Phase morphology evolution upon melt annealing treatment and corresponding mechanical performance of impact-resistant polypropylene copolymer

Yefei Tian a, Shijie Song a, Jiachun Feng a,∗, Jianjun Yi b

a State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science and Laboratory of Advanced Materials, Fudan University, Shanghai 200433, PR China
b Key Laboratory of Synthetic Resin Research, Institute of Petrochemical Technology, China National Petroleum Corporation, Beijing 100083, PR China

A R T I C L E   I N F O

Article history:
Received 21 July 2011
Received in revised form 27 January 2012
Accepted 29 January 2012

Keywords:
Polymers
Annealing
Microstructure
Mechanical properties
Structure–property relations

A B S T R A C T

The evolution of phase morphology upon melt annealing and the corresponding changes in mechanical properties of impact-resistant polypropylene copolymers (IPCs) have been systematically investigated. A distinct coarsening process is observed during melt annealing and the statistical analysis of stereology reveals that the increase of dispersed domain size well follows the Ostwald ripening mechanism. Mechanical tests suggest that the noted impact strength and elongation at break decrease gradually with increasing annealing time, while the tensile strength remains relatively constant. The decrease of toughness is consistent with the size increase of dispersed domains, which may result from the development of late-stage phase separation of IPC. However, the tensile strength, which is mainly dominated by the crystalline phase structure, remains relatively constant during the annealing treatment. On the basis of these results, the probable relationship between the change of mechanical properties and phase morphology evolution has been proposed.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

As one of the most important multiphase polymer systems, impact-resistant polypropylene copolymer (IPC) has been widely used in injection-molded parts for automotive, appliance and other durable goods applications, as well as for extruded sheet and thermoforming. IPC is typically prepared by a multi-stage polymerization process using a spherical, superactive TiCl4/MgCl2 based catalyst, which involves bulk polymerization of propylene in the first stage and gas-phase copolymerization of propylene and ethylene in the second stage [1–4]. Previous studies have verified the complexity of IPC both in its composition and phase structure [5–13]. Mirabella et al. [5] demonstrated IPC was mainly composed of isotactic polypropylene (iPP), amorphous ethylene–propylene rubber (EPR) and semicrystalline ethylene–propylene block copolymer with different sequence length (E–b–P) through temperature-rising elution fractionation technique. Yang et al. [7,8] and Urdampilleta et al. [9] testified the heterogeneous phase structure of IPC, which presented a droplet distributed phase separated structure, by means of transmission electron microscopy and atomic force microscopy. Generally speaking, as an in-reactor alloy, IPC is mainly composed of a matrix of iPP in which EPR is finely dispersed. Besides, some partially crystalline copolymers, either E–b–P block copolymers or so-called EP segmented copolymers, with different lengths of PE or PP segments are proved to exist as well [10]. The spatial entanglement of crystallizable PE segments with EPR chains, as well as E–b–P component with EPR chains, leads to the unique multi-phase core–shell structure, in which the E–b–P component usually forms as a shell around the dispersed phase and the crystallizable PE as a core of dispersed domain [8]. Our previous work also verified this multi-layered core–shell structure of IPC through investigating the mechanism of the shear-enhanced crystallization and subsequent relaxation behaviors [11–13]. So far, though it is generally accepted that the excellent rigidity–toughness balance and superior properties of IPC originate from its complex compositional heterogeneity and unique heterogeneous morphology, a complete understanding of the multi-scale phase structure and morphology in IPC as well as its evolution towards the equilibrium state has not been achieved yet.

In practical thermoplastic processing, polymer resin has to be heated to a molten state and experience both flow and shear for a certain time and then be cooled to room temperature. The multi-scale phase structure and the consequential final performance of IPC are strongly influenced by the thermal history in the molten state. Therefore, it is meaningful and necessary to investigate the evolution of phase morphology upon melt thermal treatment and further correlate the final mechanical properties...
of IPC with various phase morphologies. Considering the immiscibility of heterogeneous phase polyolefin blends, liquid–liquid phase separation (LLPS) occurred in the molten state during thermal treatment process substantially affecting the formation of new phase as well as the final phase morphology. For semicrystalline heterogeneous phase systems, the situation is more complicated since phase morphology is determined by both LLPS and crystallization. In a simple approximation, components in IPC can be divided into two categories, the crystalline ones (i.e., iPP, partially crystalline polymers with long PE or PP segments) and the amorphous ones (i.e., EPR and PP with very low isotacticity). The mechanical properties, including rigidity and toughness, of IPC are largely determined by phase structure as well as their mutual interactions. Early studies [14–17] investigating the phase separation behavior of iPP/EPR blends which involves the crystallization of iPP component suggested that the formation of final morphology was a result of competition between LLPS and crystallization. Recently, a series of excellent works which focused on the interplay and competitive relationship between LLPS and crystallization in blends of statistical copolymers, poly(ethylene-1,4-mix-hexene) (PEH) and poly(ethylene-1,4-mix-butene) (PEB) blends, have been done by Han and co-workers [18–22]. They also found that LLPS process had a dominant effect on the final crystalline morphology of an isotactic polypropylenepoly(ethylene-co-1,4-1,4-octene) (iPP/PEOc) polymer alloy [23]. Up to now, although many studies on the melt miscibility and morphology evolution during phase separation and crystallization of polyolefin blends have been reported [24–26], excepting very few systems such as the abovementioned PEB/PEHs of which phase diagrams and phase separation kinetics has been determined definitively [27,28], the phase morphology evolution of most polyolefin blends, including the complex in-reactor IPC blend, is far away from a complete understanding.

Phase separation of polymer blends can be mainly divided into two stages in sequence, namely, early-stage phase separation and late-stage phase separation. The early-stage phase separation occurs rapidly because of the thermodynamical instability of the blend, whereas the late-stage phase separation appears to be much slower [29]. In viscous melts, late-stage phase separation, which includes the coarsening of an existing separated phase and the increase of dispersed phase size, occurs spontaneously leading to a decrease in interfacial energy to reach thermodynamic equilibrium. Wang et al. [30] found that the time dependence of phase dimensions during early-stage and late-stage phase separation was different. Compared to the early-stage phase separation, coarsening presents notable time dependent manner following the theory of Ostwald ripening [31,32]. Because the slower coarsening process occurred at a time scale comparable to typical thermal processing procedures, it has attracted much attention. The time dependence of dispersed domain size evolution follows the $d \sim t^{1/3}$ law [33]. Some earlier studies concentrated on coarsening process of polyolefin blends confirmed the validity of the $d \sim t^{1/3}$ law in polymer blends system [29,34–37].

So far, the most concerned topics in the research of IPC have clarified the origination of its excellent rigidity–toughness balance property and establishing the structure–property relationship. Recently, Shangguan et al. [38] found that the molten-state annealing of IPC had a significant effect on its phase morphology architecture, and with the increase of annealing time a co-continuous structure and an abnormal ‘sea-island’ structure appeared in which the original matrix PP component became to the dispersed phase. In addition, molten-state annealing made spherulite profiles become more well-defined and caused a decrease in the nucleation ability of IPC. In previously reported research, coarsening behavior of many immiscible blends has been carefully examined, but few of them studied the correlation between the morphology evolution caused by phase coarsening and the mechanical properties. Wang et al. [30] once reported a decrease of break strength along with the late-stage phase separation in iPP/PEO blend. However, to the best of our knowledge, no similar work has been reported on IPC. In this work, the phase morphology evolution upon melt annealing and corresponding change in mechanical properties of two commercial impact–resistant polypropylene copolymers have been systematically investigated. We found that the dispersed phase coarsened with increasing annealing time and the increase of dispersed domain size followed the Ostwald ripening mechanism well. On the basis of our results, a preliminary relationship between the change of mechanical properties and phase morphologies evolution was established.

2. Experimental

2.1. Materials

A commercial IPC AW191, denoted as IPC-1, produced by the Polyolefin Company of Singapore (Singapore), was used to systematically investigate the structures evolution upon melt annealing treatment and corresponding mechanical properties. For the purpose of comparison, another IPC, 7033N, produced by the ExxonMobil Chemical Co., was also used in this work and denoted as IPC-2. The basic parameters of these materials are listed in Table 1.

2.2. Sample preparation

The IPC pellets were molded to sheets and bars at 200 °C in a press under a pressure of 15 MPa for 5 min, and were followed annealed at 200 °C with pressure for 0, 15, 30, 60, 90, 120 min (denoted as $t_a$), respectively, and then were cooled down to room temperature at a cooling rate of 5 °C/min. The 0.5 mm thick sheets are used for surface observation and specimen preparation for tensile testing. The bars with size of 100 mm × 10 mm × 4 mm are used for notched Izod impact testing after machining notches (notch depth = 2.0 ± 0.1 mm). To better understand the real phase structure of IPC in the molten state, another series of samples were prepared by molded-press at 200 °C for 5 min and then directly quenched in liquid nitrogen.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Trademark</th>
<th>MFR$^a$ (g/10 min)</th>
<th>Ethylene content$^b$ (%)</th>
<th>Mw$^c$ ($\times 10^6$)</th>
<th>Crystallizable content$^d$ (wt%)</th>
<th>Amorphous content$^d$ (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPC-1</td>
<td>AW191</td>
<td>9.8</td>
<td>10.6</td>
<td>27.5</td>
<td>76.3</td>
<td>23.4</td>
</tr>
<tr>
<td></td>
<td>7033N</td>
<td>8.3</td>
<td>9.8</td>
<td>31.8</td>
<td>81.6</td>
<td>17.2</td>
</tr>
</tbody>
</table>

$^a$ Under the condition of 230 °C/2.16 kg.
$^b$ Determined by $^{13}$C NMR.
$^c$ Determined by gel permeation chromatography (GPC).
$^d$ Determined by temperature rising elution fractionation.
2. Morphology investigation

A TESCAN 5136MM scanning electron microscopy (SEM) was used to observe the sample surface at an operating voltage of 20 kV. To remove the amorphous EPR phase [39], IPC samples were etched in an etchant containing a mixture of 0.35 wt% potassium permanganate (KMnO₄) and concentrated sulfuric acid (H₂SO₄) at room temperature for 1 h, and then washed by pure water, hydrogen peroxide (30%) and acetone in turn. Before observation, all the samples were coated with gold.

The average domain diameter and distribution were derived from the electron photomicrographs with a magnification of 2000 using an image analyzer. The number of domains chosen for calculation is approximately 100. The corresponding calculated circle diameters are assumed to be the chord length of the intercepted dispersed domain. The real dispersed domain diameter distribution moments (dₙ, dₚw, and dₚz) are calculated from the chord length (lₙ) and the number of chords (Nₙ) according to the statistical analysis methods of stereology from reference [40]. The chord lengths obtained were converted to diameter of the three-dimensional structure with the following procedure and stereological formulae:

Calculate chord length averages:

Harmonic average: \[ \bar{l}_h = \frac{\sum N_l}{\sum N_l/l} \]  
Number average: \[ \bar{l}_n = \frac{\sum N_l l}{\sum N_l} \]  
Weight average: \[ \bar{l}_w = \frac{\sum N_l l^2}{\sum N_l l} \]

Calculate dispersed domain diameter average:

Number average: \[ \bar{d}_n = \bar{l}_h \left( \frac{\pi}{2} \right) \]  
Weight average: \[ \bar{d}_w = \bar{l}_n \left( \frac{4}{\pi} \right) \]  
Z-average: \[ \bar{d}_z = \bar{l}_w \left( \frac{3\pi}{8} \right) \]

Calculate polydispersity: \[ \bar{d}_w/\bar{d}_n \] and \[ \bar{d}_z/\bar{d}_w \]

2.4. Thermal property characterization

A Mettler DSC-1 apparatus was used to analyze the thermal properties. Calibration for the temperature scale was performed using indium (T<sub>f</sub> = 156.6 °C and ΔH<sub>f</sub> = 28.45 J g⁻¹) as standard to ensure reliability of the data obtained. The accuracy of measured temperature is ±0.05 °C. All of the experiments were carried out in nitrogen atmosphere. To investigate the thickness of crystalline lamellae, the samples were heated from 25 to 200 °C at a rate of 10 °C min⁻¹ and the melting traces were recorded. The isothermal crystallization measurements were performed following the procedure: (a) samples were first heated to 200 °C at rate of 10 °C min⁻¹ and then kept there for 5 min to erase previous thermal history, (b) fast cooled down to 135 °C, at rate of 30 °C min⁻¹ and (c) isothermally kept a long enough period of time to complete the crystallization. The relative degree of crystallinity (X<sub>c</sub>) in this study is a relative value which could be defined as follows:

\[ X_c = \frac{X_c(t)}{X_c(\infty)} = \frac{\int_0^t (\Delta H/\Delta t) \, dt}{\int_0^\infty (\Delta H/\Delta t) \, dt} \]  

where the first integral is the enthalpy generated at time t and the second is the total enthalpy when the crystallization is completed.

2.5. Mechanical property testing

The dog-bone specimens used for tensile testing with dimensions of 20 mm × 4 mm × 0.5 mm were cut from the molded sheets. The tensile testing was conducted on a SANS CMT-6503 universal testing machine (Shenzhen, China) with a crosshead speed of 20 mm min⁻¹ according to GB/T1040-92. The capacity of the load cell is 10 kN in axial load. Notched Izod impact tests were carried out using an XJJ impact tester (Changchun, China) followed to ASTM D 256-04. The maximum impact energy of pendulum is 0.98 J. All specimens were placed at room temperature (23 ± 0.5 °C) for 12 h before testing. These values were measured under the same conditions and each reported mechanical result is an average value of at least 6 measurements.

3. Results and discussion

3.1. Phase structure and time-dependent phase evolution

Because of the very close refractive indices of the crystalline matrix and the amorphous dispersed components in the molten state, it is difficult to directly observe LLPS process of IPC under
molten state in situ. The indirect characterization of the samples after fast quenching from the melt is usually an effective alternative method [14]. The initial morphologies of IPC-1 sample without any further anneal treatment, which were directly quenched after molding, are shown in Fig. 1. It is obvious that the quenched IPC sample presents heterogeneous phase structures, which means that while undergoing the mold-press process for 5 min at 200 °C, the IPC systems are already not homogeneous. From the electron photomicrographs with greater magnification, the “sea-island” structures can be clearly observed. The dispersed random domains are considered as amorphous EPR, and the core structure of dispersed domains may be composed of long sequence PEs [10]. As mentioned above, the faster crystallization rate during quenching, the better the morphologies of blends under the molten state could be conserved [14–28]. In our laboratory the quenching is usually carried out by putting samples into liquid nitrogen, which could fail to keep pressure during this cooling process. However, it is necessary to cool the samples under appropriate pressure when preparing compact and tidy sheets for mechanical tests. The highest cooling rate that our press machine can be precisely controlled in the range from 200 to 20 °C is 5 °C min⁻¹. To keep consistence of the morphology observation with mechanical property tests, we prepared all these samples at a same rate of 5 °C min⁻¹. The phase morphology of IPC-1 annealing at 200 °C for different time is shown in Fig. 2. It is obvious that the dispersed phase enlarges continuously and gradually with annealing time. At the beginning, the average dispersed domain size is 2–3 μm. After undergoing 2 h annealing, the domain size of IPC increases to about 6–9 μm.

It is well known that LLPS of immiscible polymer blends from an initial homogeneous state occurs as a result of thermodynamic instability, which follows the spinodal decomposition (SD) or nucleation growth (NG) mechanism. Due to the rapid nucleation of new phase in either case, the process of early-stage LLPS of the highly immiscible system occurs rapidly. Unambiguously, the presented phase morphology evolution in this work, which starts form a pre-existing phase separated state, does not occur rapidly and has great time dependence. Hence, the phase separation in this work taking place during annealing at 200 °C, mainly undergoes the late-stage phase separation, namely phase coarsening.

3.2. Coarsening mechanism

As known, although the system has experienced early-stage LLPS from homogeneous melt and sequentially reached to the thermodynamic equilibrium state, it still has significant extra energy due to the large interface area. The driving force for this process, which is quite different from the early-stage LLPS, is considered as the extremely high surface energy of dispersed phase, in other words, the extremely high cumulative interfacial tension against the matrix. To minimize the cumulative interfacial tension, the size of dispersed domain increases spontaneously. It was generally considered that the spontaneous process by means of the diffusion of the molecules of dispersed phase in matrix followed an evaporation/condensation mechanism named Ostwald ripening [31,32].

According to the Lifshitz–Slyozov theory of Ostwald ripening, the long time coarsening regime should follow the Lifshitz–Slyozov equation [33]:

\[
\bar{r}(t) = \bar{r}(0) + Kt
\]

where \(\bar{r}(t)\) and \(\bar{r}(0)\) are the dispersed domain radii at time \(t\) and \(t=0\) respectively. The zero time is defined as the beginning of

![Fig. 2. SEM micrographs of a sample IPC-1 experienced various annealing durations at 200 °C.](image-url)
Table 2
Average dispersed domain diameter and distribution of IPC-1 annealed at 200 °C for various durations.

<table>
<thead>
<tr>
<th>Annealing time (min)</th>
<th>$d_w$ (µm)</th>
<th>$d_p$ (µm)</th>
<th>$d_n^*$ (µm)</th>
<th>$d_w/d_p$</th>
<th>$d_n^*/d_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.54</td>
<td>2.60</td>
<td>2.89</td>
<td>1.02</td>
<td>1.11</td>
</tr>
<tr>
<td>15</td>
<td>2.56</td>
<td>3.25</td>
<td>4.17</td>
<td>1.27</td>
<td>1.28</td>
</tr>
<tr>
<td>30</td>
<td>4.45</td>
<td>4.82</td>
<td>5.19</td>
<td>1.08</td>
<td>1.07</td>
</tr>
<tr>
<td>60</td>
<td>5.52</td>
<td>5.34</td>
<td>5.80</td>
<td>0.97</td>
<td>1.09</td>
</tr>
<tr>
<td>90</td>
<td>5.54</td>
<td>6.07</td>
<td>7.21</td>
<td>1.09</td>
<td>1.19</td>
</tr>
<tr>
<td>120</td>
<td>6.58</td>
<td>7.01</td>
<td>8.33</td>
<td>1.06</td>
<td>1.19</td>
</tr>
</tbody>
</table>

Fig. 3. The cube of weight-average dispersed domain diameter ($d_w$) versus annealing time. The line is the linear least-squares fit to the data.

Coarsening in the long-time regime. $K$ is a constant which is independent of the volume fraction of the coarsening phase. A careful and mathematic analysis of the development of dispersed phase size was implemented to examine whether this coarsening process is in accordance with $d \sim t^{1/3}$ law. Dispersed domain diameter distribution is determined by measuring a representative population of dispersed domain areas and then applying the aforementioned stereological methods [40]. The average size and distribution of dispersed phase of IPC-1 is presented in Table 2. Apparently, statistical data also prove the growth trend of average dispersed domain diameter with annealing time. To validate the $d \sim t^{1/3}$ law in our system, these data are plotted as $d_w^3$ versus $t$ as shown in Fig. 3. It can be seen that the $d_w^3 \sim t$ relationship exhibits linearity, which is in accordance with Eq. (8). This implies the long time coarsening mechanism for IPC-1 is in agreement with the Ostwald ripening theory.

![Fig. 4](image1.png)

Fig. 4. Notched Izod impact strength of IPC-1 (a) and IPC-2 (b) with different annealing time at 200 °C.

3.3. Evolution of mechanical performance with phase coarsening

Generally, for a rubber toughened polyolefin system, dispersed phase size and distribution have a crucial influence on material’s final mechanical property. Therefore, it is necessary to explore the corresponding changes of the mechanical performances with the variation of phase structure. To better understand these relationships, another kind of IPC, IPC-2, was also used for comparative investigation. Figs. 4 and 5 show the variations in the impact strength as well as the tensile elongation at break of both samples with the annealing durations. As expected, the notched Izod impact strength and tensile elongation at break for both IPCs decreases gradually with the increase of annealing time. For IPC-1, the values of notched Izod impact strength are 12.3, 9.3, 8.0, 7.7 and 7.2 kJ m$^{-2}$ for samples annealed at 200 °C for 0, 30, 60, 90 and 120 min, respectively, while the values of tensile elongation at break for these samples are 67.6, 46.4, 43.7, 34.8 and 30.1%. After 2 h of annealing treatment, the declines in impact strength and tensile elongation at break are approximately 42% and 55%, respectively. Similarly, the impact strength for the IPC-2 without annealing treatment is 9.9 kJ m$^{-2}$ and the value decreases to 7.8 kJ m$^{-2}$ for sample experienced 2 h of annealing, having a decline of 20%. From the beginning, IPC-1 owns a higher impact resistance, but it becomes even lower than IPC-2 after annealing for 2 h. Obviously, the notched Izod impact strength of IPC-2 is more stable than IPC-1 when undergoing thermal treatment. To understand the stability of impact strength...
of IPC-2 during annealing, the phase morphology of IPC-2 annealing at 200 °C for different time is shown in Fig. 6. By comparing Fig. 2 and Fig. 6, it was found that the dispersed phase enlarged gradually with annealing time for both IPCs. However, it is notable that the coarsening rate of dispersed domain of IPC-2 is much slower than that of IPC-1. After annealing for 2 h, the dispersed domain size of IPC-1 becomes approximately 7 μm, while the size of IPC-2 only increases to about 5 μm. From the crystallization results, as shown in Fig. 7, we found the crystallization kinetics of two kinds of IPCs were quite different. The sample of IPC-2 had a much faster crystallization rate than IPC-1 at the same crystalline temperature. Quantitatively, the half time of crystallization (\( t_{1/2} \)), which is defined as the time taken from the onset of the crystallization until 50% completion, may be used as an important parameter to indicate crystallization rate. According to the isothermal crystallization curves, we estimate \( t_{1/2} \) of IPC-1 and IPC-2 is approximately 3.8 and 1.1 min, respectively, which suggests that the IPC-2 indeed owned a relatively rapid crystallization rate. For semicrystalline polymer, the crystallization characteristics greatly influence the coarsening process. Due to the decreasing activity of diffusing molecules after crystallization, the evident faster crystallization rate of IPC-2 might largely limit the coarsening process during cooling, and sequentially lower both the coarsening rate and coarsening extent in comparison with those of IPC-1, which result in stability of the impact strength of IPC-2 samples experienced similar melt annealing treatments. In addition, the coarsening process is a diffusional mass transfer process from regions of high interfacial tension to regions of low interfacial tension [31,32]. The difference in molecular structure and composition which related to the surface tension between the dispersed domain and matrix may be also a probable factor for the different coarsening process of two IPC samples.

Evidently, the changes in mechanical properties of IPCs which experienced various melt annealing treatment are result from the different extent of phase morphology evolution. As discussed above, the decline of notched Izod impact strength of IPC-1 is much faster than IPC-2, which is consistent with its faster phase coarsening process. Therefore the change trend of impact strength may be considered as a reflection of the rate of coarsening process. Earlier studies [41–44] focused on the toughening of plastics matrix with rubber found that the dispersed phase size was a key factor determining the toughening efficiency. The brittle–ductile transition of polymer blends occurs when the rubber domain size (\( d \)) is smaller

![Fig. 6. SEM micrographs of a sample IPC-2 experienced various annealing durations at 200 °C.](image)

![Fig. 7. The plot of relative crystallinity versus crystallization time for both IPC samples.](image)
than a critical value \(d_c\) [41,42] or when the rubber volume fraction \(\phi\) is larger than a critical value \(\phi_c\) [43,44]. The \(d_c\) increases with \(\phi\) and on the other hand, \(\phi_c\) increases with decreasing \(d\). Wu et al. [45] have proposed a generalized criterion for rubber toughening based on percolation theory: the critical matrix ligament thickness \(ID_c\). If the interparticle distance \(ID\) (also called matrix ligament thickness) is smaller than the value of \(ID_c\), the blend is tough, otherwise the blend is brittle. For a given polymer matrix, the value of \(ID_c\) is a definite value which only related to its intrinsic character. However, this value is closely related to the dispersed domain size \(d\). During the coarsening process, the increase of ID caused by the increase of dispersed domain size will result in the decrease of toughness. Hence, the impact toughness of IPC gradually declines with the increase of domain size. In conclusion, from Figs. 2, 4 and 6, the increased tendency of dispersed domain size is in perfect accordance with the decline tendency of toughness. For the two samples we investigated, the toughness decrease of IPC-1 is much more pronounced than that of IPC-2, which is well consistent with the faster coarsening process of IPC-1.

The stress–strain curves of IPC-1 and IPC-2 annealing at 200 °C for different time are presented in Fig. 8. As aforementioned, the values of ultimate strain decrease with the increase of annealing time. However, the ultimate stress as well as yield stress maintains relatively constant for both samples experienced various annealing treatments. The tensile strength of IPC-1 and IPC-2 as a function of annealing time is also exhibited in Fig. 9. Compared with the pronounced decrease tendency of impact strength with annealing time, the changes in tensile strength is rather slight for both IPCs. For the multi-phase IPC system, the whole matrix may be regarded as a continuous phase of crystallizable iPP, which plays important roles in determining the final performance of materials. It is generally accepted that crystalline structure, such as lamellar thickness has a crucial influence on tensile property [30]. From the DSC results, as shown in Fig. 10, we found that the melting traces of non-annealed and 2 h annealed samples have no obvious difference in peak shape and location, which indicates that the crystalline lamellae hardly changed with annealing treatments. For semicrystalline polymer blends, the crystallization of the matrix plays a
“lock-in” effect on dispersed phase morphology. In this work, the great change in dispersed domain size and phase morphology has no obvious influence on the crystalline structures of crystalline matrix, which lead to slight decline of the tensile strength for both IPC samples.

4. Conclusion

By means of SEM observation and property tests, we systematically investigated the phase morphology evolution and corresponding change of mechanical performance of impact-resistant polypropylene copolymer during thermal treatment in the molten state. With annealing time increasing, the dispersed phases of IPC gradually enlarge themselves and the phase evolution process is in accordance with the Ostwald ripening theory, which strictly follows a $d - t^{1/3}$ time dependent law. Accordingly, the mechanical properties of IPC change with the evolution of phase morphology. Due to toughness is greatly influenced by amorphous phase, the enlargement of dispersed phase and changes in morphological structure result in a significant decrease of toughness. After 2 h of annealing treatment at 200 °C, in which the average dispersed domain size of IPC-1 increased from 2 to 3 μm to approximately 7 μm, the notch Izod impact strength and tensile elongation at break decreased by approximately 42 and 55%, respectively. The decline trends in impact strength and tensile elongation at break are consistent with the increase of dispersed domain size. However, since the annealing treatment in the molten state has slight influence on the crystalline structure of IPCs, the tensile strength of samples remains relatively constant during the annealing treatment. Our study indicates that the thermal treatment process plays a critical role in controlling the phase structure as well as the final mechanical properties of the materials.

Acknowledgments

We gratefully acknowledge the financial support from the Natural Science Foundation of China (21174032, 20874017), National Basic Research Program of China (2011CB605704), PetroChina Company Limited and PetroChina Innovation Foundation (2011D-5006-0504).

References