In Situ Compatibilization of Polypropylene/Polystyrene Blend by Controlled Degradation and Reactive Extrusion

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ABSTRACT: *In situ* compatibilization of polypropylene (PP) and polystyrene (PS) was achieved by combinative application of tetraethyl thiuram disulfide (TETD) as degradation inhibitor and di-*tert*-butyl peroxide as degradation initiator in the process of reactive extrusion. The PP/PS blends obtained were systematically investigated by rheological measurement, scanning electron microscopy, and differential scanning calorimetry. The results indicate that peroxide-induced degradation of PP can be effectively depressed by adding TETD, which may favor the formation of PP-*g*-PS copolymer during melt processing. The PP-*g*-PS copolymer formed may act as an *in situ* compatibilizer for PP/PS blends, and subsequently decreases the size of dispersed PS phase and changes both rheological and thermal properties of the blends. Based on the present experimental results, the mechanisms for the controlled degradation of PP and *in situ* formation of PP-*g*-PS copolymer in the PP/PS blends have been proposed. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 826–832, 2009

Key words: polypropylene/polystyrene blends; controlled degradation; reactive extrusion; *in situ* compatibilization

INTRODUCTION

Polypropylene (PP) has been widely used as a commodity plastic because of its desirable properties. However, the PP polymerized with conventional Ziegler-Natta catalyst generally has a high molecular weight and broad molecular weight distribution, which results in high melt viscosity and elasticity, and limits its application in some fields,[1,2] e.g., high-velocity melt spinning. Degradation is known as a simple method to change the fluidity of PP melt. Many literatures have already referred to this issue,[3–8] including the degradation variety (thermal degradation, mechanical degradation, oxidation degradation, etc.), degradation mechanism, influence on PP properties of degradation, and so on. Peroxide-induced degradation, as one means of degradation, can effectively reduce molecular weight and molecular weight distribution, and further change the rheological properties of PP. Effects of peroxide concentration and processing conditions such as degradation temperature, reaction residue time, screw rotation speed and configuration on the rheo-

logical, thermal, and mechanical properties of PP have been extensively investigated.[9–18]

The process of peroxide-induced degradation of PP is mostly carried out in a mixer or extruder, which is one type of the so-called reactive extrusion (REX). REX plays many important roles in the processing of polyolefin.[19–25] Not only controlled degradation of PP can be realized but also modified PP materials with predesigned chain structures and enhanced physicochemical properties can be effectively and economically prepared by this method. Polypropylene-*g*-polystyrene (PP-*g*-PS), as a conventional compatibilizer for PP/PS blends, can be prepared via two approaches. One is that styrene monomers can be polymerized to PP main chains by manners as follows:[26–31] reactor granule technology, solid-state polymerization, and solution reactions, etc. On the other hand, the direct grafting of PS long chains to PP backbones also have been extensively investigated.[32–35] Sun et al.[32] and Díaz et al.[33,34] reported the *in situ* compatibilization of PP and PS using Friedel-Crafts alkylation through reactive extrusion, and found improvement of mechanical properties of PP/PS blends. Xie and Zheng[35] studied the effect of multifunctional monomers on one-step REX of PP/PS blends. Results showed that the PP chain degradation is effectively suppressed and the formation of PP-*g*-PS copolymer is accelerated.

Otsu[36] investigated the effect of sulfides and disulfides on the copolymerization of St and MMA and

found that the sulfides behave as not only initiators but also retardants, terminators, and transfer agents. They gave the concept "Iniferter" and eventually proposed a polymerization mechanism for such systems. Thiuram disulfides have been classically used for the synthesis of block copolymers or telechelic polymers.[37–39] Dithiocarbamate radicals from thiuram disulfides decomposition can react with polyolefin macroradicals, which is generally reversible.[40] Such reaction will result in the instantaneous decrease of PP free radicals concentration and thus suppress the β-scission of PP chains in PP existed system, favoring other reactions of PP macroradicals such as branching.[41] Among the thiuram disulfides, tetraethyl thiuram disulfide (TETD) is an excellent thermal- and photoinitiator for the polymerization of many monomers and allows obtaining branched structures.[36]

Approaches to realize the grafting of styrene monomers or PS long chains to PP backbones have been vastly reported. In the present work, di-*tert*-butyl peroxide (DTBP), one of the commonly used peroxides, was applied as degradation reagent in the controlled degradation of PP. And TETD was adopted as both degradation inhibitor and chain transfer agent. The combinative application of DTBP and TETD can promote the formation of PP-*g*-PS copolymer as a compatibilizer so as to achieve the *in situ* compatibilization of PP/PS blends. Consequently, the rheological behavior, morphological characteristic, and thermal property of the PP/PS blends were systematically investigated. Based on the experimental results, mechanisms for the controlled degradation of PP and *in situ* formation of PP-*g*-PS copolymer have been proposed.

EXPERIMENTAL

Materials

PP S1003 (MFR = 3.6 g/10 min, ASTM 1238L: 230°C, 2.16 kg) and PS 666D (MFR = 7.8 g/10 min, ASTM 1238G: 200°C, 5 kg) were commercial products of Sinopec Beijing Yansan Petrochemical Co. Ltd. (Beijing, China) TETD and DTBP were purchased from Northeast Auxiliary Chemical Industry Co. Ltd. (Shenyang, China) and Lanzhou Auxiliary Agent Plant (Lazhou, China), respectively.

Reactive extrusion of PP/PS blends

Reactive extrusion (REX) was carried out through a corotating twin-screw extruder (TSE-30A) with 10 heating zones. The diameter of the screw is 30 mm and the length-to-diameter ratio (L/D) is 40/1. Reactive mixtures were premixed and then fed into the extruder with constant flux. The screw rotating

TABLE I
Composition and MFR Values of Degraded PP

Composition (wt %)			
PP	DTBP	TETD	MFR (g/10 min)
100[a]	0	0	3.6
100[b]	0	0	4.6
100	0	0.2	4.8
100	0.2	0	9.9
100	0.2	0.08	6.6
100	0.2	0.2	7.1
100	0.2	0.32	6.0
100	0.2	0.41	6.8
100	0.2	0.57	6.8

[a] Neat PP S1003.
[b] Neat PP S1003 extruded through twin-screw extruder.

speed was 150 rpm. Temperature settings along the barrel of the extruder were as follows: 160, 190, 200, 200, 210, 210, 200, 200, 190, 190°C.

Characterization

Melt flow rate

According to ASTM 1238L, the melt flow rates (MFR) of PP and PP/PS blends were measured with a Haake-swo556-0031 melt indexer at 230°C under 2.16 kg load.

Rheological properties

The dynamic rheological measurements of the PP/PS blends were carried out at 190°C on a Rheometric Scientific rheometer (ARES) using the parallel-plate geometry with diameter of 25 mm and gap of 1 mm. To maintain the mechanical behavior of the investigated polymer blends within the region of linear viscoelasticity, the applied strain was 10%. All experiments were performed with a frequency sweep between 0.05 and 100 rad/s. The sample granules were first hot-pressed into 2 mm thick discs with diameter of 25 mm, and then submitted for rheological experiments. Dynamic storage modulus G', dynamic loss modulus G'', tangent of loss angle tan δ, and complex melt viscosity η^* were recorded.

Scanning electron microscopy

The cross sections of PP/PS blends were observed using a scanning electron microscope (SEM) (JSM-6700F JEOL) at an acceleration voltage of 5 kV. The samples were cryogenically fractured in liquid nitrogen and the cross sections were coated with a conductive platinum layer before observation.
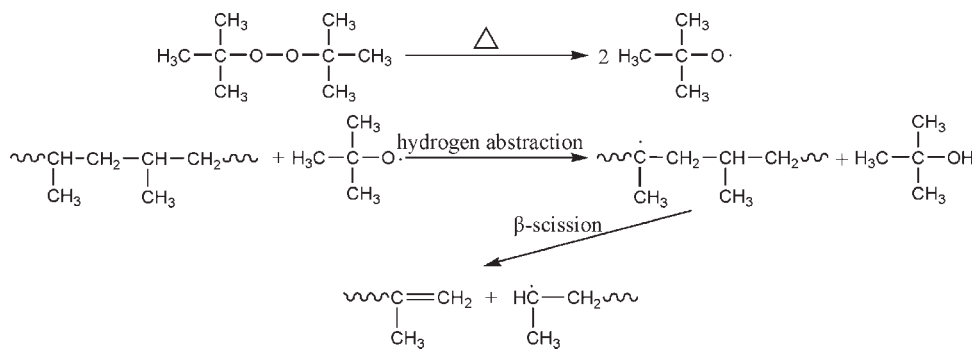
Scheme 1   DTBP-induced degradation of PP.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurement of PP/PS blends was performed with a Perkin–Elmer differential scanning calorimeter (DSC-7). Samples were first heated from 20 to 200°C and held at this temperature for 5 min to eliminate thermal history, then cooled to 20°C and held for 5 min, and finally heated again from 20 to 200°C. Both the heating and cooling rates were 10°C/min. The thermograms of cooling and second heating runs were recorded.

RESULTS AND DISCUSSION

Controlled degradation of polypropylene

Table I shows the MFR values of series of degraded PP with different amount of TETD and DTBP. MFR values of neat PP and PP only added TETD increase slightly after twin-screw extrusion, compared with neat PP. The addition of DTBP, as expected, resulted in obvious increase of MFR from 4.6 to 9.9 g/10 min. To control the degradation of PP, TETD was added as a degradation depressor during melt processing. It can be seen that the addition of TETD can inhibit the degradation of PP effectively and cause the decrease of MFR. MFR of the series of PP added both DTBP and TETD fall into the range of 6.0–7.1 g/10 min, an intermediate value between neat PP and PP with only DTBP. It is also noticed that the content of TETD has little influence on the MFR of degraded PP when DTBP concentration fixed at

0.2%, implying that TETD even at very low concentration can effectively depress the degradation of PP. Therefore, PP with desired MFR can be obtained by controlling the ratio of DTBP/TETD reasonably. And PP/PS blends in next section were prepared by adding TETD only 0.08% to investigate the influence of different DTBP concentration and different ratios of PP to PS on PP degradation and grafting reaction. The mechanism for controlled degradation of PP by DTBP/TETD pair is proposed below in detail.

It is generally recognized that the free radicals generated by thermal decomposition of DTBP abstract the tertiary hydrogen atoms from PP backbone and accelerate β-scission of PP. The schematic illustration of DTBP-induced degradation of PP is shown in Scheme 1. On the other hand, dithiocarbamate radicals formed by thermal decomposition of TETD can promptly capture PP macroradicals,[41] which reduces the instantaneous concentration of free radicals of PP and consequently depresses the β-scission of PP. Therefore, the addition of TETD can control the degradation of PP, and the reaction between dithiocarbamate radicals and PP macroradicals is reversible,[40] which is beneficial to the following grafting and other polymerization process under appropriate conditions. Scheme 2 shows the reaction between TETD and PP macroradicals.

In situ compatibilization of PP/PS blends

Based on the role of TETD in controlling degradation of PP, PP/PS blends with different DTBP/TETD
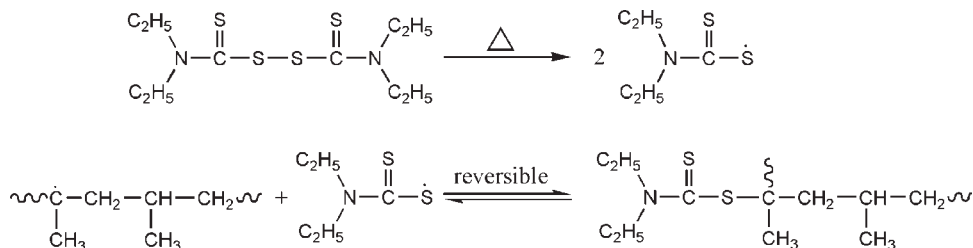
Scheme 2   Reaction between TETD and PP macroradicals.

TABLE II
**Composition and MFR Values of**
PP/PS/DTBP/TETD Blends

Composition (wt %)				
PP	PS	DTBP	TETD	MFR (g/10 min)
98	2	0.2	0.08	13.9
95	5	0.2	0.08	12.9
92	8	0.2	0.08	13.6
90	10	0.2	0.08	17.7
85	15	0.2	0.08	16.9
90	10	0.1	0.08	9.5
90	10	0.4	0.08	60.0
90	10	0.6	0.08	94.2
90	10	0	0	5.6
90	10	0.2	0	48.4
90	10	0	0.08	8.4

ratios were prepared by reactive extrusion. The aim of adding TETD is to both reduce the β-scission of PP macroradicals and increase the opportunity of grafting reaction between PP and PS.

MFR values of PP/PS blends with different amount of DTBP and TETD are shown in Table II. Obviously, the MFR of PP/PS/DTBP (90/10/0.2) is much higher than that of PP/PS/DTBP/TETD (90/10/0.2/0.08), which accords with the conclusion that adding TETD can depress the degradation of PP. The MFR values rise dramatically with the increase of DTBP from 0.1 to 0.6% for the series of PP/PS/TETD (90/10/0.08) blends, whereas the increase of PS content from 2 to 15% has little influence on the MFR values of the blends with the same DTBP/TETD (0.2/0.08) ratio. Therefore, it is easier to achieve the controlling of MFR by regulating the ratio of DTBP/TETD than changing the content of PS, and PP/PS blends with desired MFR values can be obtained through such a method.

Figure 1 presents the variations of dynamic moduli (G' and G''), tan δ, and complex viscosity η* against angular frequency ω of PP/PS blends at 190°C. Both storage and loss moduli of PP/PS/DTBP (90/10/0.2) decrease distinctly compared with pure PP/PS (90/10) blend, indicating that the former blend has much lower molecular weight caused by peroxide-induced degradation. PP/PS/DTBP/TETD (90/10/0.2/0.08) has moderate dynamic moduli due to the controlled degradation of PP by adding TETD. The decrease of tan δ at low frequency generally corresponds to the increase of relaxation time and for polymer melts, relaxation time is correlated with the macromolecular structure, including molecular weight, long chain branches, and so on.[42–44] Figure 1(b) shows that the tan δ of sample with both DTBP and TETD is much lower than that of PP/PS blend only with DTBP, indicating the enhancement of elastic deformation whereas the relative decrease of viscous flow. The change of complex viscosity of

PP/PS blends is consistent with that of dynamic moduli and tan δ [Fig. 1(c)]. With the decrease of the molecular weight of PP by peroxide-induced degradation, the viscosity of PP/PS blends decreases
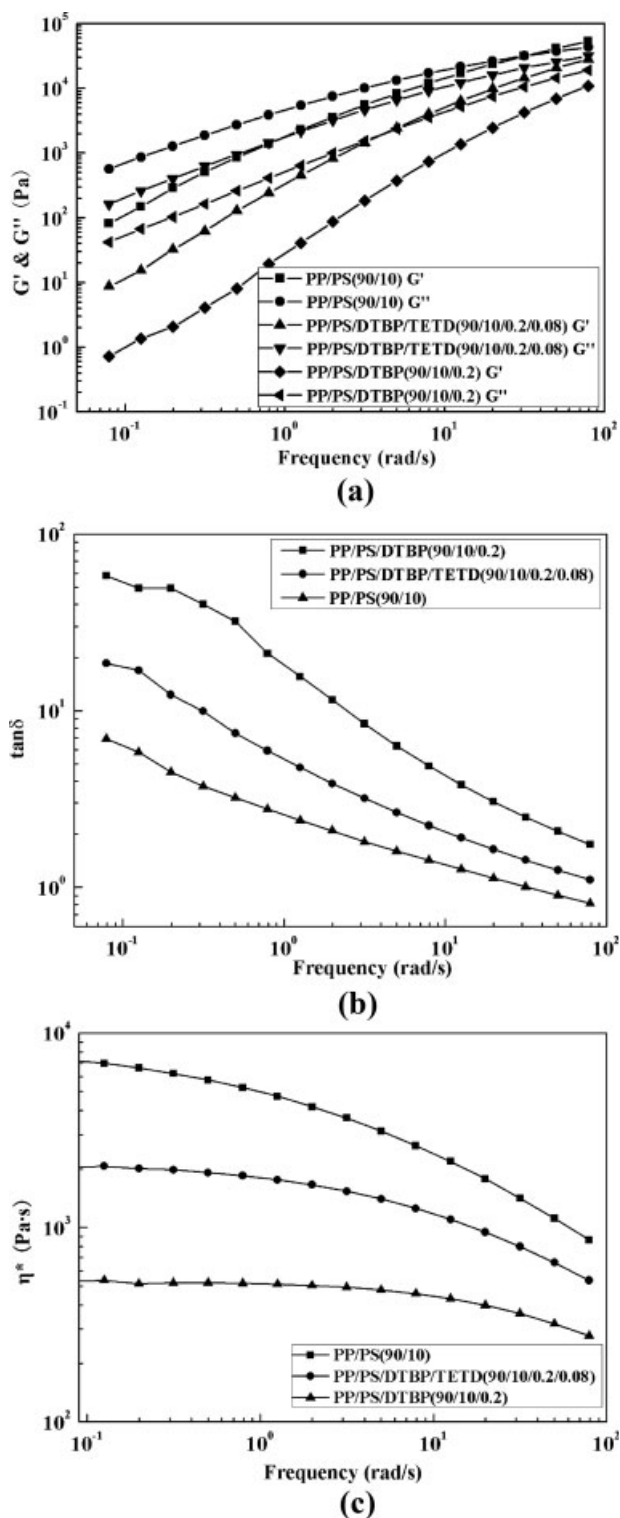

Figure 1 (a) Storage modulus G' and loss modulus G'', (b) tan δ, and (c) complex viscosity η* versus angular frequency ω of PP/PS (90/10) blends at 190°C.
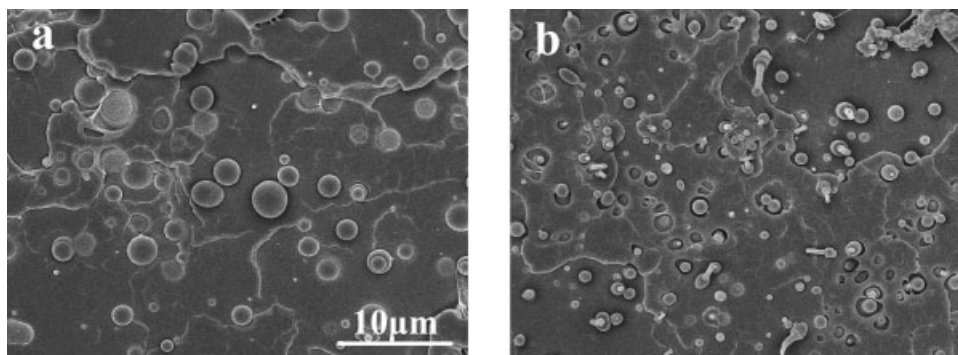
Figure 2 Influence of TETD on the morphology of PP/PS/DTBP (90/10/0.02) blends: (a) without TETD; (b) with TETD.

distinctly. The present rheological results further confirm that the degradation of PP in the PP/PS blends can be effectively controlled by the addition of TETD, implying the potential formation of PP-*g*-PS copolymer.

The phase structure of PP/PS blends also changes with the existence of different additives (Fig. 2). Both the PP/PS/DTBP (90/10/0.2) blends with or without TETD exhibit typically incompatible sea-island bi-phase structure; however, with the addition
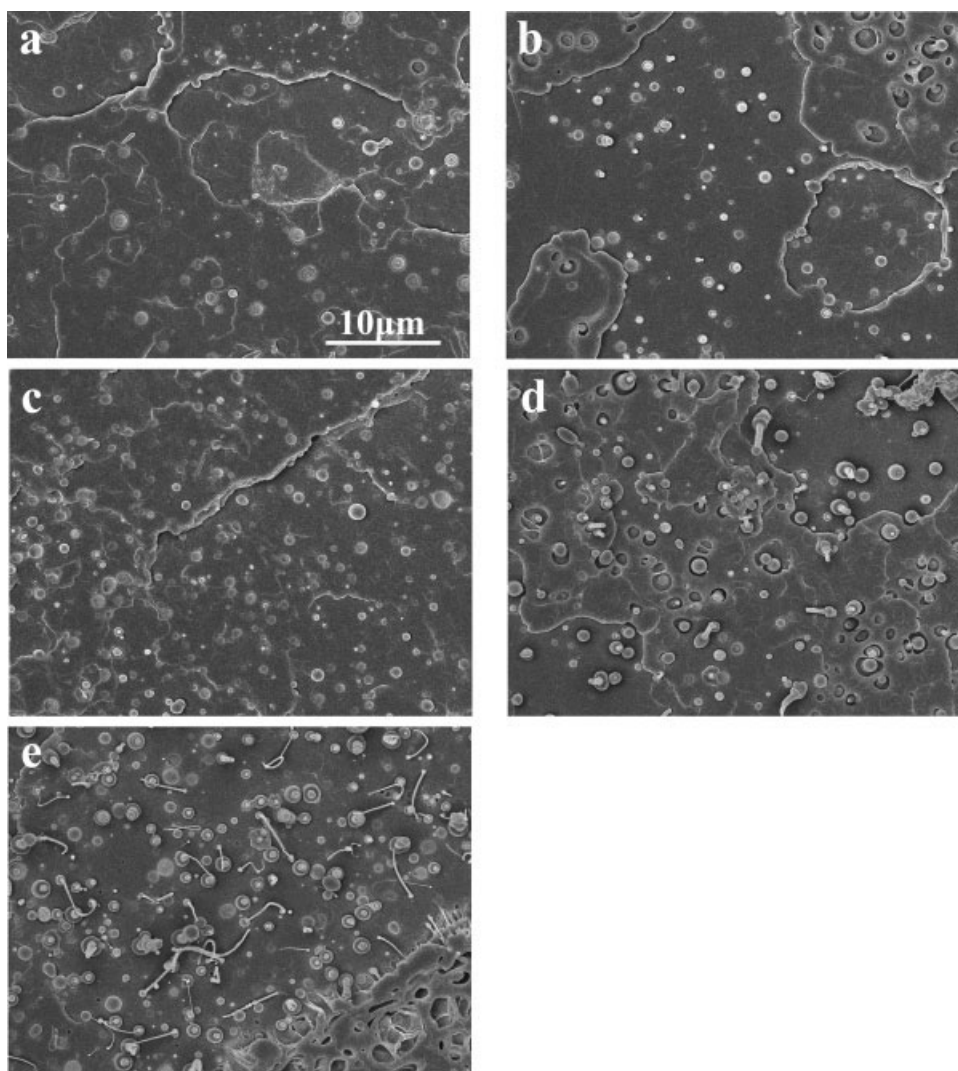
Figure 3 SEM micrographs of PP/PS blends with different PS content: (a) PP/PS/DTBP/TETD = 98/2/0.2/0.08; (b) PP/PS/DTBP/TETD = 95/5/0.2/0.08; (c) PP/PS/DTBP/TETD = 92/8/0.2/0.08; (d) PP/PS/DTBP/TETD = 90/10/0.2/0.08; (e) PP/PS/DTBP/TETD = 85/15/0.2/0.08.
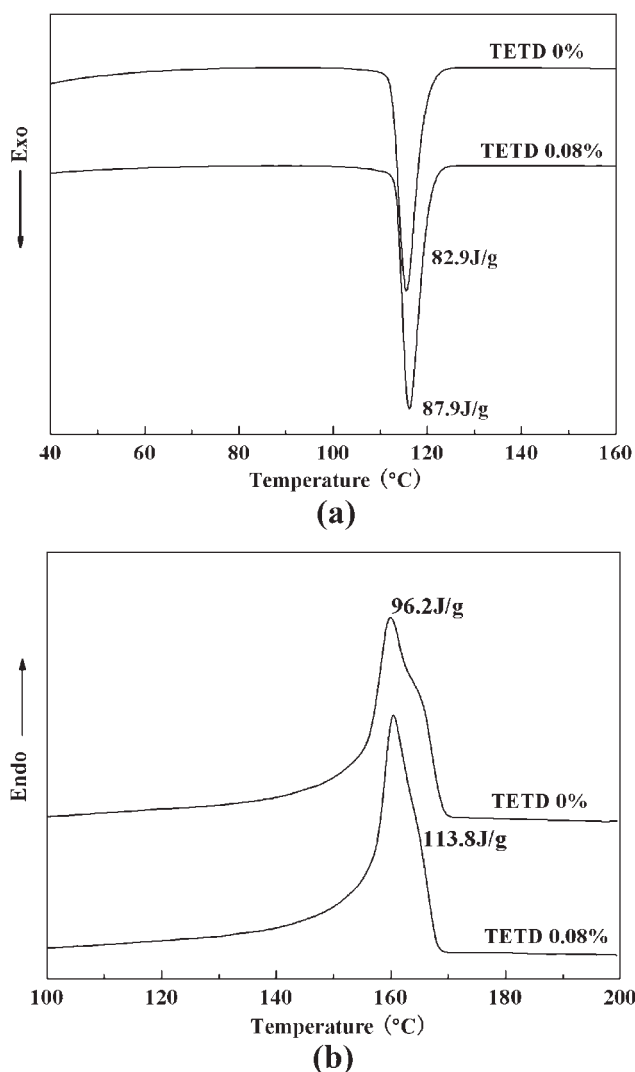
Figure 4 DSC thermograms of PP/PS/DTBP (90/10/0.2) and PP/PS/DTBP/TETD (90/10/0.2/0.08) blends: (a) crystallization scan; (b) melting scan.

of TETD, the average particles size of PS phase decreases clearly and some fibrous structures emerge in the fractured surface. Two reasons might be taken into account to explain the results. On one hand, the existence of TETD promotes the formation of PP-*g*-PS copolymer which behaves as an efficient compatibilizer for PP/PS blend and enhances the interfacial interaction of PP and PS. On the other hand, the dispersion of PS must be related to the viscosity ratio $\lambda = \eta_{PS}/\eta_{PP}$ in the blends, and the bigger λ in PP/PS/DTBP (90/10/0.2) owing to serious degradation arouses the aggregation of PS phase. Micrographs in Figure 3 demonstrate that under the constant ratio of DTBP/TETD (0.2/0.08), the size of PS particles in all the five blends is much smaller compared with the sample without TETD [Fig. 2(a)]; whereas PS content has no obvious influence on the particles size just like MFR, indicating that the combinative application of DTBP and TETD

causes limited and similar degradation of PP, and leads to formation of PP-*g*-PS for samples with different PS content. According to Figures 2 and 3, it can be concluded that TETD plays important roles in controlling the degradation of PP and promoting compatibilization of PP/PS blends by the possible formation of PP-*g*-PS copolymer.

The crystallization and melting behaviors of PP must be greatly influenced by the possible formation of PP-*g*-PS copolymer under the coexistence of DTBP and TETD. Figure 4 shows the DSC thermograms of PP/PS/DTBP (90/10/0.2) and PP/PS/DTBP/TETD (90/10/0.2/0.08). Both crystallization and fusion enthalpy of PP are all higher for blend with TETD than the one without. It indicates that the crystallinity of PP has been improved. Furthermore, both the crystallization and melting peaks of PP become sharper when the sample PP/PS/DTBP (90/10/0.2) added TETD, which means that the existence of TETD also increases the crystallization and melting rates of PP as well as the perfection of crystals. The reason for above results might be also ascribed to the addition of TETD which enhances intermolecular interaction and optimizes the interface of PP and PS.

Based on the above results and discussion, the mechanism for the REX of PP/PS blends with the coexistence of DTBP and TETD is proposed. As mentioned earlier, the dithiocarbamte radicals can react with PP macroradicals, and the reaction is reversible. After adding PS, the reverse reaction of PP macroradicals bonding with dithiocarbamte radicals in Scheme 2 can be easier to occur, providing enough PP radicals and promoting the opportunity
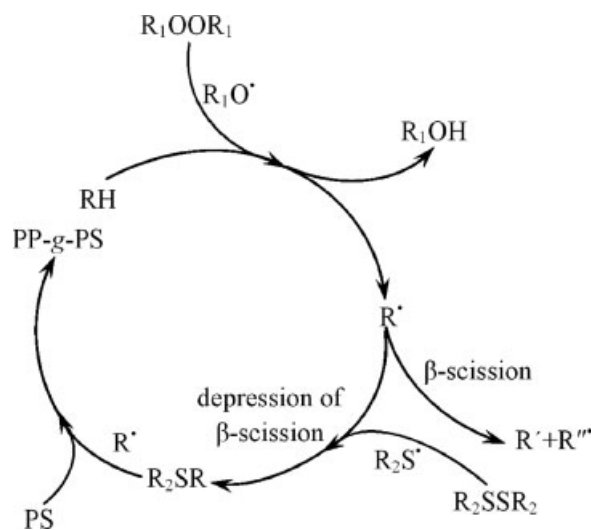
Scheme 3 Schematic illustration for the possible formation of PP-*g*-PS copolymer during the reactive extrusion of PP and PS controlled by the coexistence of DTBP and TETD.

of PS grafting to PP macromolecules and formation of PP-*g*-PS copolymer. Scheme 3 illustrates the formation of PP-*g*-PS copolymer in PP/PS blends with the coexistence of DTBP and TETD in detail, where RH, R_1 and R_2 refer to PP, $(CH_3)_3C$, and $(C_2H_5)_2$ NC=S, respectively.

CONCLUSIONS

In situ compatibilization of PP/PS blends by controlled degradation and REX has been carried out in this work. Peroxide-induced degradation of PP can be effectively controlled by the addition of tetraethyl thiuram disulfide. With the coexistence of DTBP and TETD, PP-*g*-PS copolymer can be *in situ* formed in PP/ PS blends. As a compatibilizer for PP/PS blends, the PP-*g*-PS copolymer optimizes the dispersion of PS in PP matrix and reduces its particles size. Furthermore, the crystallinity, perfection of crystals, and crystallization and melting rates of PP are all increased due to the enhanced compatibility of PP and PS.

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