

INFLUENCE OF SHEARING ON IMPACT POLYPROPYLENE COPOLYMER: PHASE MORPHOLOGY, THERMAL AND RHEOLOGICAL BEHAVIOR*

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Abstract The influences of shearing conducted by a Brabender rheometer on phase morphology, thermal and rheological behavior of a commercial impact polypropylene copolymer (IPC) were studied. The crystallization and melting traces show that short-time annealing at 210°C is unable to completely erase the influence of shearing on the samples. When the samples which were treated at a rotation speed of 80 r/min crystallize at a cooling rate of 10 K/min, their T_c s and corresponding T_m s obviously rise with the increase of shearing time. Furthermore, the POM results reveal that the shearing can lead to the formation of shish-kebab and the shish-kebab amount is proportional to shearing time. The rheological measurement results show that the treated samples exhibit different $G' \sim \omega$ dependences. The 'second plateau' appears when the sample is treated at a rotation speed of 60 r/min or 80 r/min for 10 min, and linear $G' \sim \omega$ dependence is observed at other rotation speeds. In addition, it is found that the appearance of the 'second plateau' depends on the shearing time when the rotation speed is fixed. According to SEM observations, it is proposed that the 'second plateau' of IPC samples should be ascribed to the aggregation of dispersion particles.

Keywords: Impact polypropylene copolymer (IPC); Shish-kebab; Phase morphology; Second plateau.

INTRODUCTION

In order to improve the toughness of polypropylene, many modifications by physical or chemical methods have been made in past several decades^[1–5]. As a multiphase polymeric system, impact polypropylene copolymers (IPC) produced in a continuous process possesses excellent mechanical properties, especially toughness, which allows them to be made into some important auto elements such as radiator's water chamber, air filter's shell, storage battery's shell and cooling fan *etc.* In the first stage of the process, propylene is polymerized to homopolymer in a variety of environments, including liquid or gaseous reactors^[6, 7]. However, the second reactor is almost always a gas-phase reactor to avoid dissolution of the amorphous copolymer, and a rubbery ethylene-propylene copolymer phase is dispersed in the homopolymer matrix^[8].

In general, IPC consists of mainly polypropylene homopolymer, ethylene-propylene random copolymer and ethylene-propylene segmented copolymer (or ethylene homopolymer)^[4, 9]. It is believed that as a compatibilizer, ethylene-propylene segmented copolymer can improve the miscibility between dispersion phase and matrix. Furthermore, it is important that the segmented copolymer consists of macromolecules with different segment lengths^[10]. In the past decade, studies on composition, morphology and crystallization of IPC have been reported

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by many researchers^[11–14]. Nevertheless, to our knowledge, little attention has been paid to the morphologic development of dispersion phase and rheological behavior of IPC under processing conditions. In our previous work^[4], it was found that the static annealing may lead to a change in IPC morphology. Usually, the shape, size and distribution of dispersion phase are related to the crystallization behavior, rheological behavior and mechanical properties of polymer materials. Since the shearing occurs during the processing of polymeric materials and has been proved to greatly affect the morphology^[15, 16], microstructure^[17, 18], thermal behavior^[19, 20] and rheological properties^[21–23] of multicomponent polymers, it is necessary to investigate the influences of processing factors (such as shear rate, shear time *etc.*) on the morphology and other properties of IPC. In the present article, a Brabender rheometer is adopted to obtain the various IPC samples with different shearing histories. The phase morphology, rheological behavior and thermal behavior of these samples are investigated, and the influences of processing factors including shear rate and shear time on them are discussed.

EXPERIMENTAL

Material and Sample Preparation

The material used was a commercial impact polypropylene copolymer (SP179, Sinopec Qilu Petrochemical Co. of China). Shearing was carried out on a Brabender rheometer (Brabender Measurement & Control System) to simulate practical process at 210°C. The original IPC about 50 g was filled in the chamber when two rotors' speeds reach to the preset value. To obtain samples subjected to different shear histories, various rotation speeds (40–100 r/min) and shear time (10–40 min) was applied. The samples were scratched out and cooled down to room temperature after the shearing was done. Finally, the IPC samples were cut to pieces for further measurements.

Differential Scanning Calorimetry

A modulated differential scanning calorimeter (Q100, TA Instruments Corporation) with N₂ as purge gas was used to probe the nonisothermal crystallization and melting behavior of IPC specimens. Pure indium and zinc were used as reference materials to calibrate both the temperature scale and the melting enthalpy before the specimens were tested. First, the IPC specimens were heated to 200°C at a heating rate of 10 K/min and held for 10 min, and then the nonisothermal crystallization was conducted at a cooling rate of 10 K/min. After the crystallization was completed, the samples were reheated to 200°C at 10 K/min again and their melting traces were recorded.

Dynamic Rheological Measurements

The dynamic rheological measurements were conducted on a Modular Advanced Rheometer System (MARS, HAAKE, Germany) with parallel plates of 25 mm in diameter under air. The samples for rheological tests were prepared by heat-molding at 210°C for 5 min and then cooled down to room temperature under pressure. The selected rheological testing mode was isothermal ω sweep from 100 rad·s⁻¹ to 0.01 rad·s⁻¹, and a strain of 5% was applied in all tests, which falls within the linear viscoelastic range^[10]. All rheological tests were conducted at 210°C.

Morphology Analysis

The crystalline morphologies and phase morphologies of the IPC samples were observed by using a polarized optical microscope (POM, BX51, Olympus) equipped with an Olympus camera and a temperature controlled hot stage (THMS600, Linkam Co.) and a scanning electron microscope (SEM, H-7000, Hitachi, Japan), respectively. After the nonisothermal crystallization of the samples at a cooling rate of 10 K/min, the morphologies of samples were observed. The samples used for SEM observation were fractured in liquid N₂, and then etched in xylene at room temperature for 12 h. The dried drawing sections of samples were coated with gold before observation.

RESULTS AND DISCUSSION

In previous work^[24], it was found that obvious degradation happened in IPC when it was exposed to air at high temperatures. In present work, the GPC measurements of the samples treated at 210°C for different time have been conducted and the results do not show obvious degradation of IPC during these processes. The reason may lie in that the working chamber of Brabender rheometer is nearly hermetic and there is no too much air. Since the rheological measurement requires specimens with certain shape, the IPC samples treated by Brabender rheometer must undergo the heat-molding procedure. However, the heat-molding procedure possibly removes or reduces the influence of shearing on IPC samples. Thus, it is necessary to understand whether the influences of shearing on IPC samples can survive after they experience the heat-molding procedure. The thermal behavior of IPC samples was investigated first, especially the crystallization and melting behavior following the annealing at 210°C.

Effect of Shearing on Thermal Behavior of IPC

The thermal behavior of IPC samples which were treated in rheometer at different rotation speeds was investigated. Figure 1 gives the first melting, nonisothermal crystallization and the second melting traces of IPC samples treated at the rotation speed of 80 r/min for different time, respectively. As shown in Fig. 1(a), these samples present similar melting traces and their melting peak temperatures (T_m) are almost the same. Since the difference among these T_m s is no more than 0.5 K and falls into the range of ordinary experimental error, these results show that the IPC samples subjected to different treatments have similar lamellar thickness. Taking into

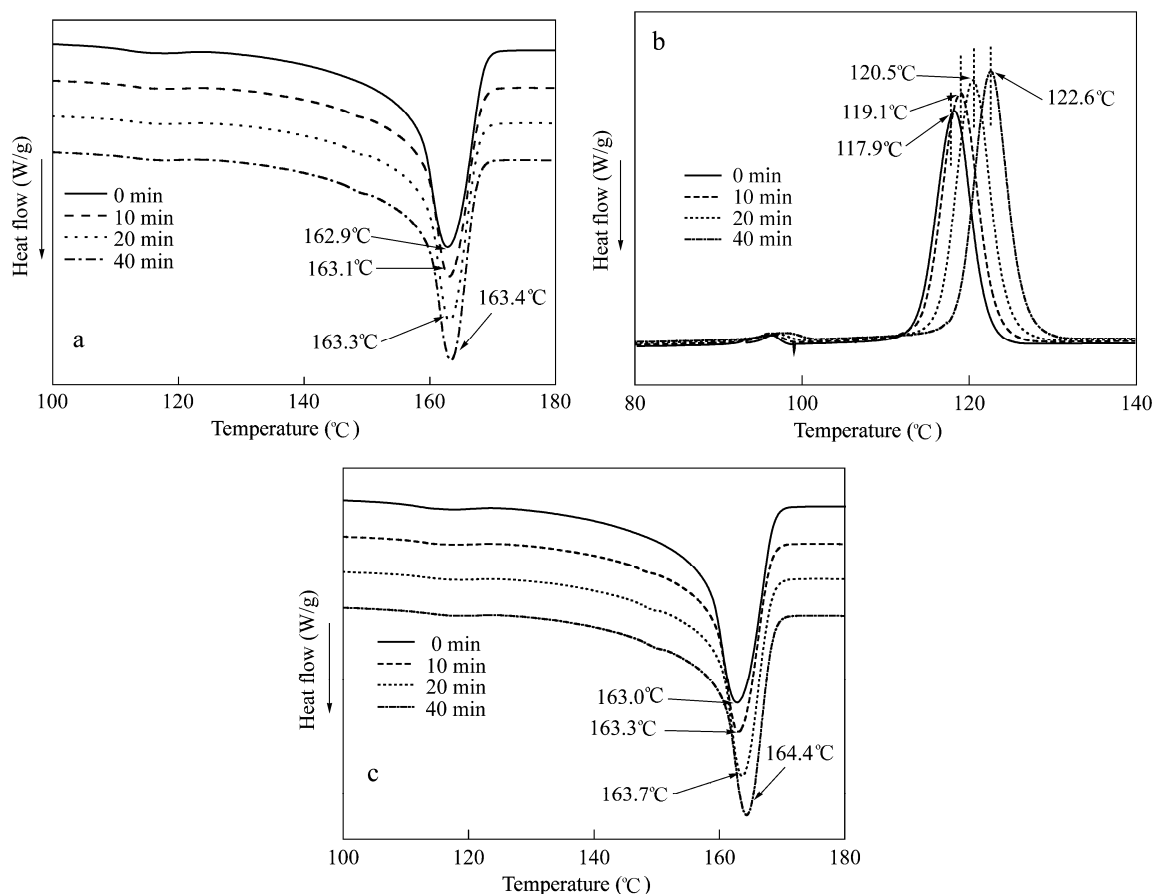


Fig. 1 DSC traces for IPC samples treated at the rotation speed of 80 r/min for different time: (a) the first melting traces, (b) crystallization traces, (c) the melting traces after nonisothermal crystallization (cooling/heating rate: 10 K/min)

account the fact that these samples were quickly cooled down to room temperature after being treated in rheometer, these melting traces may be explained as follows: during these crystallization courses the thermal condition plays a more important role than the shearing, and the effects of shearing on the crystallization behavior of IPC samples were covered by rapid cooling, so these IPC samples show almost the same melting traces. However, when the IPC samples crystallized nonisothermally at 10 K/min after being annealed at 210°C for 10 min, they presented distinct exotherms shown in Fig. 1(b). With the increase of shearing time, the crystallization peak gradually becomes stronger and the crystallization peak temperature (T_c) remarkably rises. Furthermore, the area of crystallization peak increases with the increase of shearing time. Since the peak area represents the crystallinity of the sample and the higher T_c implies the stronger crystallization ability when no nucleating agent is added, the nonisothermal crystallization results show that the introduction of shearing can improve the crystallization ability of IPC samples and the improvement becomes more obvious with the increase of shearing time. To understand the influence more, the melting traces of the IPC samples crystallized nonisothermally are given in Fig. 1(c). It is seen that the second melting traces are similar to those in Fig. 1(a) and only their T_m s increase more or less. The longer treatment time is, the higher T_m is. For the sample treated in rheometer for 40 min, T_m of the second melting is about 1 K higher than that of the first melting.

Figure 2 gives polarized optical micrographs of nonisothermally crystallized IPC samples treated at the rotation speed of 80 r/min for different time. It can be found that the samples show different crystalline morphologies. The untreated IPC sample presents relatively clear birefringence character of spherulite and its crystalline phase almost consists of spherulites. For the samples treated for 10 and 20 min, besides spherulites some shish-kebabs could be found in the POM images, as indicated by white arrows in Figs. 2(b) and 2(c). The only difference is that the amount of shish-kebab in Fig. 2(c) is more than that in Fig. 2(b). When the sample was treated for 40 min, it is seen that its crystalline morphology almost consists of shish-kebabs and no obvious spherulite exists. Based on the above crystalline morphology results, it is believed that the formation of shish-kebab structure in treated IPC samples results from the shearing in rheometer and the amount of shish-kebab depends on the shearing time. Furthermore, considering that during nonisothermal crystallization T_c s of treated IPC samples rise with the increase of shearing time, it is suggested that the formation of shish-kebab is the main reason of the increase of T_c . The above thermal analysis results show that the short-time annealing at 210°C could hardly completely erase the influence of shearing on the IPC samples and it is possible to understand the influence of shearing on the rheological behavior of IPC samples.

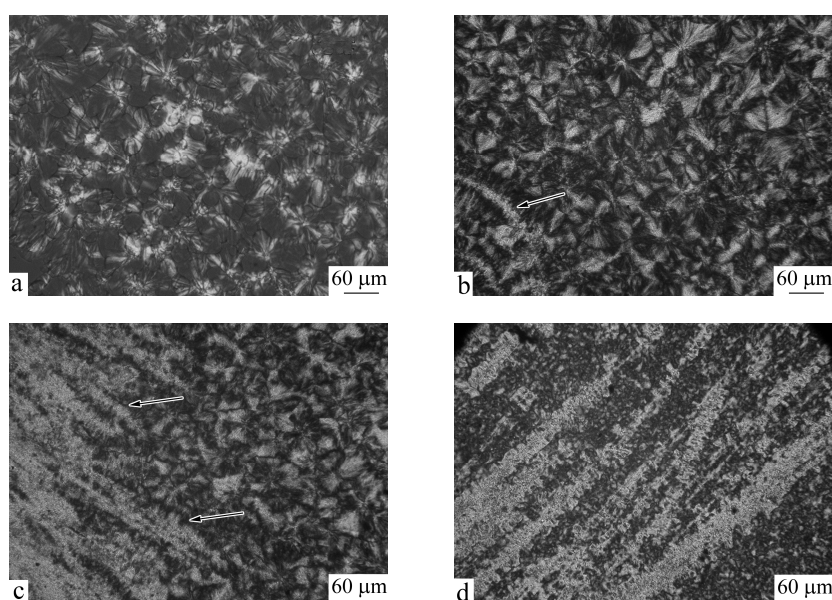


Fig. 2 POM images of nonisothermally crystallized IPC samples treated at the rotation speed of 80 r/min for different time: (a) 0 min, (b) 10 min, (c) 20 min and (d) 40 min

Effect of Shearing on Rheological Behavior of IPC

Figure 3 gives the frequency (ω) dependences of the dynamic storage modulus (G') and loss modulus (G'') for IPC samples treated at different rotation speeds. It can be seen in Fig. 3(a) that these IPC samples exhibit different $G' \sim \omega$ dependences in low ω region. The samples treated at the rotation speeds of 60 and 80 r/min present obvious raise of G' with the decrease of ω , and other samples present linear $G' \sim \omega$ dependence. Usually, for homopolymers in low ω region, G' and G'' are proportional to ω^2 and ω , i.e. $G' \propto \omega^2$ and $G'' \propto \omega$, respectively^[25]. The rise of G' in low ω region for multi-phase polymer systems is named ‘second plateau’ which is often ascribed to the formation of a higher ordered structure, such as cross-link^[10], phase-separation^[26] or filled network^[27]. However, it is interesting that although the IPC is in a phase-separated state^[4, 10, 14], no ‘second plateau’ appears for as-received IPC at 210°C, which may be attributed to the good dispersion of ethylene-propylene copolymer in original IPC. Furthermore, according to our previous studies^[10], these results imply that there is no chemical crosslink in IPC under this condition. It is noted that although the IPC samples at 60 and 80 r/min present ‘second plateau’, for the samples with lower (40 r/min) and higher rotation speeds (100 r/min) no ‘second plateau’ appears. These results indicate that there exist some ordered structures in the samples with 60 and 80 r/min treatments and the lower (40 r/min) or higher rotate speeds (100 r/min) don’t facilitate the formation of this ordered structure. Similar to G' , only the $G'' \sim \omega$ curves of IPC samples at 60 and 80 r/min exhibit a weak rise in low ω regions, being another sign of the formation of ordered structure in IPC samples.

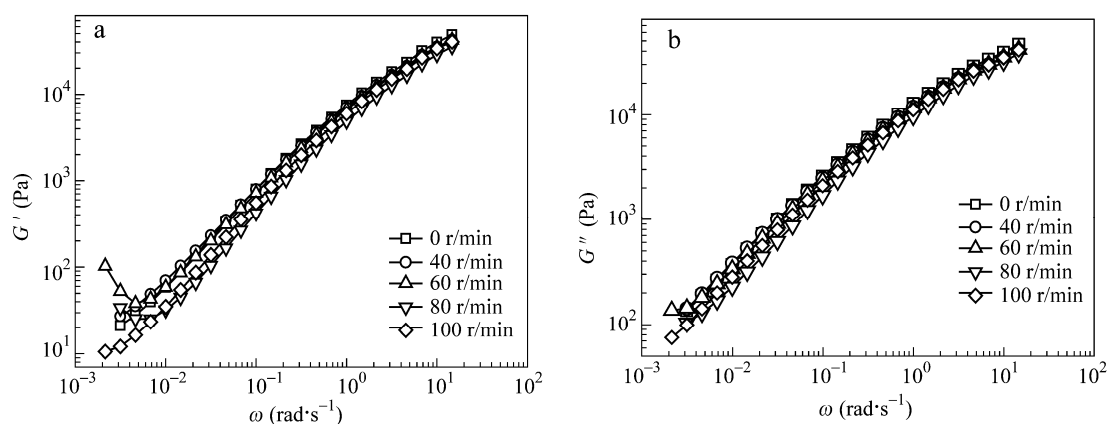


Fig. 3 Dependences of (a) storage modulus (G') and (b) loss modulus (G'') on frequency (ω) for IPC samples treated at different rotation speeds for 10 min

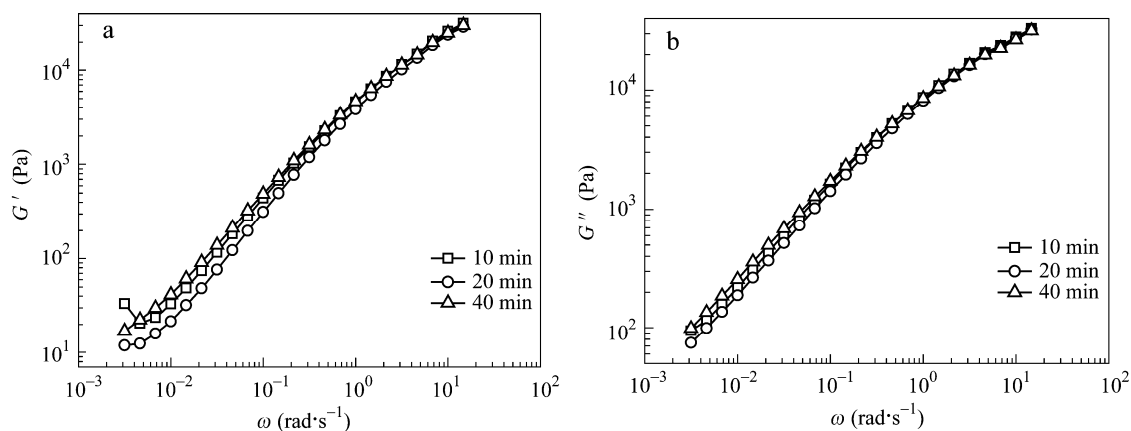


Fig. 4 Dependences of (a) storage modulus (G') and (b) loss modulus (G'') on frequency (ω) for IPC samples treated for different shearing time

Figure 4 presents the $G' \sim \omega$ dependences of IPC samples treated at rotation speed of 80 r/min for different time. It is found that the 'second plateau' appears for the samples subjected to shearing for 10 and 20 min, and disappears when the shearing time approaches 30 min. The influence of long shear time is similar to that of high rotation speed. These results indicate that besides rotation speed, shear time is also important to the formation of ordered structure in IPC samples. According to the above rheological measurement results, it is believed that the morphology of the dispersion phase in IPC must have changed to some extent under shearing. To probe the ordered structure in IPC samples, the morphologies of IPC samples exposed to shearing will be investigated and discussed in next section.

Effect of Shearing on Phase Morphology of IPC

It is well known that when the melt of multiphase polymer is subjected to shearing, its dispersion phase will deform or orient. Usually, the deformation or orientation degree is related to the viscosity and interfacial tension between two phases^[28]. The role of interfacial tension is to make the dispersion phase spherical, whereas the viscosity forces the dispersion phase to deform along the flow direction. It has been reported that the dispersion phase in IPC is a mixture of ethylene-propylene copolymers and in most cases exists as a shell-core structure^[10, 29, 30]. The soft 'shell' is EPR and the hard 'core' is ethylene homopolymer or crystallizable ethylene-propylene block copolymer.

SEM observation was carried out to examine the effect of shearing on the morphology of dispersion phase. Figures 5 and 6 demonstrate the SEM images of IPC samples subjected to shearing with different rotation speeds and time, respectively. As seen in Fig. 5(a), a randomization of dispersion phase could be observed in the origin IPC sample and the size distribution of dispersion phases appears relatively uniform. For the sample with rotation speed of 40 r/min, the aggregation of a few dispersion particles appears. As the rotation speed increases to 60 and 80 r/min, the aggregation of dispersion particles becomes more obvious than that in sample with 40 r/min. However, when the rotation speed reaches 100 r/min, a relatively uniform dispersion appears again and the sizes of dispersion particle are similar to those of the original IPC sample. Based on these morphological images of IPC samples, their rheological behavior mentioned in previous section may be interpreted. The 'second plateau' in IPC samples with 60 and 80 r/min should be ascribed to the aggregation of dispersion

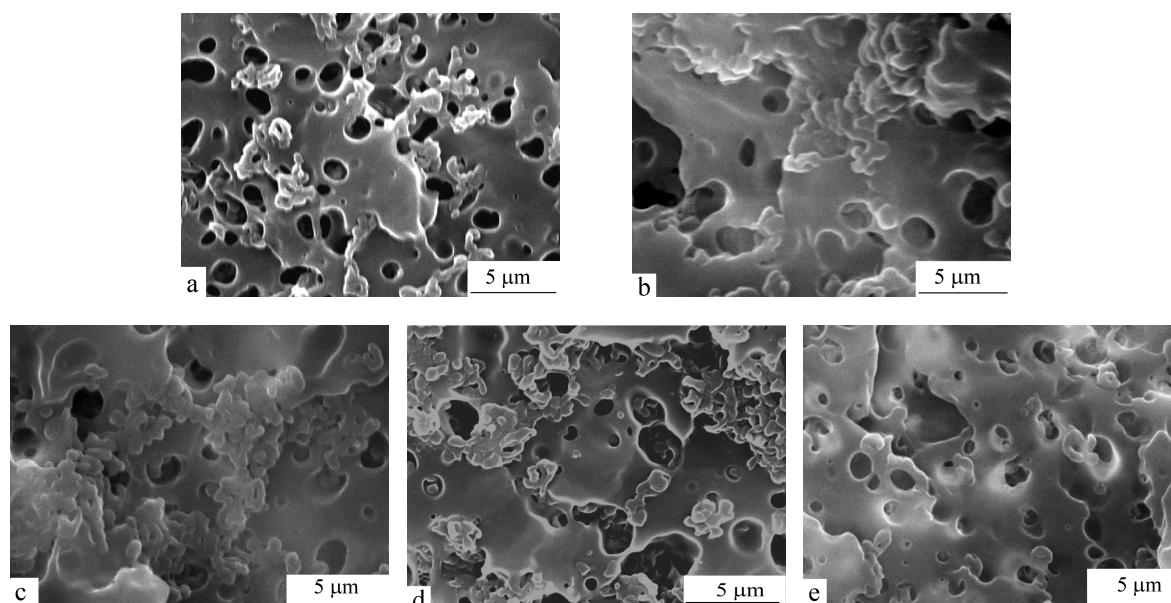


Fig. 5 SEM images of IPC samples treated by different rotation speeds: (a) 0 r/min, (b) 40 r/min, (c) 60 r/min, (d) 80 r/min and (e) 100 r/min for 10 min at 210°C

particles. Furthermore, although there have some aggregations of dispersion particles in IPC samples with 40 r/min, the amount of aggregation is so few that no ‘second plateau’ appears. For the sample with 100 r/min, since there is no aggregation of the dispersion particles the sample also presents a linear $G' \sim \omega$ dependence in low ω region. These results indicate that the too strong shearing doesn’t probably facilitate the aggregation of dispersion particles.

Figure 6 gives the SEM images of IPC samples treated at a rotation speed of 80 r/min for different time. As described above, compared with the good dispersion in original IPC, the dispersion phase of the sample subjected to shearing for 10 min exhibits obvious aggregation. However, as shown in Figs. 6 (c) and 6(d), the aggregated dispersion particles seem to separate one another again when the treatment time increases. Compared with the original IPC, the sizes of dispersion particles in the samples treated for 20 and 40 min become more ununiforme, and some particles with larger sizes appear. These results show that with increase of shear time, the evolution of dispersion phase may undergo a two-step course, *i.e.* aggregation of dispersion particles and subsequent destroy of the aggregation. When the IPC samples were treated on Brabender rheometer, it was found that the melt viscosity decreased with the increase of time until a constant viscosity appeared. Thus, it is thought that the effect of shearing time on morphology is also related to the melt viscosity. When the treatment time is shorter, the shearing and the higher viscosity simultaneously affect the phase morphology and lead to the aggregation of the dispersion phase. When the samples were treated for 40 min, duo to the lower viscosity and shearing, these aggregated particles were destroyed. Considering that only the sample subjected to shearing for 10 min presents an obvious ‘second plateau’ phenomenon, these results again show that the ‘second plateau’ of IPC under shearing should be ascribed to the aggregation of dispersion phase and long-time shearing would destroy the aggregation at a rotation speed of 80 r/min.

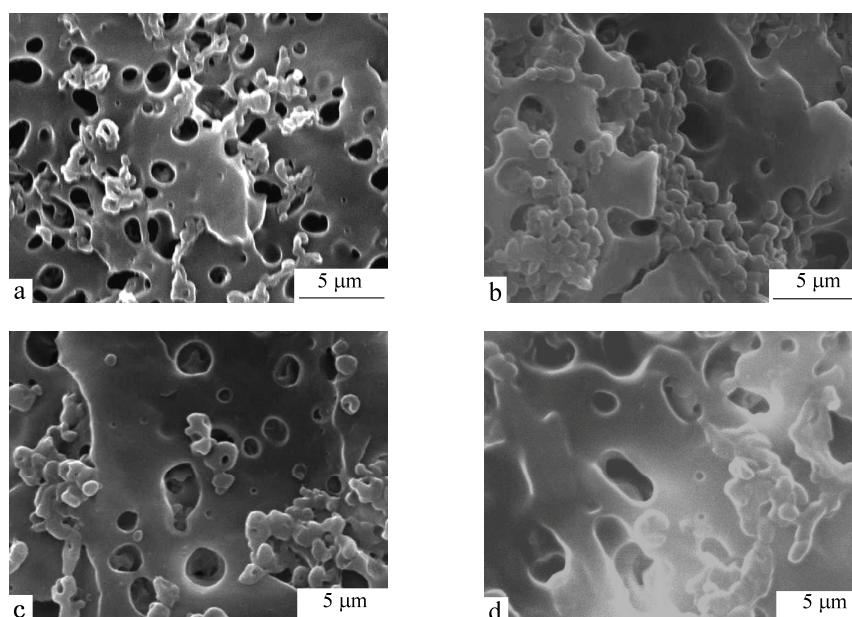


Fig. 6 SEM images of IPC samples treated for different shearing time at a rotation speed of 80 r/min at 210°C: (a) 0 min, (b) 10 min, (c) 20 min and (d) 40 min

CONCLUSIONS

The short-time annealing at 210°C could hardly completely erase the influence of shearing on the IPC samples. The nonisothermal crystallization and melting results show that with the increase of shearing time, T_c and T_m of IPC samples increase. The shearing can result in the formation of shish-kebab in samples. Depending on rotation speed and shearing time in rheometer, the IPC samples show different $G' \sim \omega$ dependences. A ‘second plateau’

could be observed when the sample was treated at rotation speeds of 60 r/min or 80 r/min for 10 min. Contrarily, a linear $G' \sim \omega$ dependence appears when the rotation speed is higher than 80 r/min or lower than 60 r/min. In addition, it is found that the appearance of 'second plateau' is also related to the shearing time when the rotation speed is fixed. The 'second plateau' appears when the shear time is 10 min or 20 min, and disappears when the shear time approaches to 30 min. According to SEM observation, it is suggested that the 'second plateau' in IPC samples results from the aggregation of dispersion particles.

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