Polymer 51 (2010) 500–506

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Study on degradation and crosslinking of impact polypropylene copolymer by dynamic rheological measurement

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ARTICLE INFO

Article history:
Received 10 December 2008
Received in revised form
15 September 2009
Accepted 30 November 2009
Available online 4 December 2009

Keywords:
Dynamic rheological behavior
Degradation
Crosslinking

ABSTRACT

The structural stability of impact polypropylene copolymer (IPC) melt under high temperatures was explored by dynamic rheological measurement. The structure changes including degradation and crosslinking of IPC were discussed through examining the influence of temperature and additive antioxidant on dynamic rheological functions. A plateau of dynamic storage modulus (G') appeared in low frequency region at high temperatures under air atmosphere. Furthermore, when IPC sample was annealed at 230 °C, its viscoelasticity presented a dramatic change. The time dependences of G' for pure IPC at different temperatures were investigated. At 190 °C, a slight drop and a succedent rise of G' for IPC0 appeared. The decrease period of G' generally shorted and the increase of G' became more remarkable with the increase of temperature. The decrease of G' was ascribed to the degradation in IPC and the G' increase was due to the crosslink reaction. Through incorporation of antioxidant into IPC, the crosslinking in IPC could be effectively inhibited, and the degradation and crosslinking in IPC were believed to result from PP component.

1. Introduction

Most of polymeric materials need undergo melt processing before being employed. Usually, the processing conditions, such as elevated temperature, the presence of oxygen, and mechanical stresses *etc*, would lead to the changes in chemical structure of macromolecule, which can considerably influence the liquid and solid-state properties of polymers. Since it is important to understand the effects of processing conditions on the chemical structure for optimizing the properties of polymeric materials, much attention has been paid to thermal and thermo-oxidative degradation of polymer melts in the past several decades. Various analytical techniques, including thermogravimetric analysis (TGA) [1–3], gel permeation chromatography (GPC) [3–6], differential scanning calorimetry (DSC) [6,7], Fourier-transfer infrared spectra (FT-IR) [7,8], scanning electron microscopy (SEM) [8–10], nuclear magnetic resonance spectroscopy (NMR) [6,7,11], temperature rising elution fractionation (TREF) [6,9,11] and rheology [12–19], have been employed to detect the change in chemical structure of macromolecule. Among these, dynamic oscillation rheology, especially under the low frequency, was found to be one of the most efficient techniques for detecting chemical reactions and microstructural transformation of polymers due to chain scission and recombine, because different polymer chains could behave diagnostic viscoelastic response in long time regime due to the difference of relaxation rate [16–22]. In addition, another excellence of dynamic oscillate rheological measurement is that its strain is too small to damage the structure of a polymer [16,17,19,21,22].

Impact polypropylene copolymer(IPC), also so-called polypropylene catalloys (PP-cats) or polypropylene impact copolymer, is an *in situ* polypropylene copolymer prepared by two-step polymerization: bulk polymerization of propylene and then gas-phase copolymerization of ethylene and propylene with a spherical superactive $TiCl_4/MgCl_2$ based catalyst systems [23–26]. Since IPC can provide better mechanical properties i.e. impact strength and production costs than general modified polypropylenes by mechanical blending with thermoplastic elastomer, in last decade, many studies on composition, microstructure, morphology, crystallization and melting behavior of IPC have been conducted [23,27–34], and it was found that the IPC mainly consisted of three compositions: *propylene homopolymer*(*PP*), *ethylene–propylene random copolymer* (*EPR*) and *ethylene–propylene block copolymer with different segment lengths* (*E-b-P*) [23–26,34]. It is noticed that both propylene homopolymer and ethylene–propylene random copolymer are prone to

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doi:10.1016/j.polymer.2009.11.066

thermal and thermo-oxidative degradation at high temperatures, as reported by many researchers [35–37]. Furthermore, being an *in situ* catalloy, IPC has a broad molecule weight distribution and there probably exist some copolymers with low molecule weight, thereby, it is reasonably suspectable that these copolymers with low molecule weight would lead to the instability of IPC melt at high temperatures. Based on the above-mentioned aspects, it is necessary to investigate the possible change in chemical structure of IPC under conditions of high temperatures and oxygen atmosphere as well their effects on melt properties.

Recently, Terano et al. [38] reported thermal degradation of polypropylene impact copolymer through atomic force microscopy (AFM) observation. It was found that degradation behavior of the copolymer was heterogeneous and the PP matrix was degraded selectively whereas the EPR phase was hardly degraded. Nakatani et al. [11] studied the thermal oxidative degradation of polypropylene impact copolymer with its fractions obtained using TREF and found that the rate of degradation was dominated by the content of tertiary C–H bonds (propylene unit). Tochacek et al. [9] studied the effect of processing on molecular structure and properties of polypropylene impact copolymer and found that the biggest portion of the degradation changes took place in the PP homopolymer phase and crosslinking took place in the rubbery phase.

In our previous work, the abnormal viscoelastic behavior of IPC melt at high temperatures has been reported [39]. In present article, the changes in molecular structure including degradation and crosslinking of IPC melt at high temperatures are investigated by dynamic rheological measurement, and the effects of temperature, atmosphere and antioxidant on stability of IPC melt are discussed to understand the origins of degradation and crosslinking in IPC melt.

2. Experimental

2.1. Materials and sample preparation

A commercial impact polypropylene copolymer (EPS30R, $\overline{M}_n = 9.16 \times 10^4$ and $\overline{M}_w = 3.81 \times 10^5$, supplied by Sinopec Qilu Petrochemical Co. of China) was used in this work. The isotactic polypropylene (*i*PP) with granule form (T300, $\overline{M}_n = 1.14 \times 10^5$, $\overline{M}_w = 3.83 \times 10^5$, supplied by Sinopec Shanghai Petrochemical Co. of China) was selected as a reference. A complex antioxidant, B215, combined substance of antioxidant 1010 (terakis[methylene-β-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate]methane) and antioxidant 168 (tri(2,4-di-tert-butylphenyl)phosphate), was used as stabilizer system in this study and supplied by Nanjing Milan ChemEng. Ld co. The IPC samples containing different antioxidants (0, 1, 3 and 5 wt%) were named as IPC0, IPC1, IPC3 and IPC5, respectively. All the IPC samples were prepared by mixing on a Haake Rheomix at 165 °C for 5 min. The rotor rate was set at 45 rpm. Disks about 1.5 mm in thickness and 25 mm in diameter were prepared by compression molding at 170 °C under 10 MPa for the following rheological measurements. The specimens with rectangle shape of 30 mm × 12 mm × 1.5 mm for pure *i*PP and IPC0 were prepared by compression molding at 170 °C for DMA test.

2.2. Dynamic rheological tests

The DMA measurements were carried out on a Q800 Dynamic Mechanical Analyzer (TA Instruments Corporation, USA). The single cantilever clamp and the bend mode were used to the temperature sweep under a heating rate of 5 °C/min and a frequency of 1 Hz.

The dynamic rheological tests were conducted on an Advanced Rheometric Expansion System (ARES, TA Instruments Corporation, USA) with parallel plate geometry of 25 mm diameter under air and N_2 respectively. Here, without special indication, the experiments always were carried out under air atmosphere. Two sorts of tests were performed under conditions as follows: 1. isothermal frequency sweeps from 100 to 0.01 rad s^{-1} at the temperature range from 190 to 230 °C; 2. isothermal time sweeps at a frequency of 0.05 rad s^{-1} at the temperature range from 190 to 230 °C. A strain of 5% was applied in all tests, which was ensured within the linear viscoelastic range.

2.3. GPC measurements

Weight-average molecular weight ($\overline{M}_w$) and polydispersity of molar mass for virgin and treated IPC samples were determined by gel permeation chromatography (GPC) at 150 °C. The GPC system used is a PL-GPC220 equipped with three PLgel 10 mm MIXED-B columns using polystyrene as standards and 1,2,4-trichlorobenzene (1.0 mL min^{-1}) as the eluent. Table 1 lists the molecular weight and polydispersity data of virgin IPC and dissoluble parts of treated IPC samples.

2.4. SEM observations

Fracture surfaces of IPC specimens at liquid nitrogen were etched in xylene for 4 h at 50 °C, and were observed by means of a scanning electron microscope (JSM-5510LV, JEOL, Japan) after coating gold–palladium. An operating voltage of 25 kV and the magnifications of 1000 and 10 000 were used.

3. Results and discussion

3.1. Composition and phase structure of IPC

As reported previously [23–26,34], IPC has a complex composition and contains three components: propylene homopolymer, ethylene–propylene random copolymer and ethylene–propylene block copolymer with different segment lengths. Fig. 1 gives the plots of tan δ versus temperature for virgin IPC and *i*PP samples. Two obvious peaks corresponding to glass transitions of different components could be seen at −34 and 25 °C. This result is in accordance with our previous report about another IPC (polypropylene catalloys), in which its glass transition was detected by a modulated DSC [30]. Therefore, the tan δ peak at −34 °C for IPC is ascribed to the ethylene–propylene random copolymer (EPR) and the other peak at 25 °C to propylene homopolymer (PP). To prove this deduction, the DMA curve of pure *i*PP sample was also demonstrated in Fig. 1 and a single tan δ peak at about 23 °C could be observed. These results suggest that EPR and PP are main components in IPC and their contents are high enough so their glass transitions could be detected. Contrarily, although the existence of E-*b*-P component has been proposed [23,24,26], and E-*b*-P copolymer was confirmed through extraction fractionation and thermal analysis [30], its glass transition behavior could hardly be

Table 1
Molecule weight and molecular weight distribution of virgin IPC and IPC0 samples treated at different temperatures for 130 min.

Sample	Peak No	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	PD
IPC0-190	–	6.29	22.55	3.58
IPC0-210	1	8.17	22.11	2.70
	2	0.11	0.14	1.42
IPC0-230	1	6.85	17.31	2.52
	2	0.10	0.14	1.42
IPC		9.16	3.81	4.38

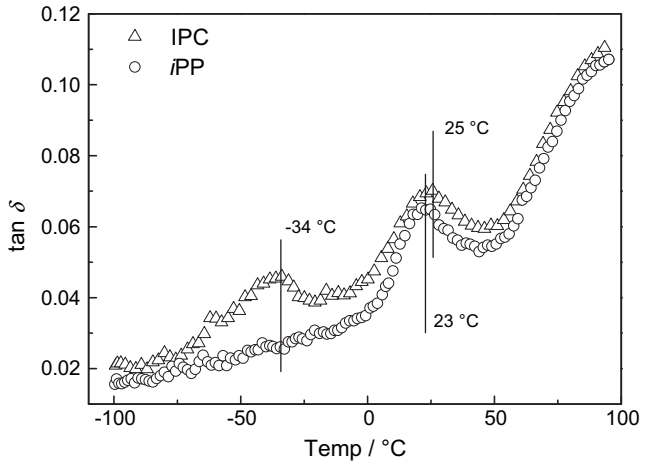

Fig. 1. Temperature dependences of tan δ for pure IPC and *i*PP at a frequency of 1 Hz and a heating rate of 5.0 °C/min.

observed in Fig. 1. There are three possible explanations; i. The E-*b*-P content in IPC is so low that DMA couldn't detect its glass transition; ii. The E-*b*-P couldn't exhibit an unaided glass transition because it consists of a series of block copolymers with different ethylene and propylene segment lengths; iii. The polymer chain motions of E-*b*-P are restricted by EPR and PP and couldn't independently move since E-*b*-P is believed to play a role of compatilizer between EPR and PP [23,32,34]. Furthermore, the detected glass transitions of IPC in Fig. 1 show that EPR and PP are phase-separated in IPC.

Fig. 2 demonstrates the morphology of fracture surface for IPC after being etched. A two-phase structure with good dispersion could be found from Fig. 2a. The EPR spherical granules uniformly disperse in PP matrix. Fig. 2b gives an enlarged micrograph of this morphology. A dimension distribution from 0.5 to 1 μm could be observed. For rubber-toughening in polypropylene, Jang et al. [40]. proposed that 0.5 μm was a critical particle diameter of elastomer and only the rubber particles with larger dimensions than the critical diameter could promote crazing and improve the fracture resistance of PP. It is obvious that the sizes of EPR particles in IPC are almost beyond the above critical dimension. Thus, it is believed that the excellent toughness of IPC (12.55 kJ m^{-2} under 28 °C and 4.01 kJ m^{-2} under −20 °C, simply supported beam) results from the uniform dispersion and appropriate size of EPR.

3.2. Instability of IPC melts at high temperature

Fig. 3 gives isothermal frequency (ω) dependence of the dynamic storage modulus (G') for IPC0 at different temperatures under air and N_2, respectively. Under air atmosphere, it can be seen that G' drops with the decrease of ω at 190 °C. However, an obvious raise of G' could be observed in low ω region at 210 °C, indicating the appearance of a 'second plateau'. In addition, the G' plateau appears earlier and the value of G' at lower ω is higher when temperature increases to 230 °C. According to common understanding, the appearance of the 'second plateau' results from the existence of a higher-order structure in multicomponent system, such as sol–gel transition, crosslinking and phase-separation etc [18]. It is interesting that under N_2 condition no second plateau appears on the $G' \sim \omega$ curve of IPC1 sample and its $G' \sim \omega$ curve shape is similar to that of PP homopolymer. These results show that the second plateau appearing under air has nothing with the phase-separation structure of IPC and should be attributed to some changes in chemical structure of IPC0 at higher temperatures.

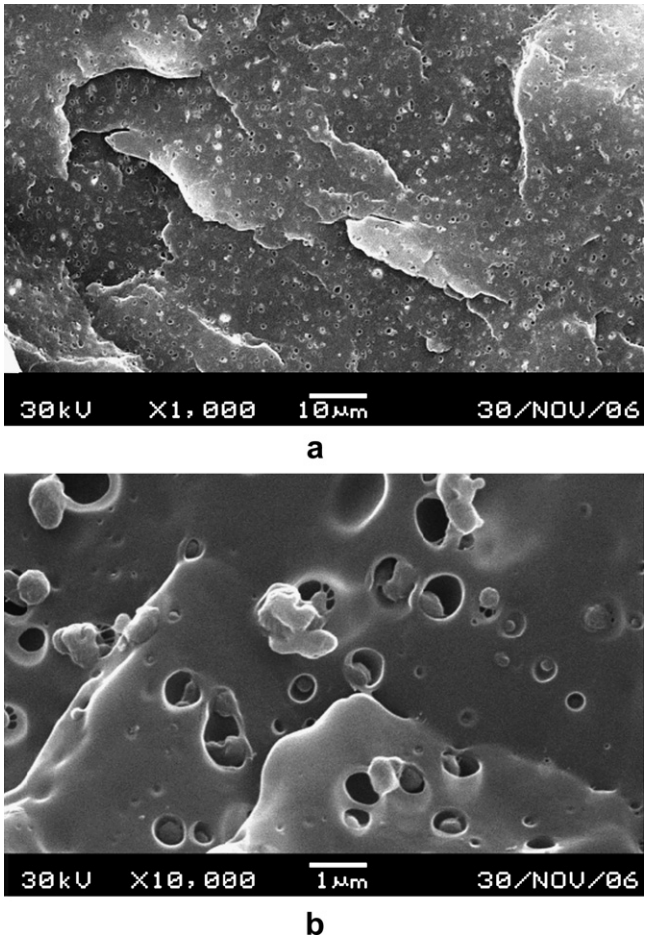

Fig. 2. SEM micrographs of fracture surface of the IPC in different magnifications.

Fig. 4 gives the evolutions of rheological functions, G' and dynamic loss modulus (G''), of IPC0 under 230 °C. It can be seen that G'' of IPC seems unchanged at the early stage and then rises slowly with time. Contrarily, an evident increase of G' appears after a 10 min standstill at the early stage. It is noted that at the early stage, the value of G'' is higher than that of G', showing that the viscosity of IPC0 dominates in melt. Since G' increases much faster than G'' during most of test period, a critical time at which the value of G' and G'' is equal appears and it divides the curves into two parts. The value of G' becomes higher than that of G'' after 73 min, indicating that the elasticity of the melt is dominant at this stage. The above facts show that IPC melt has different viscoelasticity with time under isothermal condition. Usually, similar situations only take place in sol–gel transition, cure or crosslinking of polymeric materials. Thus, the change in viscoelasticity is definitely regarded as a sign of instability for IPC melt. Moreover, Compare to G'', the variation of G' is more obvious, indicating that G' is suit for describing the change of IPC structure.

3.3. Degradation and crosslinking in IPC melts at high temperature

Fig. 5a shows the influence of temperature on time dependence of G' for IPC0 samples, and two different situations appear. Under isothermal condition of 190 °C, the storage modulus of IPC0 appears a slight drop before it begins a much minor rise. With the increase of temperature, the drop period of G' generally shortens and the increase becomes more remarkable. When temperature reaches to 230 °C, the modulus starts to rapidly increase after only

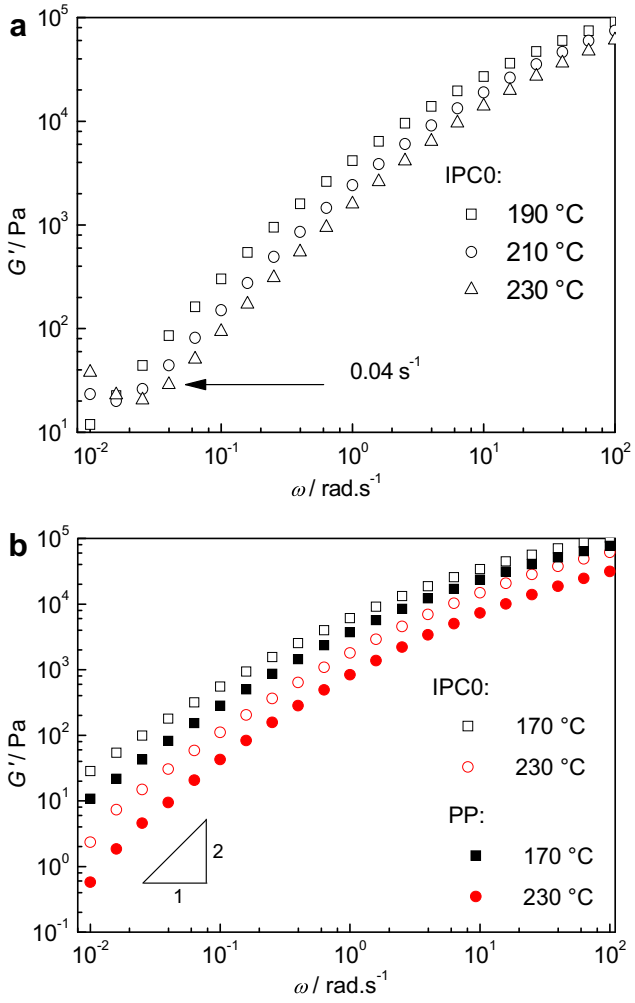

Fig. 3. Relationship between G' and ω for IPC0 at different temperatures under air (a) and under N2 (b).

a transitory constant. Under isothermal condition, the decrease of G' for polymer melt may result from the stress relaxation [12,13] or degradation [13,15,16]. However, the result of relaxation experiment for IPC0 at 190 °C shows that achieving this relaxation only needs no more than 100 s [39]. Taking the fact that polymer melts have usually faster relaxation rate at higher temperature into account, the decrease of G' is impossibly ascribed to the stress relaxation of IPC melt.

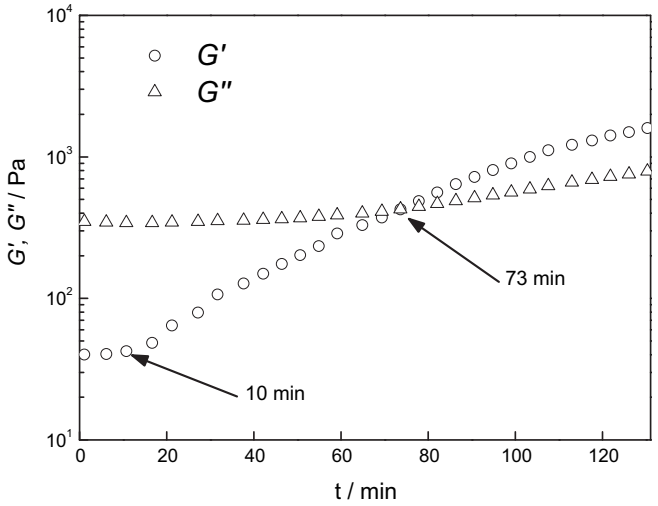

Fig. 4. Time dependences of G' and G'' for IPC0 samples at 230 °C.

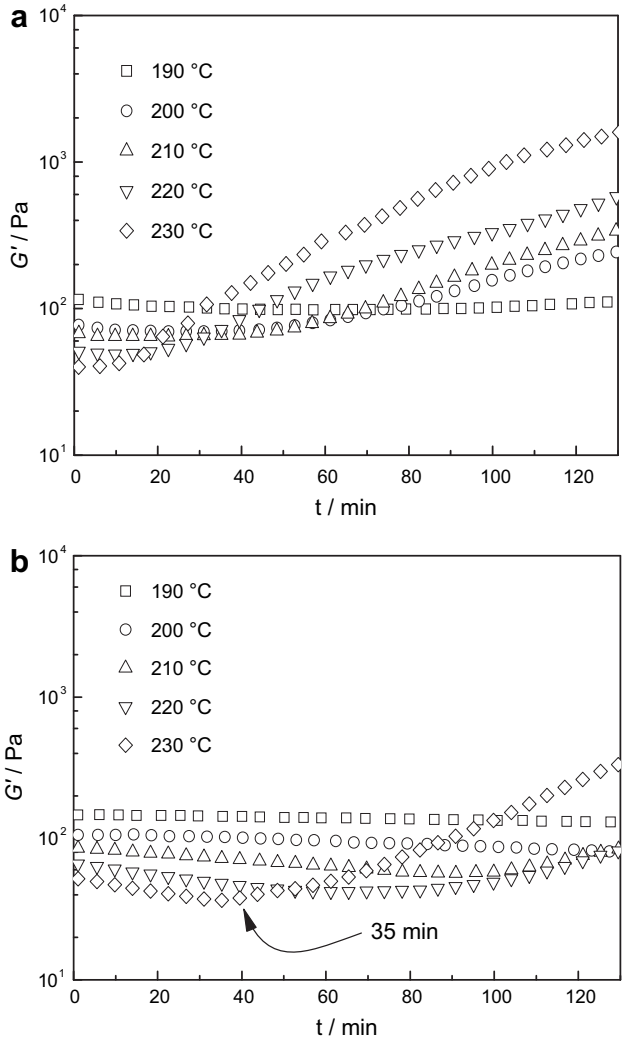

Fig. 5. Time dependences of G' for IPC0 (a) and IPC1 (b) at different temperatures.

It is well-known that EPR is prone to thermal degradation at above 150 °C and PP is apt to thermo-oxidative degradation at high temperatures [35–37]. Because IPC contains EPR, E-*b*-P and PP and there is air around samples in rheological test, the decrease of G' results likely from the degradation reaction in IPC melt. Fig. 6 gives the GPC results of IPC0 samples subjected to isothermal time sweep for 130 min at different temperatures. As shown in Fig. 6a, except the sample treated at 190 °C, both the plots of response versus retention time (*RT*) for IPC0 samples at 210 and 230 °C show two peaks, a strong one at 19 min and a weak one at 24 min. Because the sample treated at 190 °C presents a single strong peak and the longer *RT* means the lower molecular weight, these results prove the occurrence of degradation reaction in IPC samples at high temperatures and the mass with lower molecular weight is the resulting product of IPC degradation. Furthermore, as shown in Table 1, the degraded products have similar molecular characteristic under different temperatures. Fig. 6b gives the fraction plots of molecular weight distributing for IPC0 sample treated at 230 °C. It can be seen that the proportion of lower molecular weight is about 10%, indicating that the degradation in IPC is considerable at this temperature.

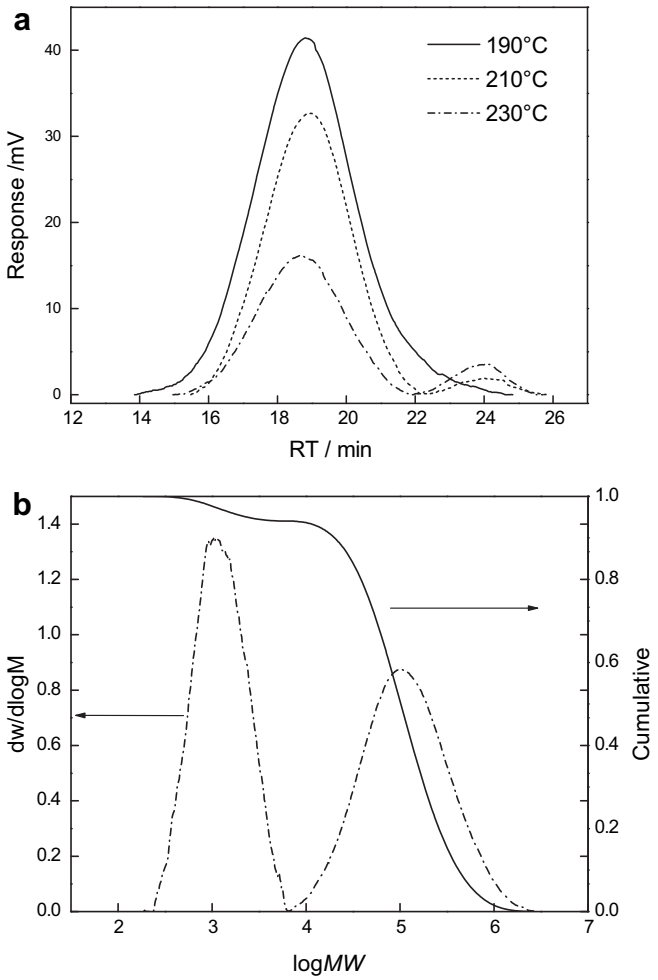

Fig. 6. (a) Plots of *Response* vs. *t* of IPC0 treated at different temperatures for 130 min; (b) Molecular weight distribution of IPC0 treated at 230 °C for 130 min.

As seen in Fig. 5, the increase of G' becomes much obvious with increase of test temperature. Considering the crosslink tendency of EPR and PP at high temperature, this change of G' may result from the crosslink reaction in IPC melt. To prove this deduction, the IPC0 samples subjected to dynamic time sweep experiments at 210 and 230 °C were extracted in boiling xylene by a Soxhlet extractor for 48 h. Through extracting, some undissolved yellow and black substances remained. It is clear that the insoluble substances are the crosslinked products from rheological measurement at high temperatures, indicating the occurrence of crosslinking within IPC0 under high temperatures.

For EPR and PP, their crosslink mechanism has been extensively studied in past decades [35–37]. The crosslink of PP follows two steps: oxidative degradation at high temperature and recombination of the degraded products. However, the crosslink of EPR could be initiated in two routes: additional crosslinking agent or the free radical produced from its thermal degradation. To understand the origin of crosslink reactions in IPC system, the samples containing antioxidant were prepared, and Fig. 5b gives their time dependences of G' at various temperatures. Compared with IPC0, some clear differences could be found; i. The increases of G' at 190 and 200 °C disappear and only a drop of G' could be observed; ii. The increments of G' become smaller when temperature is higher than 200 °C; iii. The onset time of G' increase clearly delays; iv. For all test temperatures, the decreases of G' become more obvious. These results show that the incorporation of antioxidant could effectively

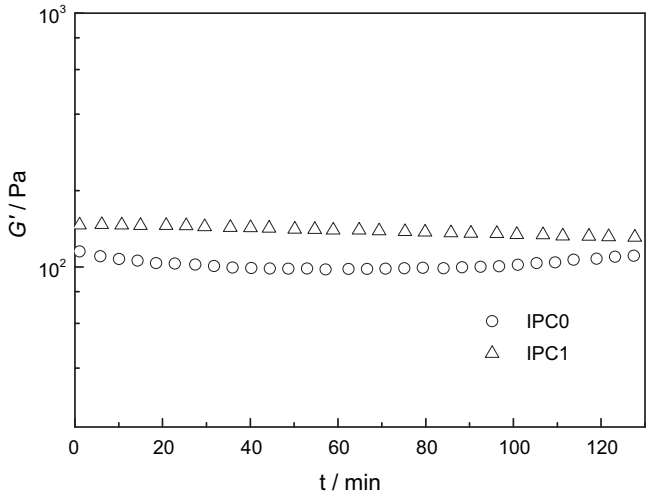

Fig. 7. Time dependences of G' for IPC0 and IPC1 at 190 °C.

inhibit the crosslinking in IPC. It needs to be pointed out that the used antioxidant only consumes the free radical, $RO_2^{\cdot}$, which produced from the oxidative degradation, and could avoid further degradation or crosslinking induced by $RO_2^{\cdot}$ [41,42]. Considering the insensitivity of EPR to oxygen and the lower E-*b*-P content in IPC, the above results indicate that the crosslinking reaction in IPC should result mainly from the PP component.

Fig. 7 shows the time dependences of G' for IPC0 and IPC1 samples at 190 °C. A continuous drop of G' for IPC1could be found at 190 °C. However, Compared with that of IPC0, the G' decrease of IPC1 is more inconspicuous. The used antioxidant has little influence on the thermo degradation product of EPR, thus, the slight decrease of G' of IPC1 indicates that few EPR degrade at 190 °C and thermal degradation of EPR could be ignored. In other words, the G' decrease of IPC0 should be ascribed to the oxidative degradation of PP component at 190 °C. Fig. 8 gives the time dependences of G' for IPC0 and IPC1 samples at 230 °C. The beginning of crosslink reaction at 230 °C could be effectively delayed to 40 min through adding antioxidant into IPC. Furthermore, the plot of G' versus time for IPC0 in N_2 is also demonstrated in Fig. 8. It can be seen that the modulus of IPC0 is almost invariant, and neither obvious degradation nor crosslinking happens under N_2. These results imply that

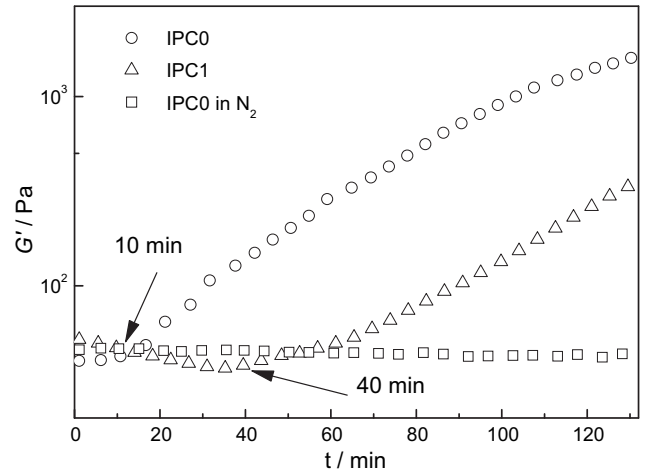

Fig. 8. Time dependences of G' for IPC at 230 °C in air and N_2.

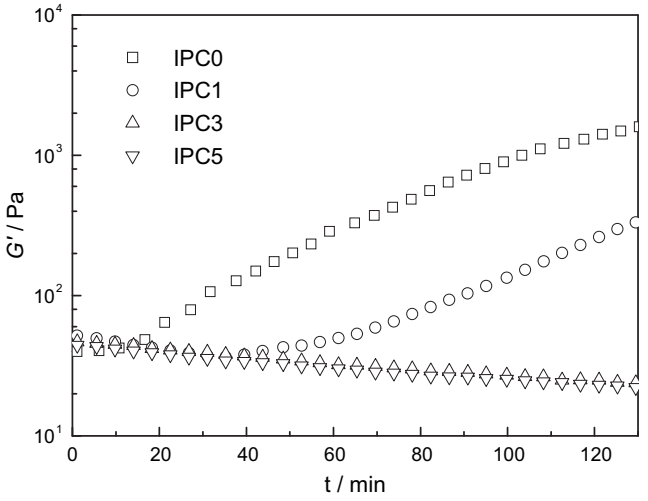

Fig. 9. Dependences of G' on time for IPC samples with different antioxidant amounts at 230 °C.

the oxidative degradation and crosslinking are the main reasons for the instability of IPC0 melt at high temperatures, and the degradation and crosslinking mainly occur in PP component.

3.4. Influence of antioxidant amount on stability of IPC melts

Fig. 9 gives the influence of antioxidant amount on rheological behavior of IPC. At 230 °C, the incorporation of 1 wt% antioxidant into IPC could effectively inhibit the crosslinking until 40 min. Once the antioxidant exhausts, the crosslinking of PP component happens and leads to an increase of G'. Furthermore, when the additive antioxidant is more than 3 wt%, the same rheological behavior could be observed, and both IPC3 and IPC5 present an obvious drop of G'. Just as mentioned above, the used antioxidant could effectively eliminate $RO_2^{\cdot}$ and avoid further degradation or crosslinking resulting from $RO_2^{\cdot}$, but it couldn't completely remove the oxidant-degradation. Considering the stability of IPC in N_2 at 230 °C shown in Fig. 8, the drops of G' for IPC3 and IPC5 seem to only be ascribed to the oxidant-degradation of PP. In other words, these results show that the used antioxidant could effectively prevent the crosslinking, but couldn't completely prevent the oxidant-degradation of PP.

In this work, it is noticed that E-*b*-P and PP components are similar in structure to some certain extent, and the oxidant-degradation of E-*b*-P component is possibly easier to happen. However, since the content of E-*b*-P is lower compared to PP, the roles of PP and EPR in degradation and crosslinking are emphasized.

4. Summary

The degradation, crosslinking and stability of IPC were investigated by dynamic rheological measurements and the influences of temperature, atmosphere and additive antioxidant on dynamic rheological functions were discussed. The DMA results show that ethylene–propylene random copolymer (EPR) and propylene homopolymer (PP) are main components and are in phase-separated state. The SEM observations indicate that EPR has a good dispersion in PP matrix.

Under high temperatures, a 'second plateau' of G' in low ω range appeared, indicating a formation of higher-order structure. Furthermore, the time sweep result at 230 °C shows that the IPC melt presents different viscoelasticity at the early and late stage, implying the instability of IPC melt at high temperatures. The time dependences of G' for pure IPC were investigated at temperature range from 190 to 230 °C. It is found that pure IPC presents different rheological behavior at various temperatures. At 190 °C, a slight drop and a succedent rise of G' for IPC0 appears. When temperature rises, the decrease period of G' generally shortens and the increase becomes more remarkable. At 230 °C, G' increases rapidly after a transitory standstill. The decrease of G' is ascribed to the degradation in IPC and the G' increase is attributed the crosslink reaction. The possible contribution of stress relaxation to the decrease of G' is excluded. The experimental results imply that the oxidative degradation and crosslinking are the main reasons for the instability of IPC0 melt at high temperatures, and the degradation and crosslinking mainly occur in PP component. The incorporation of the antioxidant could effectively prevent the crosslinking, but couldn't completely prevent the oxidant-degradation of PP.

Acknowledgements

This work was supported by National Nature Science Foundation of China (Grant 50603023) and National Basic Research Program of China (No. 2005CB623800).

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