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Grafting of polypropylene with *N*-cyclohexylmaleimide and styrene simultaneously using supercritical CO_2

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Abstract

Monomer mixture of styrene (St) and *N*-cyclohexylmaleimide (ChMI) and initiator benzoyl peroxide (BPO) were first impregnated into isotactic polypropylene (iPP) films simultaneously using supercritical carbon dioxide (SC CO_2) as a solvent and swelling agent at 35.0 °C. The composites were obtained after the monomers were grafted onto the iPP matrix at 70 °C. The effects of various conditions, such as pressure, monomer concentration, and the molar ratio of the two monomers in the soaking process, on the composition of the composites were determined. The molar ratios of St to ChMI in the composites were estimated by Fourier transform infrared spectroscopy. The thermal properties, the morphology, and the mechanical properties of the composites were characterized by different techniques. The results demonstrated that the phase size of the grafted St–ChMI was very small and the phase boundary was very ambiguous. The composites had better thermal stability than the original iPP film. The Young's modulus and tensile strength of the film increased continuously with increasing grafting percentage. The two grafted monomers in the composites had good synergetic effect.

Keywords: Supercritical CO_2; Grafting; Polypropylene

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1. Introduction

There has been increasing interest in using supercritical carbon dioxide (SC CO_2) as the solvent/processing aid in polymer processing and polymer chemistry [1–5]. The advantages of using SC CO_2 include that it has high diffusivities, low viscosity, and near zero surface tension, mild critical parameters ($T_c = 31.1$ °C, $P_c = 73.8$ bar), and it is nontoxic, nonflammable, and inexpensive. Moreover, it can be easily removed from the system after reaction. Although SC CO_2 is a poor solvent for most polymers, it can swell most polymers [6]. SC CO_2 has been used to impregnate polymer matrices with different organic molecules, and chemical [7–10] and physical [11–13] modifications of the polymers have been carried out. McCarthy and coworkers [11,12,14] are the first to prepare polymer composites by impregnating monomer and thermal initiator into polymer substrates, followed by thermal free radical polymerization.

As one of the most important general-purpose polymers, polypropylene (PP) is widely used in various fields. However, PP is restricted in its applications because of the lack of chemical functionalities, nonpolarity and poor compatibility with other polymers. Graft copolymerization offers an effective approach to overcome these disadvantages [15–18]. The conventional methods, like reactive extrusion process and solution process, often require high temperature or organic solvents. Recently, modifications of PP in a SC CO_2 medium have been carried out. For example, Spadaro and coworkers [19] charged maleic anhydride (MA) and dicumyl peroxide (DCP) into polypropylene matrix using SC CO_2 at 80 °C, and successfully grafted MA onto polymer chains through gamma irradiation. Our group [20] has prepared polypropylene/polystyrene (PP/PS) composites by impregnating styrene (St) and initiator into the PP matrix with the aid of SC CO_2. It was demonstrated that the composites showed improved mechanical properties and special microstructure. However, the PP/PS composite had a decreased thermal stability compared to the pure PP due to the poor thermal stability of the incorporated PS [21].

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In this paper, we describe the grafting of St and *N*-cyclohexylmaleimide (ChMI) onto PP backbone using SC CO_2 as a carrier and swelling agent. The composition, mechanical property, thermal property, and morphology of the composites have been studied, and very satisfactory results have been obtained. As far as we know, this is the first report for preparing a polymer composite consisting of more than two components using a supercritical fluid.

2. Experimental

2.1. Materials

Isotactic polypropylene (iPP) films were provided by Yanshan Plastic Institute The thickness of the films was 80 μm *N*-cyclohexylmaleimide (ChMI) was prepared from the reaction of maleic anhydride and the cyclohexylamine according to the method described in the literature [22], followed by repeated sublimation. Styrene (St, Beijing Chemical Reagent Center, A. R. grade) was vacuum distilled from calcium hydride. Benzoyl peroxide (BPO) was recrystallized twice from methanol. Tetrahydrofuran (THF, Beijing Chemical Reagent Center, A. R. grade) was used as received. CO_2 with a purity of 99.95% was supplied by Beijing Analytical Instrument Factory and used as received.

2.2. Composites synthesis

Preweighed iPP films were placed into a high-pressure stainless steel vessel of 30 ml together with styrene/ChMI/BPO solution (0.3 mol% BPO). The vessel was put into a constant temperature water bath of 35.0 °C. The air in the vessel was replaced by CO_2, and then CO_2 was compressed into the vessel to a desired pressure using a high pressure pump. CO_2 was released after the system had been equilibrated for a desired time. Then the vessel was heated to 70 °C. After a reaction time of 12 h, the samples were taken out and Soxhlet-extracted using THF for 48 h to remove the ungrafted polymers. The products were dried at 60 °C under vacuum, and were weighed until the weight was constant. The above procedures were repeated until the weight of the products was independent of extraction time. We assumed that all the ungrafted polymers were removed by the extraction process. The grafting percentage (*G*) was calculated from the following equation

$$G(\mathrm{wt}\%) = (W_1 - W_0)/W_0 \times 100 \quad (1)$$

where W_0 and W_1 stand for the weight of origin iPP film and that of the composite after the Soxhlet-extraction, respectively.

2.3. Characterization

Fourier transform infrared spectroscopy (FTIR) analysis of the PP and grafted films were run on a Perkin–Elmer 180 IR spectrometer in transmission mode. The FTIR spectra were recorded in the wavenumber range from 2000 to 500 cm^{-1} with resolution of 4 cm^{-1}. Differential scanning calorimetry (DSC) was conducted on a Perkin–Elmer DSC-7. Initially, the samples were heated to 220 °C and kept at this temperature for 10 min to remove all prior thermal history. Subsequently, they were quenched to −30 °C and then reheated to 200 °C at a rate of 20 °C/min. The second heating scan was recorded. Thermal gravimetric analysis (TGA) was carried out on a Perkin–Elmer TGA 7 from room temperature to 500 °C with a heating rate of 10 °C/min under dry nitrogen. Tensile tests were conducted using an Instron 1122 universal tensile tester with a crosshead speed of 100 mm/min. Tests were carried out at 25 °C and 30% relative humidity. The results of five specimens were averaged. The morphology of the composite was observed by means of TEM (Hitachi H-800). Cryoultrathin sections were cut from the film and stained in OsO_4 vapor for 24 h.

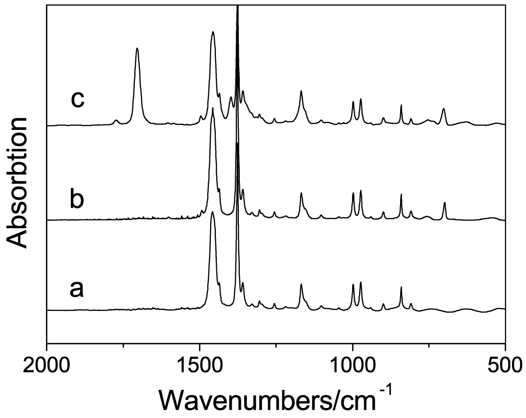


Fig. 1. FTIR spectra of (a) PP, (b) PP-*g*-PS composite (4.2% grafted) and (c) PP-*g*-(St–ChMI) composite (12.3% grafted).

3. Results and discussion

Maleimide and its *N*-substituted derivatives can polymerize and copolymerize easily in spite of their 1,2-disubstituted ethylene structures. Their interesting polymerization and copolymerization behavior and the excellent thermal stability of the polymers have been extensively studied [23–27]. Polymers of *N*-phenylmaleimide (PMI) have been reported to be superior in thermal stability [25–27]. However, the coloration of the polymer containing PMI was unavoidable due to the conjugated structure of the PMI. In order to obtain an organic transparent material, we use ChMI and St as monomers to modify the PP matrix.

3.1. Composites synthesis

The FTIR spectra of pure PP, PP-*g*-St, and PP-*g*-(St–ChMI) are shown in Fig. 1. In the case of PP-*g*-St, new absorption band appeared at 702 cm^{-1}, which can be

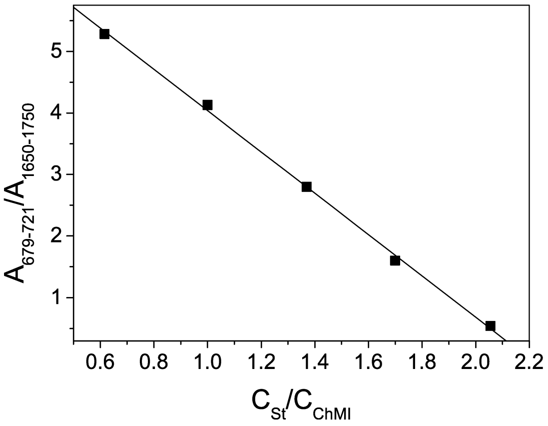


Fig. 2. Calibration plot for St and ChMI content in PP-*g*-(St–ChMI) composites.

assigned to the absorption of substituted phenyl ring. For the composite of PP-*g*-(St–ChMI), in addition to the band at 702 cm^{-1}, the characteristic band of carbonyl at 1704 cm^{-1} was also observed, indicating the successful incorporation of St and ChMI.

The absorbance ratio of the areas of the bands at 1704 and 702 cm^{-1} shows the content ratio of the St and ChMI in the composite. The calibration curve was obtained by determining the IR spectra of PS/poly(ChMI) thin films of known compositions, which were prepared by casting method using THF as the solvent. The films were subjected to transmission IR analysis and the results are shown in Fig. 2. As expected, a linear relationship between the absorption ratio and concentration ratio is observed, which can be expressed as follows:

$$A_{679-721}/A_{1650-1750} = 7.39 - 3.36(C_{St}/C_{ChMI}) \qquad (2)$$

The overall graft percentage of ChMI and St (*G*) was obtained gravimetrically. Therefore, the graft percentage of ChMI and St can be easily obtained.

Fig. 3 shows the effect of the molar concentration ratio of ChMI and St in the fluid phase on the grafting percentage.

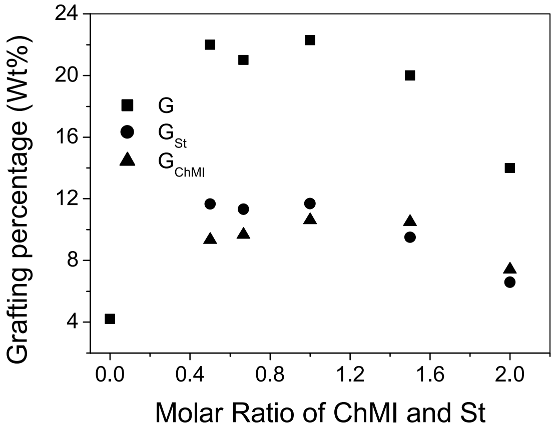


Fig. 3. Effect of molar concentration ratio of ChMI and St in the fluid phase on the grafting percentage. (The total concentration of the monomers in the fluid phase during soaking process is 0.3 mol/l.)

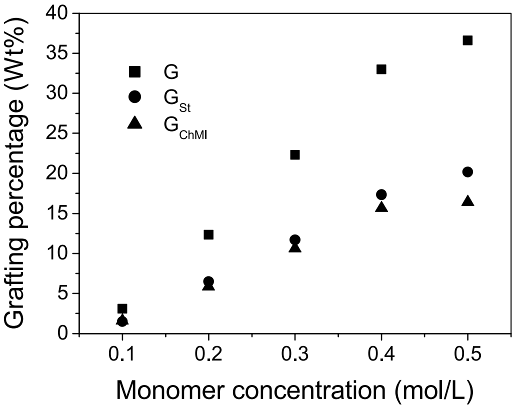


Fig. 4. Effect of monomer concentration during the soaking process on the grafting percentage.

The total concentration of the two monomers in the fluid phase is 0.3 M with 0.3 wt% initiator (monomer-basis), and the pressure is 10 MPa during the soaking process. The graft level of St in the absence of ChMI is 4.2 wt%. When ChMI is introduced into the system, both the overall graft level, *G*, and the individual graft level of St, G_{St}, are increased, and the highest graft level occurs as the equimolar of ChMI and St are added. When there is more ChMI than St in the system, the *G*, G_{St} and G_{ChMI} began to decrease, but the molar ratio of St and ChMI remains nearly unchanged. This can be explained in the following.

It has been well established that the radical grafting of a monomer onto PP in the presence of a peroxide initiator starts with the formation of macroradicals along with the PP chains by a so-called hydrogen abstraction mechanism. The reactivity of ChMI towards free radical is low due to its structural symmetry and deficiency of electron density around the double bond. In the presence of St, a good electron-donating monomer, the two monomers, St and ChMI, can interact with each other one-to-one to form a charge transfer complex (CTC) [28], which has a higher reactivity than St and ChMI. Therefore, the grafting percentage is significantly improved in the presence of ChMI. When the amount of St is larger than ChMI in the system, part of St interacts with ChMI to form CTC and the others can graft onto the PP due to its relatively high reactivity. When equimolar St and ChMI are added, the two monomers interact easily with each other and the grafting percentage is the highest. In the case that more ChMI is added than St, the formed CTC can graft easily, but it is difficult for the free ChMI to graft onto the PP backbone due to its low reactivity. Therefore, the grafting level begins to decrease and the concentration ratio of the grafted St and ChMI remains nearly unchanged. It should be mentioned that the grafting level was less that 1% when pure ChMI monomer was used. Therefore, the two monomers exhibit good synergetic effect for enhancing the grafting.

The dependence of the graft degree of St and ChMI on the monomer concentration at St/ChMI = 1:1 is shown in Fig. 4. The graft percentage increases with the monomer

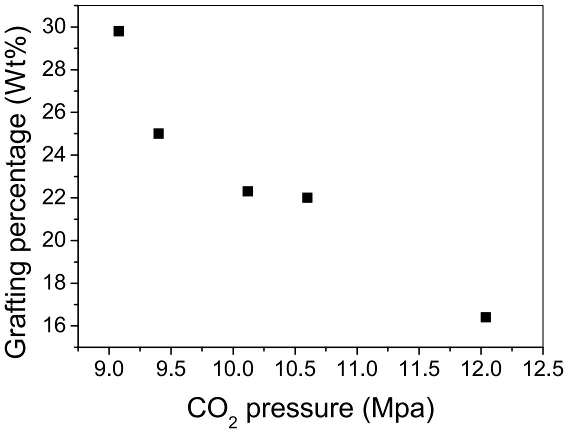


Fig. 5. Effect of CO_2 pressure on the grafting percentage. (The monomer concentration is 0.3 mol/l.)

concentration in the fluid phase. This is easy to understand because the monomer distributes between the fluids phase and the polymer solid phase during the soaking process, and higher concentration is favorable to impregnate more monomers into the PP substrate.

Fig. 5 shows the effect of soaking pressure on the graft degree. As can be known from the figure, the graft degree decreases with increasing CO_2 pressure. This results from the fact that the stronger solvent power of CO_2 at higher pressure makes the sorption of the monomers in the polymer phase more difficult.

3.2. TEM micrographs

Fig. 6 shows the TEM micrographs of the composite samples with graft percentages of 12.3 and 22.3%, respectively. The dark phase is the OsO_4-stained St–ChMI phase, which is uniformly distributed in the PP matrix. Though the St–ChMI phase exists, the phase boundary is extremely ambiguous. This can be attributed to the special method used in this work, which is discussed in the following.

SCFs have high diffusivity, low viscosity, and near zero surface tension. Thus, the monomer and the initiator molecules can diffuse into any inter-chain spaces in the PP matrix with a faster rate, provided that the size of the gap is larger than the molecules. Therefore, the monomers are more uniformly distributed in the PP matrix before polymerization. For semicrystalline polymers, SC CO_2 can only swell the amorphous phase [5,14]. Therefore, the monomer cannot enter the crystalline regions. Thus, the grafting and the chain growth occur solely within the amorphous region. Meanwhile, the existence of the rigid iPP crystallites prevents the formation of the large St–ChMI domains.

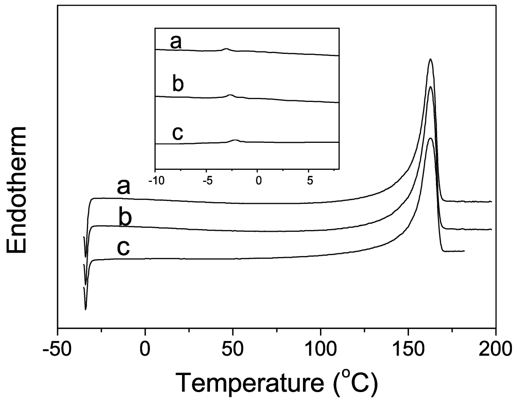
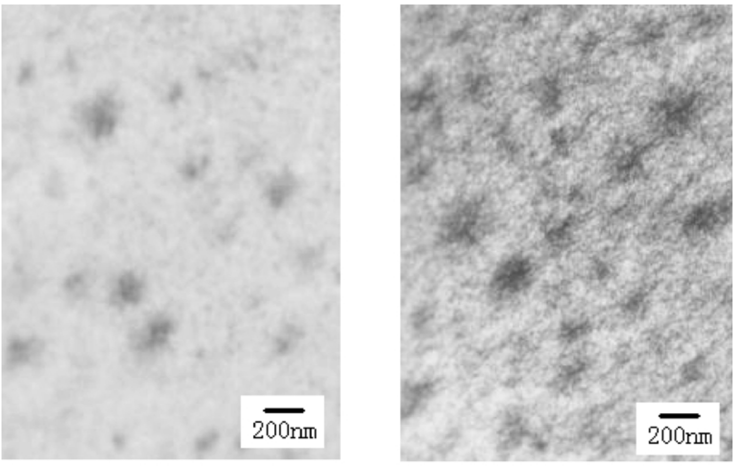


Fig. 7. DSC curves of (a) PP, (b) 12.3% grafted PP-*g*-PS composite and (c) 22.3% grafted PP-*g*-(St–ChMI) composite.

3.3. DSC and TGA

Fig. 7 shows the DSC thermograms of pure iPP and PP-*g*-(St–ChMI) samples with grafting degree of 12.3 and 22.3 wt%, respectively. The glass transition temperature (T_g) of the PP matrix can be observed on the magnified



(a) (b)

Fig. 6. TEM images of PP-*g*-(St–ChMI) composites with grafting percentage of (a) 12.3% and (b) 22.3%.

Table 1
Parameters of iPP and composites

Sample[a]	T_g (°C)	ΔH_m (J/g)	T_m (°C)	Crystalline degree (%)	
				C_a	C_{iPP}
iPP	−2.9	88.25	163.3	42.2	
Sample A	−2.8	67.15	162.6	32.1	36.6
Sample B	−2.1	57.70	162.5	27.6	35.5

[a] The grafting levels of Sample A and Sample B are 12.3 and 22.3%, respectively.

endotherm curves. The T_g, melting point (T_m), and apparent enthalpy of melting (ΔH_m) obtained from the DSC curves in Fig. 7 are listed in Table 1. The T_g of the grafted St–ChMI units cannot be detected, although the T_g of St/ChMI with an alternating structure was reported to be about 180 °C [29]. It is difficult to determine the molecular weights of the grafted St–ChMI branches, but it is reasonable to assume that the molecular weights of the St–ChMI branches formed in the restrained space are small. Thus, the T_g of the St–ChMI chains should be below 180 °C, and it is likely that the glass transition was obscured by the large endothermic peak between 120 and 170 °C for the fusion of iPP. In addition, we cannot exclude the possibility that the change in heat capacity was too small to be detected by DSC.

The apparent crystallinity (C_a) of the iPP and the grafted iPP were calculated from Eq. (3)

$$C_a(\%) = \Delta H_m / \Delta H^0 \qquad (3)$$

where ΔH_m is the apparent enthalpy of melting. ΔH^0 is the heat of fusion per gram of 100% crystalline iPP, which is 209 J/g [30]. It can be seen from C_a (Table 1) that the apparent crystallinity of the composites decreases with increasing grafting level. The reduction may be due to dilution by the addition of the incorporated St–ChMI. To eliminate the effect of the dilution, the crystallinity of the iPP portion is calculated as follows:

$$C_{iPP} = C_a / W_{iPP} \qquad (4)$$

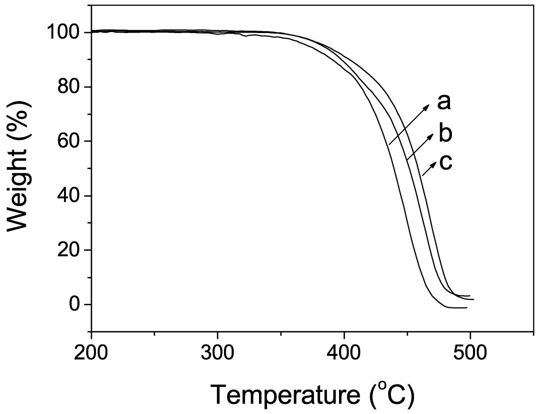


Fig. 8. TG curves of (a) PP (b) 12.3% grafted PP-*g*-PS composite and (c) 22.3% grafted PP-*g*-(St–ChMI) composite.

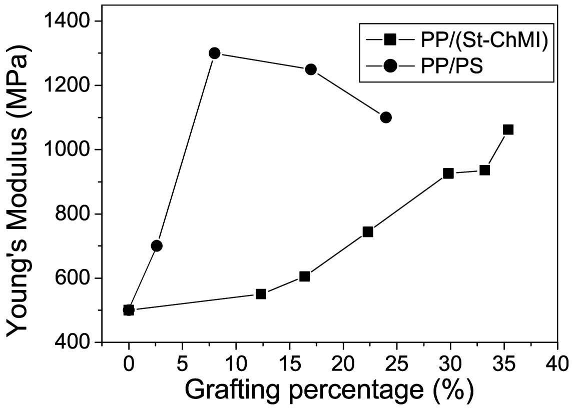


Fig. 9. Young's modulus of the composite as a function of grafting percentage.

where W_{iPP} is the weight fraction of the iPP in the composites. It can be seen from C_{iPP} (Table 1) that the crystallinity of the iPP portion in the composites decreases by about 16% as a result of amorphous St–ChMI grafts onto PP.

Fig. 8 shows the TGA curves of pure iPP, PP-*g*-(St–ChMI) samples with different graft percentages. It can be seen that the modified samples show a higher onset thermal degradation temperature and a lower weight loss at a particular temperature, indicating the PP-*g*-(St–ChMI) have a better thermal stability than the iPP.

It has been reported [21] that when only St was grafted onto the PP backbone, the resulting polymer showed a lower onset degradation temperature and underwent more weight loss than pure PP due to the poor thermal stability of the incorporated PS. Clearly, the improved thermal stability of the PP-*g*-(St–ChMI) results from the incorporated St–ChMI branches.

3.4. Tensile properties

The dependence of the Young's modulus, tensile strength, and elongation-at-break of the composites on the graft percentage is shown in Figs. 9–11, respectively. Young's modulus and the tensile strength of the samples

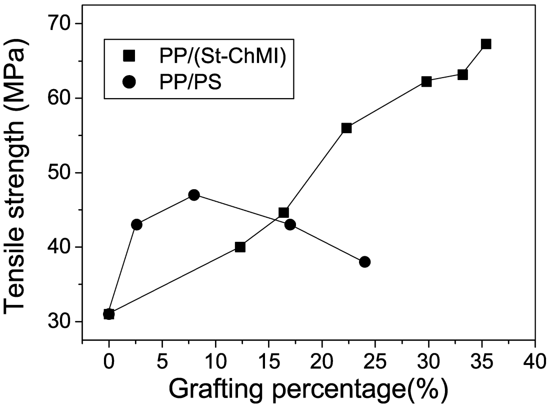


Fig. 10. Tensile strength of the composite as a function of grafting percentage.

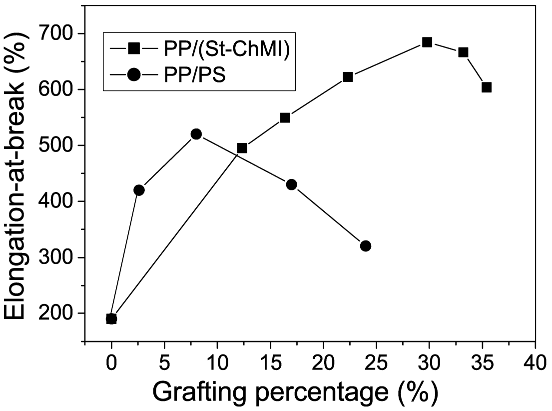


Fig. 11. Elongation-at-break of the composite as a function of grafting percentage.

increase continuously with grafting percentage in the entire concentration range (up to 35 wt%). The elongation-at-break is also improved, although a maximum occurs at the grafting level of 30 wt%. We prepared the PP/PS composites using the similar procedure [20]. The composites also showed improved mechanical properties, but the Young's modulus, tensile properties, and elongation-at-break tend to decrease when the PS content in the composite was higher than 10 wt%. We believe there are mainly two reasons for this. The first is the rigidity of the ChMI unit and the strong inter- and intra-molecular chain interaction caused by the carbonyl groups in the ChMI unit. Second, it is well known that the mechanical properties of polymer composites are closely related to their microstructures and morphologies. The size of the St–ChMI phase is very small and the phase boundary is very ambiguous as observed, which is favorable for the improvement of the mechanical properties. As discussed above, the graft percentage is very low when pure ChMI was used, and the thermal and mechanical properties of PP-*g*-(St–ChMI) are much better than that of PP-*g*-St. Therefore, the two grafted monomers show a strong synergetic effect in increasing both graft level and improving the properties of the PP.

4. Conclusions

St and ChMI can be grafted onto the iPP films simultaneously with the aid of SC CO_2, although the graft percentage is very low when pure ChMI is used. The graft level can be controlled by various factors, such as pressure of CO_2, monomer concentration in the fluid phase, and the molar ratio of the two monomers during the soaking process. The phase size in the composites is very small and the phase boundary is ambiguous. The composites show a better thermal stability than the pure PP and the PP/PS composites. The Young's modulus and the tensile strength of the composites increase continuously with the graft percentage in the concentration range studied (0–35 wt%). The elongation-at-break is also improved significantly, although a maximum is observed at the graft percentage of 30 wt%. The two grafted monomers show a strong synergetic effect.

Acknowledgements

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