W*. Also, PPC was subjected to the same mixing treatment so as to obtain a reference material compared with the blends. After mixing, all of the compounds were cut into small pieces. Then, all the samples were compression-molded into sheets with thicknesses of 1.0 mm for various tests at 160 °C, a hold pressure of 10 MPa and a hold time of 3 min, followed by quenching to room temperature between two thick-metal blocks kept at room temperature. The specimens were then sealed in plastic bags awaiting the processing and analysis.
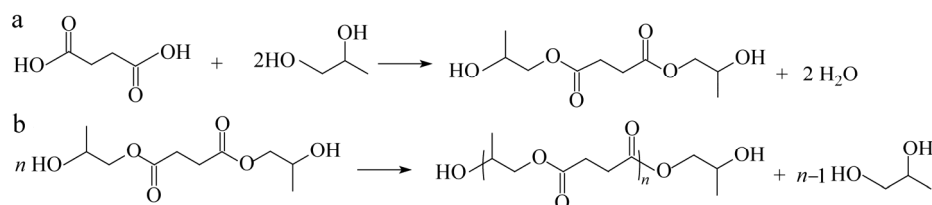
Scheme 1 Synthesis of poly(1,2-propylene succinate) from succinic acid and 1,2-propylene glycol

Characterization

Differential scanning calorimetry

Thermal behavior of the blends and PPC was studied by differential scanning calorimetry (DSC) (TA Instruments DSC Q20 USA) under N_2 atmosphere. The specimens were sliced from compression molded samples and the sample weights varied between 5 mg and 8 mg. All the specimens were cooled to −65 °C at a cooling rate of 10 K/min. Then, the specimens were heated form −65 °C to 100 °C at a heating rate of 10 K/min to study the variation of T_gs.

Dynamic mechanical properties testing

Dynamic mechanical analysis (DMA) was carried out with a dynamic mechanical analyzer NETZSCH DMA 242C (Selb, Germany) in the shear mode. The samples have gauge dimensions of the diameter of 10 mm and thickness of 1 mm. The dynamic loss factor (tanδ) were determined at a frequency of 1 Hz and a constant heating rate of 3 K/min as a function of temperature from −90 °C to 70 °C.

Thermal stability

Thermogravimetric analysis (TGA) was performed using a Netzsch STA 409 PC simultaneous thermal analysis instrument. All samples with weight of 10 ± 0.2 mg were heated from room temperature to 800 °C at 10 K/min under nitrogen.

Mechanical properties testing

The uniaxial tensile tests were carried out on an Instron 1121 testing machine (Canton MA). Specimens (20 mm $\times 4$ mm $\times 1$ mm) were cut from the previously compression-molded sheets into a dumbbell shape. All tests were conducted at a cross-head speed of 50 mm/min at room temperature according to ASTM D638-2008. At least five specimens for each sample were measured to get an average value.

Rheological properties

Melt flow indices (MFIs) of the PPC and PPC/PPSu blends were determined with a μPXRZ-400B melt flow indexer (Changchun, China) equipped with a standard die. The die had a smooth straight bore with a diameter of 2.0955 ± 0.005 mm and a length of 8.000 ± 0.025 mm. The measurements were performed according to ASTM D1238-82. The conducted temperature was 160 °C.

Rheological measurements of the samples were carried out on a Physica MCR 2000 rheometer (AR 2000ex USA). Frequency sweep for the all samples was carried out under nitrogen using 25 mm plate-plate geometry. The gap distance between the parallel plates was 0.9 mm for all tests. The sheet samples were about 1.0 mm in thickness. A strain sweep test was initially conducted to determine the linear viscoelastic region of the materials. The angular frequency range used during testing was 0.1−100 rad/s. The temperatures were set at 160 °C.

RESULTS AND DISCUSSION

Miscibility

Figure 1 shows the DSC thermograms for PPC, neat PPSu, and PPC/PPSu blends. Both PPC and PPSu are amorphous materials with no crystallization and melting peaks. The glass transition temperature (T_g) as an indicator for mobility of chain segment is very important. Also, plasticizing effect has been evaluated by the decrease of T_g due to the incorporation of plasticizer for broadening the application field of PPC.
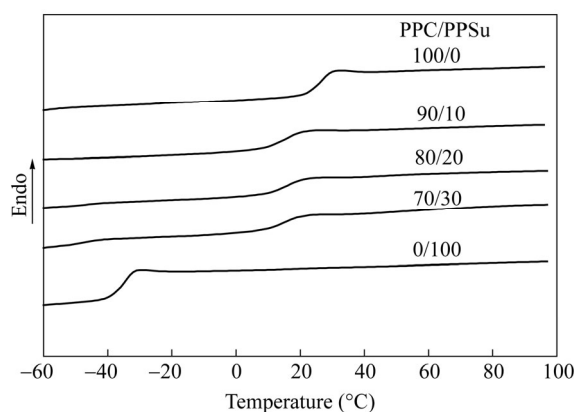

Fig. 1 DSC thermograms of PPC, neat PPSu, and their blends

The Hildebrand solubility parameter[28] can be calculated as follows:

$$\delta = (E_{coh} / V)^{1/2} \tag{1}$$

where δ is solubility parameter, E_{coh} is the cohesive energy density and V is the molar volume. The solubility parameter of PPC was 21.2 $(J/cm^3)^{0.5}$ and the solubility parameter of PPSu was 20.0 $(J/cm^3)^{0.5}$.

T_g can be calculated by Fox equation for the PPC/PPSu system. The Fox equation[29] is listed as follows:

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \tag{2}$$

where W_i is weight fraction of each component, in the copolymer composition, T_g is the glass transition temperature of the copolymer and T_{gi} is the glass transition temperature of each homopolymer. T_g values of the PPC/PPSu blends, taken from the curves of Fig. 1, are plotted in Fig. 2 as a function of the blend composition. When the content of PPSu was lower than 10 wt%, it could be seen that the variation of T_gs with the composition of PPC-rich blend conformed to the Fox equation, and the result indicated that PPSu was miscible with PPC at low content. However, when the content of PPSu increased to 20 wt%, the experimental results of T_g exhibited a decreased trend and gradually deviated from the theoretical values, and this indicated that PPC was partially miscible with PPSu.
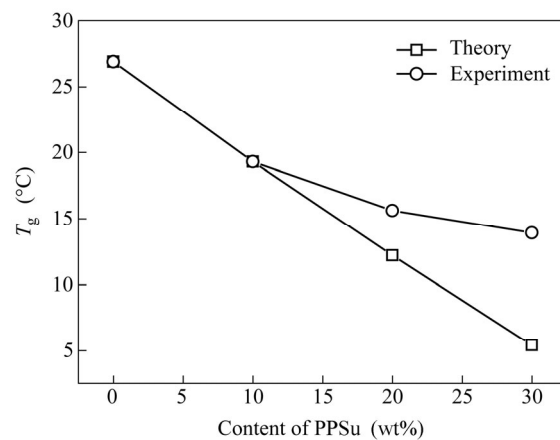

Fig. 2 T_g as a function of PPSu weight fraction

Figure 3 displays the curves of dynamic loss tangent versus temperature of the PPC/PPSu blends. The glass transition temperatures could also be determined from the peak temperature of the dynamic loss ($\tan\delta$) curves.
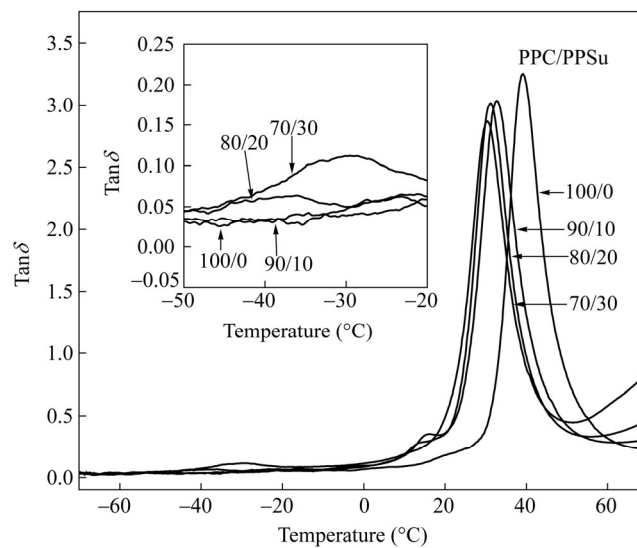

Fig. 3 $\tan\delta$ versus temperature traces of PPC/PPSu blends with different PPSu contents

The plasticization of PPSu led to glass transition temperature of PPC/PPSu blends shifting to lower temperatures. It can be seen that PPC and 90/10 PPC/PPSu blend exhibited a single glass transition peak. In case of the 80/20 and 70/30 PPC/PPSu blends, the tanδ curves revealed two glass transitions peaks, the higher T_gs was corresponding to PPC component and the lower one was corresponding to PPSu component. It could also be seen that the glass transition (T_gs) of PPC component in blends appeared at a lower temperature than that for the PPC homopolymer and it gradually decreased to lower temperatures with increasing PPSu content in the blend. For 70/30 blend, the T_g of PPC decreased by about 8.9 K. Moreover, the T_gs of both PPC and PPSu components in the blends slightly shifted toward each other with the increase of PPSu content, suggesting that PPC was partially miscible with PPSu, which is consistent with the DSC analysis.

Thermal Stability

Thermal stability is of particular importance for any materials in the melting-process. The TGA trace for PPC, neat PPSu and PPC/PPSu blends in the nitrogen flow is shown in Fig. 4. The corresponding characteristic temperatures are given in Table 1. The thermal degradation behaviors of PPC, neat PPSu and the blends with changing composition were compared using the 5% weight loss temperature ($T_{-5\%}$) and the temperature corresponding to the maximum rate of mass loss (T_{max}) in order to explain the effects of PPSu on the thermal degradation process of PPC. The $T_{-5\%}$ of PPC was at 261 °C. After that, there was a quick weight loss, and the T_{max} occured at 285 °C. The $T_{-5\%}$ of PPC/PPSu blends tended to decrease with increasing PPSu content. The thermal degradation process of all blends had two stages in the temperature ranges of 230–260 °C and 260–380 °C. The first stage might belong to the degradation of PPC and the second stage was the degradation of PPSu. At temperatures higher than 400 °C, PPC was decomposed completely. The thermal decomposition temperatures ($T_{-5\%}$) of the PPC/PPSu blends decreased dramatically by 30–40 K compared with that of the PPC matrix. Both $T_{-5\%}$ and T_{max} showed that the thermal stability of PPC decreased with the incorporation of PPSu.
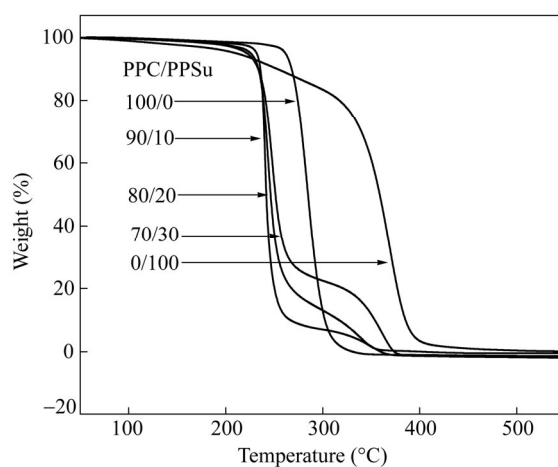

Fig. 4 The TGA curves of PPC and PPC/PPSu blends

Table 1. Characteristic temperatures of TGA curves

PPC/PPSu (W/W)	$T_{-5\%}$ (°C)	T^1_{max} (°C)	T^2_{max} (°C)
100/0	261.3	285.5	–
90/10	231.7	240.9	351.6
80/20	225.5	244.2	338.2
70/30	221.4	248.5	361.0
0/100	209.7	–	369.6

T^1_{max} and T^2_{max} were denoted as the thermal decomposition temperature with the max rate of the PPC-rich phase and PPSu-rich phase, respectively.

Mechanical Characterization

The tensile properties for PPC and neat PPSu and the PPC/PPSu blends are shown in Fig. 5 and the corresponding data of mechanical properties are listed in Table 2. The elongation at break of the PPC/PPSu blends showed a sharp increase with increasing PPSu content which accounted for that the good ductility was obtained by the addition of PPSu.
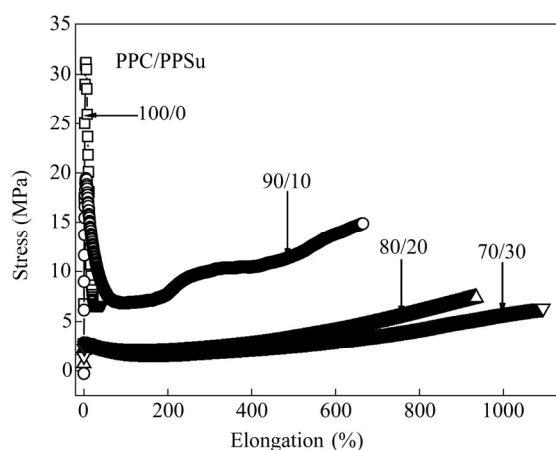

Fig. 5 Tensile behavior of PPC and PPC/PPSu blends

PPC showed low elongation at break of 46%, with tensile strength of 31 MPa. PPC fractured at low strain, while the PPC/PPSu blends exhibited a ductile behavior with yielding and a subsequent plastic deformation. The elongation at break value of PPC increased with the addition of PPSu. The highest elongation at break was increased to 1100% for the 70/30 PPC/PPSu blend, which is 24 times higher than that of PPC, while the tensile strength decreased to 6.3 MPa. The satisfactory results of plasticizing with PPSu was attributed to the molecular level miscibility between PPSu and PPC. PPSu increased the molecular chain mobility of PPC which resulted in the decrease of T_gs in the blends. Due to enhancing the mobility of chain segments, the interaction among molecular chains was reduced. During the tensile process, molecular chains gradually disentangled and were oriented, which could disperse fracture energy more effectively and delayed the final rupture of the material. In Fig. 5, it could be seen that the plastic deformation stress platform was extended with the increase of the content of PPSu. Although the elongation at break changed significantly, the increased flexibility of the PPC/PPSu blends was accompanied with a decrease in tensile strength and yield stress.

Table 2 presented the Young's modulus, tensile strength and elongation at break of PPC with different PPSu contents. It could be seen that the increase of PPSu from 10% to 30% led to the decrease of the modulus value from 1070 MPa to 72 MPa. The increased flexibility of the PPC/PPSu blends was accompanied with a decrease in tensile strength, yield stress, and modulus.

Table 2. Mechanical properties of PPC/PPSu blends

PPC/PPSu (*W/W*)	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
100/0	1020 ± 43	35 ± 4.2	45 ± 22
90/10	940 ± 25	19 ± 2.9	650 ± 25
80/20	640 ± 22	7.6 ± 3.7	930 ± 56
70/30	70 ± 12	6.3 ± 1.1	1100 ± 20

Rheological Measurement Results

The MFIs of PPC and the PPC/PPSu blends were determined, and the results are shown in Fig. 6.

Figure 6 demonstrated the effect of PPSu content on MFI. With the addition of PPSu, the MFI of PPC/PPSu blends had a sharp increase. The MFI of PPC was 0.4 g/10 min, and the MFI increased to 23 g/10 min for the

70/30 PPC/PPSu blend. The experimental results indicated that the melt flow ability of PPC was increased with the addition of PPSu. The increased MFI exhibited that the system of the melt flow resistance was reduced and the melt viscosity was decreased. Therefore, PPSu was a good plasticizer for PPC.
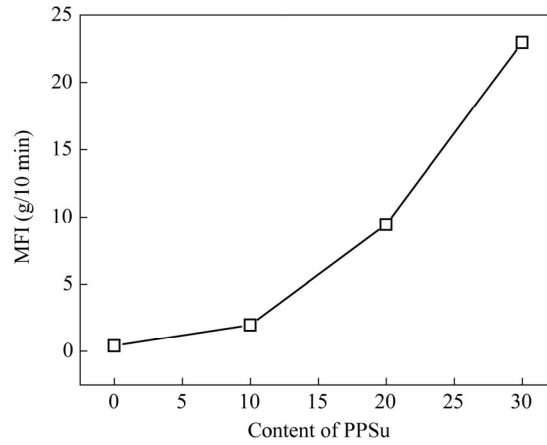

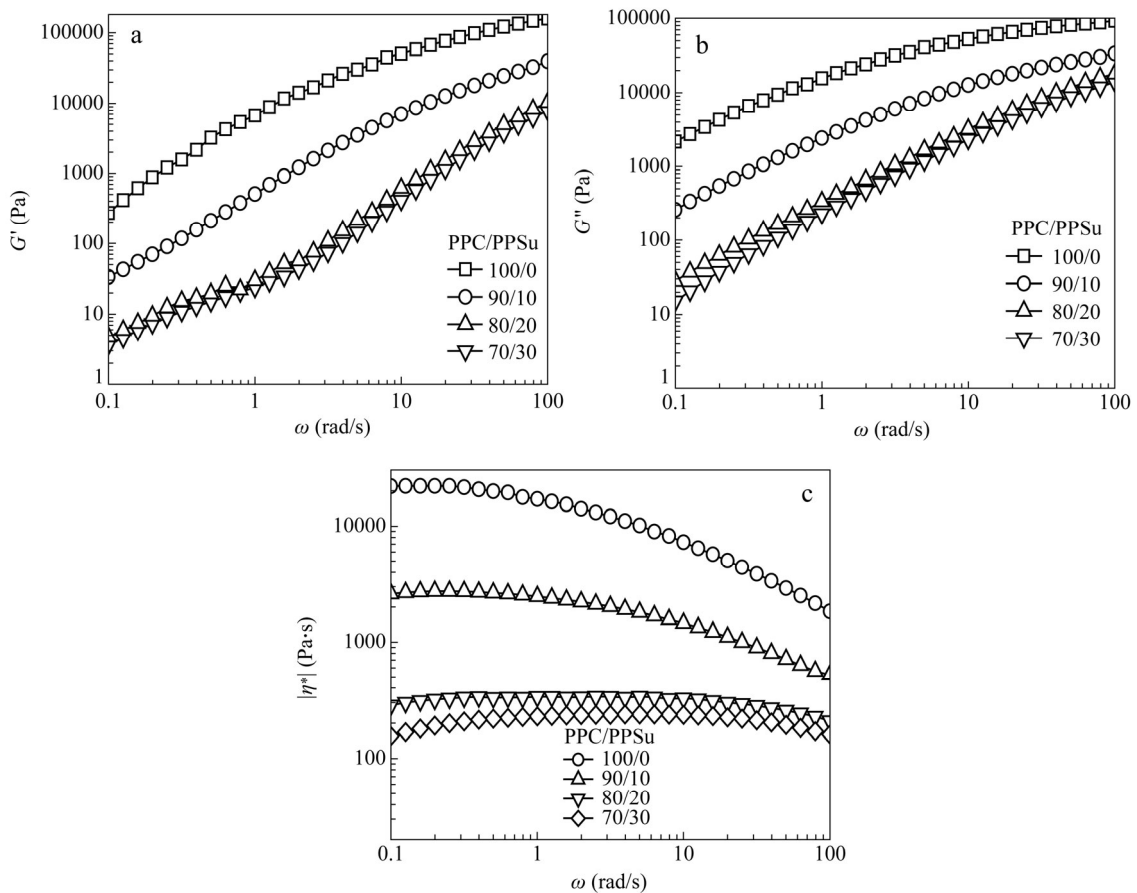**Fig. 6** Variations of MFI for PPC and PPC/PPSu blends

Fig. 7 Plots of (a) dynamic storage modulus G', (b) loss modulus G'', and (c) complex viscosity $|\eta^*|$ versus frequency

The dynamic rheological experiments were carried out for all the samples. The rheograms of dynamic storage modulus G', dynamic loss modulus G'', and complex viscosity η^* versus oscillatory frequency were carried out by conducting dynamic frequency sweep test ($\omega = 0.1-100$ rad/s) on the blends at the temperature of 160 °C, as shown in Fig. 7.

It can be seen that G' and G'' of PPC/PPSu blends increased with angular frequency, but they decreased with the increase of PPSu content in the blends. At the whole frequency range, the G' of PPC/PPSu blends was much lower than that of PPC. Meanwhile, the frequency dependence of G'' also showed the same tendency as G'. The G' of the 70/30 PPC/PPSu blend decreased by about two orders due to the low modulus of PPSu. The lower storage modulus of the blends was supposed to be originated from the decrease in molecular entanglements in the blends.

The much lower G'' indicated lower viscosity. PPSu acted as an effective plasticizer and decreased both elastic and viscous modulus of PPC/PPSu blends. Because of PPSu as plasticizer increased the polymer free volume which increased the ability of polymer chains' mobility. However, the G' and G'' of the the PPC/PPSu blends were nearly unchanged with the PPSu content above 20%. It could be explained that there might be a maximum of plasticizing effect at the whole angular frequency range.

Figure 7(c) presents the relationship between complex viscosity and angular frequency of the PPC/PPSu blends. It exhibited that the melt viscosity of the blends was substantially lower than that of PPC. It also demonstrated a stronger shear thinning effect comparing with other blends. PPC melt showed non-Newtonian behavior at the whole frequency region. However, the 80/20 and 70/30 PPC/PPSu blends exhibited a pronounced Newtonian response with an extended Newtonian plateau compared with PPC. The decreased melt viscosity of the blends could be related to the free volume increase due to the plasticization of PPSu.

The effect of the plasticizer content is further explored in Fig. 8 where the zero-shear viscosity is presented as a function of the plasticizer content. It was obvious that the viscosity follows an exponential decay with plasticizer content which is a typical plasticizer content effect. At high plasticizer content, a leveling off of the viscosity is expected if the plasticizer saturation point is reached which is in agreement with the results of Fig. 7.
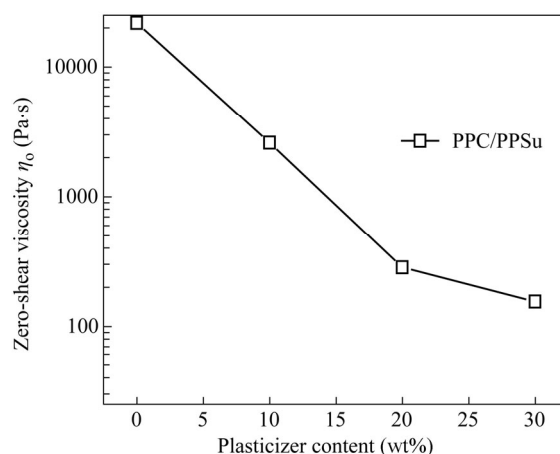

Fig. 8 Effect of plasticizer content on the zero-shear viscosity of PPC/PPSu blends at 160 °C

CONCLUSIONS

In this paper, an emerging plasticizer of PPSu was added to PPC matrix by melt blending. MFI revealed that the melt flow ability of the blends was improved. The melt viscosity of the PPC/PPSu blends was significantly lower than that of PPC in the rheological measurements. DMA and DSC results demonstrated that PPSu was partially miscible with PPC. The thermal stability of PPC was decreased by the introduction of the PPSu phase, as shown by TG measurements. All of the PPC/PPSu blends showed pronounced stress yielding and noted necking. For

the 70/30 blend, the elongation at break was markedly increased to 1100% which was expected to extend the practical application of PPC in the future.

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