# Online Study of the Formation of PA6 Droplets in PP Matrix Under Shear Flow

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**ABSTRACT:** Breakup process of polyamide 6 (PA6) in polypropylene (PP) matrix under shear flow was online studied by using a Linkam CSS 450 stage equipped with optical microscopy. Both tip streaming and fracture breakup modes of PA6 droplets were observed in this study. It was reported that the droplet would break up by tip streaming model when the radio of the droplet phase viscosity to the matrix phase viscosity ($\eta_r = \eta_d/\eta_m$) is smaller than 0.1 (Taylor, Proc R Soc London A 1934, 146, 501; Grace, Chem Eng Commun 1982, 14, 225; Bartok and Mason, J Colloid Sci 1959, 14, 13; Rumscheidt and Mason, J Colloid Sci 1961, 16, 238; de Bruijn, Chem Eng Sci 1993, 48, 277). However, the tip streaming model was observed even when the viscosity ratio was much greater than 0.1 ($\eta_r = 1.9$). In this study for the tip streaming mode, small droplets were ruptured from the tip of the mother droplet. On the other hand, the mother droplet was broken into two or more daughter droplets with one or several satellite droplets between them for the fracture mode. It was found that PA6 droplet was much elongated at first, and then broke up via tip streaming or fracture to form daughter droplets or small satellite droplets with the shape of fiber or ellipse. Stopping shearing, those elongated droplets began to shrink, and finally became spheres. Moreover, it was found that the average domain size of those PA6 spheres considerably decreased with increasing shear time. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 2690–2695, 2007

**Key words:** liquid droplet; breakup; shear flow; polyamide 6; polypropylene

## INTRODUCTION

In the past decades, the effect of shear flow on the morphology and phase behavior in immiscible polymer blends is of considerable interest to polymer science and engineering.[1–16] Break-up[17,18] and coalescence[19,20] of the dispersed droplets were two contrary trends in the melt blending. For instance, break-up would occur when the shear forces exerted on the droplet beyond the interfacial forces that tend to maintain the droplet in a spherical shape. The detailed analysis of this process was described by Taylor,[17,18] through the capillary number as following:

$$\mathrm{Ca} = \eta_m \, \dot{\gamma} \, R/\nu \tag{1}$$

where $\eta_m$ is the matrix phase viscosity, $\dot{\gamma}$ is the applied shear rate, $R$ is the droplet radius, and $\nu$ is the interfacial tension between the two phases. Once Ca exceeds a critical value approximately 0.5,[20] break-up will occur under steady shear until reaching a stable steady-state droplet diameter $D_s$, which was defined as following:

$$D_s = \frac{2\nu \mathrm{Ca}_{\mathrm{crit}}}{\eta_m \dot{\gamma}} \approx \frac{\nu}{\eta_m \dot{\gamma}} \tag{2}$$

Moreover, coalescence is possible when the droplet size is less than the steady-state droplet size given by eq. (2). It is known that there is a distribution of the droplet sizes created by break-up.[21,22] Therefore, the coalescence of the small droplets may occur during steady shear.

Recent quantitative measurements of retraction,[23,24] deformation,[25,26] and breakup[27–44] of droplets in polymer mixture have been widely investigated. In general, there are two breakup modes for Newtonian systems in a simple shear flow field. One mode is tip streaming where a stream of very small droplets is

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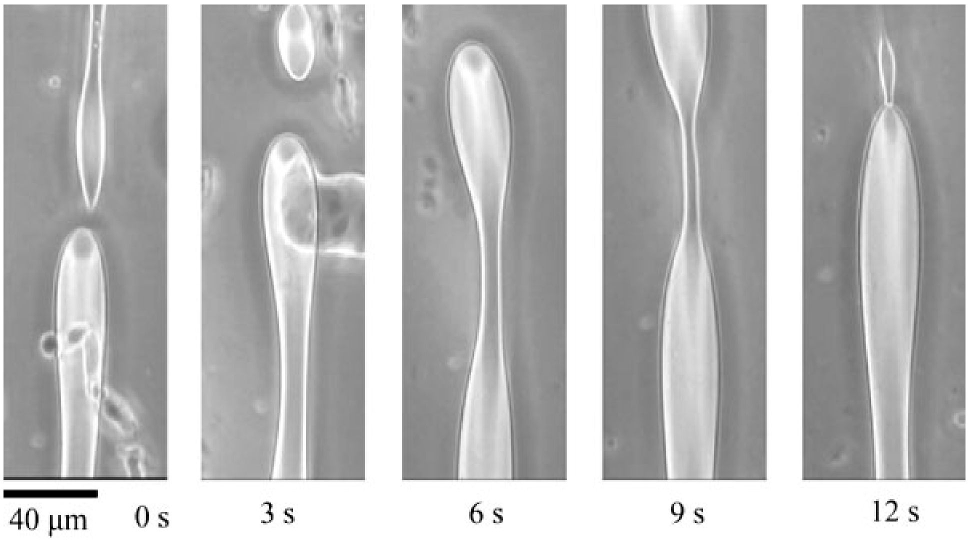

**Figure 1** Breakup occurred at the head of the PA6 droplet via fracture mode for $\dot{\gamma} = 5\ s^{-1}$ at 250°C.

ruptured off the tips of the mother droplet.[18,27–31] The other mode is droplet fracture when the droplet is extended into a cylinder, and then breaks up into two or more daughter droplets with one or several satellite droplets between them.[27,32] When the ratio of the droplet phase viscosity to the matrix phase viscosity ($\eta_r = \eta_d/\eta_m$) is smaller than 0.1,[18,27–31] the droplet will break up by tip streaming model, whereas the fracture model will occur for $10^{-6} < \eta_r < 3.5$.[27] Recently, shear-induced droplet break-up and coalescence processes were investigated by optical microscopy.[33] It was demonstrated that no permanent droplet size hysteresis occurs and the steady-state droplet size produced by coalescence was essentially equal to that produced by break-up. Ramic et al.[34] studied the droplet breakup and coalescence processes in model ternary blends of two homopolymers and a copolymer compatibilizer. They pointed out that a very small amount of copolymers adsorbed to the interface are dramatically effective in suppressing coalescence. More recently, Son et al.[24] described an improvement of technique to measure interfacial tension in immiscible polymer blends. Breakup and filaments in blends under shear flow have also been probed by Van Puyvelde et al.[38] and Cristini et al.[39] Zhang et al.[40] investigated morphology development of straight and folded molten fibers in an imposed external shear flow by using a numerical modeling.

On the other hand, the fabrication of multiphase plastics generally offers a route to combine several good properties of individual polymer components. It can be achieved by mixing two or more than two polymers, leading to the formation of polymer blends or composites.[45–47] The combination of the advantageous properties of polypropylene (PP) with those of polar polymers such as nylon has resulted in the development of available PP/polar polymer blends.[48–55] In general, morphology is a key factor that determines the properties of the resulting blends.

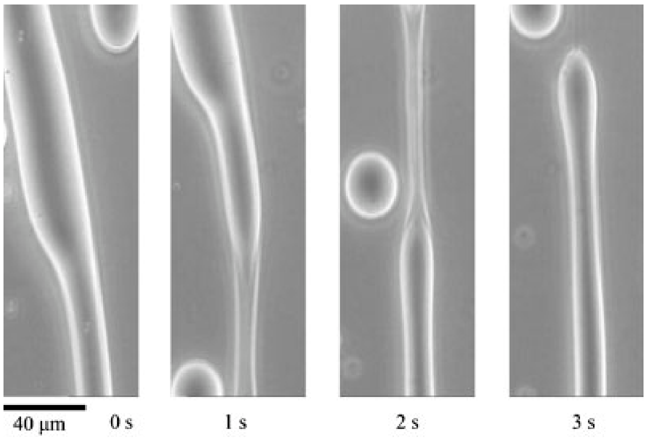

**Figure 2** Breakup occurred at the middle of the PA6 droplet via fracture mode for $\dot{\gamma} = 5\ s^{-1}$ at 250°C.

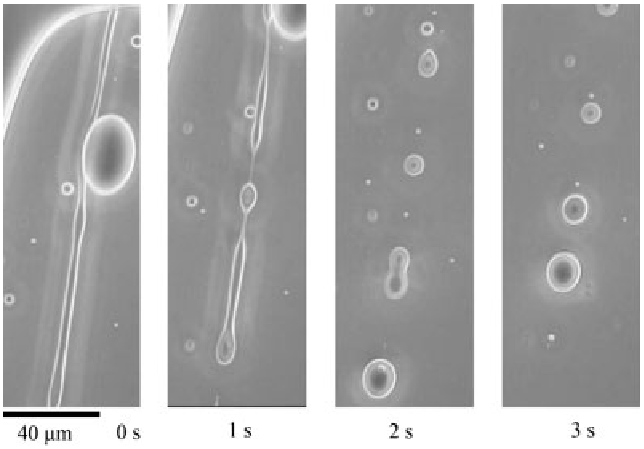

**Figure 3** Breakup for a long and thin PA6 ligament via fracture mode for $\dot{\gamma} = 5\ s^{-1}$ at 250°C.

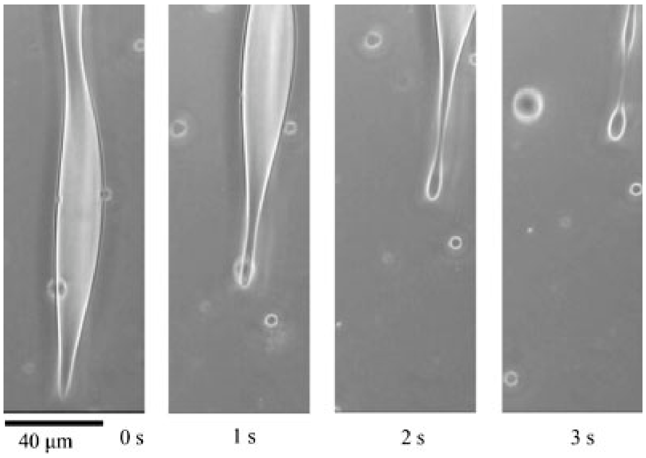

**Figure 4** Breakup occurred at the end of the PA6 droplet via tip streaming mode for $\dot{\gamma} = 5\ \mathrm{s}^{-1}$ at 250°C.

In this study, Linkam CSS 450 equipped with optical microscopy was used to online study the morphology evolvement of polyamide 6 (PA6)/PP blends. The purpose is to reveal the formation of PA6 droplets in PP matrix under shear flow.

## EXPERIMENTAL

### Materials

Polyamide 6 (PA6) sample was obtained from Heilongjiang Nylon Plastic Factory (China). Its number average molar mass is $2.4 \times 10^4$ g/mol. The isotactic polypropylene used in this work was supplied by Jinlin Petrochemical Co. Ltd (China).

### Experimental measurements

The morphologies of PA6/PP blends under shear flow were online observed at 250°C by using a Linkam CSS-450 shearing stage equipped with an Olympus BX-51 optical microscope. Steady shear mode and 40 μm gap thickness were employed in this study. The composition of PA6/PP blends was fixed at 16.7/83.3 by weight. The rheological behavior at 250°C was investigated using a Physica-200 rheometer and a 25-mm parallel plate.

## RESULTS AND DISCUSSION

Figures 1–4 show a series of breakup processes in the PA6/PP blends under steady shear flow. From Figure 1, it is seen that the breakup occurred at the head of the PA6 droplet. This phenomenon agrees with Zhang's simulation result,[40] i.e., the droplet was firstly stretched along the shear orientation subjected to the shear flow, then, bottleneck shape formed adjacent to the head of the droplet. With the further drawing against shear flow, breakup of the fiber occurred at the bottleneck site. Therefore, the PA6 drop was broken into two big daughter droplets. And we can also find that some small satellite droplets were formed between the two daughter droplets. Similarly, from Figure 2 it is found that the breakup can also occur in the middle of the PA6 droplet, namely long PA6 fiber was broken into two separated big daughter droplets. Moreover, a long and thin PA6 ligament between the two daughter droplets can be broken into a series of small satellite droplets (Fig. 3). These breakups (Figs. 1–3) belong to a same breakup mode, i.e., fracture mode. On the other hand, the tip streaming mode was also observed (Fig. 4). It can be seen that breakup occurs at the tail of the PA6 droplet, and the tail of the droplet was much elongated, then broken up and separated to form small droplets from the tip of mother droplet.

Figure 5 presents the shear viscosities at 250°C for the pure melt components. The viscosity ratio ($\eta_r = (\eta_0)_{\mathrm{PA6}}/(\eta_0)_{\mathrm{PP}}$) in this work was 1.9, where the terms $(\eta_0)_{\mathrm{PA6}}$ and $(\eta_0)_{\mathrm{PP}}$ represent the viscosities of PA6 and PP, respectively, at $0.0791\ \mathrm{s}^{-1}$. It is well established that the droplet subject simple shear flow will breakup by tip streaming model for $\eta_r < 0.1$.[18,27–31] However, in our present work, it is found that the tip streaming model occurs even when the viscosity ratio is greater than 0.1 (In present work, $\eta_r = 1.9$.). It may be inferred from these studies[56,57] that the critical breakup condition for polymer systems is different from that for Newtonian system since the polymers are viscoelastic and shear-thinning.

After shear stopping, from Figure 6, it is found that those elliptical droplets shrink quickly (1 s) to spherical droplets due to the high interfacial tension between the two immiscible polymers. However, the

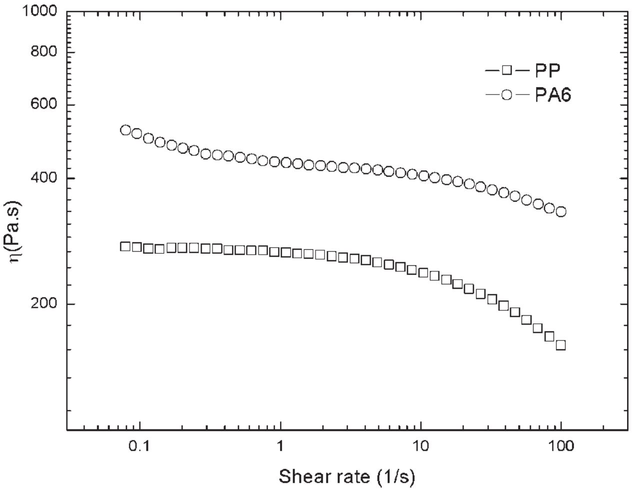

**Figure 5** Steady-shear viscosity as a function of shear rate for the pure melt components at 250°C.

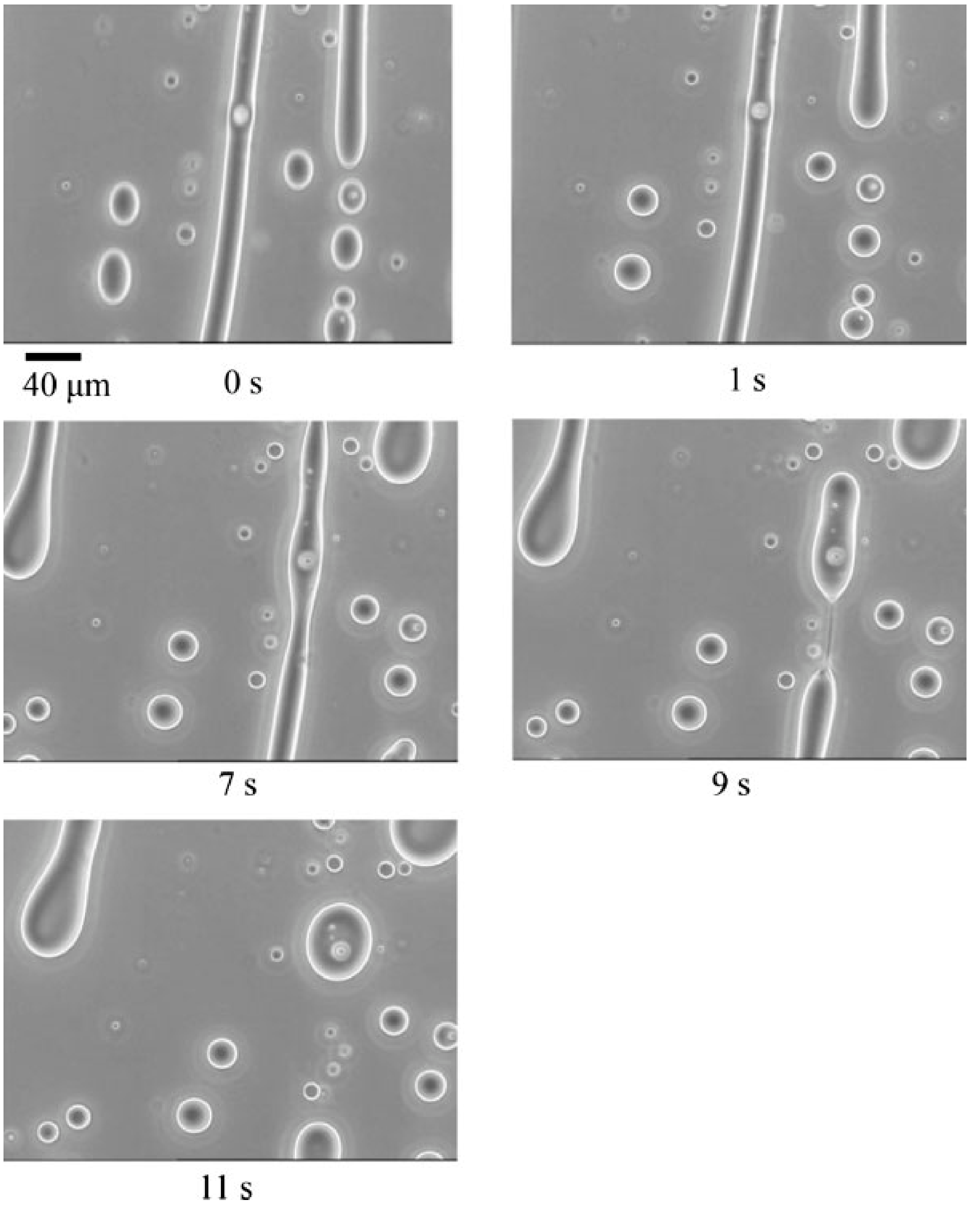

**Figure 6** Morphology evolvement for the PA6/PP blends after shear stopping at 250°C. The blend had been sheared for 960 s at 5 $s^{-1}$ shear rate.

fiber shape droplets began to rupture into some daughter droplets, which also shrink to spherical droplets. On the basis of the experimental observations, we present a schematic diagram (Fig. 7) showing the formation of the PA6 droplets in the PP matrix under shear flow. At first, the PA6 droplets are elongated. With the time going on, mother droplets begin to rupture into daughter droplets, small satellite droplets or a streaming of small droplets via fracture or tip streaming breakup mode. However, once the shear stops, the elliptical droplets begin to shrink to spherical droplets.

Figure 8 shows the morphology change with time for the PA6/PP blends at the shear rate of 20 $s^{-1}$. It can be found that the PA6 domain size decreases with increasing of shearing time. To quantitatively study the relation between the PA6 domain size and shear time and rate, the PA6 domains were statistically analyzed and the average domain sizes were reported. Figure 9 shows the variation of the average PA6 domain size with shear time for various shear rates. The results indicate that shear time and shear rate are two important factors that determine the formation of PA6 droplets in the PP matrix. It is found that the PA6 domain size decreases to 15 μm within 240 s at 20 $s^{-1}$ shear rate. Moreover, the higher the shear rate, the shorter shear time is needed to reach a stable steady-state droplet diameter.

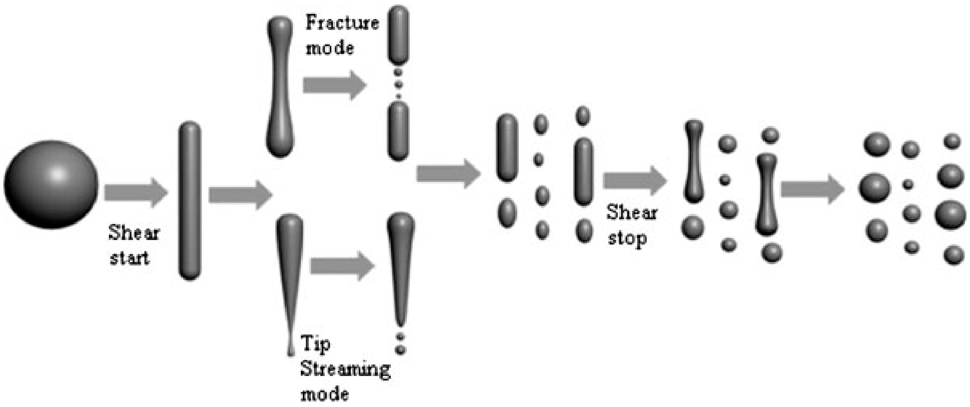

**Figure 7** Schematic diagram showing the morphological evolvement of PA6 droplets in PP matrix.

## CONCLUSIONS

Formation of PA6 droplets in PP matrix under shear flow was online studied by varying shear time and rate. In this work, both tip streaming and fracture breakup modes of PA6 droplets were observed when the viscosity ratio was much greater than 0.1 ($\eta_r = 1.9$). This finding is quite different from the prevenient conclusion,[18,27–31] i.e., the tip streaming model will occur only when $\eta_r < 0.1$. For the tip streaming mode, small droplets were ruptured from the tip of the mother droplet. On the other hand, the mother droplet was broken into two or more daughter droplets and formed a series of satellite droplets between them for the fracture mode. It was found that PA6 droplet was much elongated at first, and then broken up via tip streaming mode or fracture mode to form daughter droplets or small satellite droplets with the shape of fiber or ellipse. When shearing stopped, these elongated droplets began to shrink, and finally from spheres. Moreover, it was found that the average domain size of those PA6

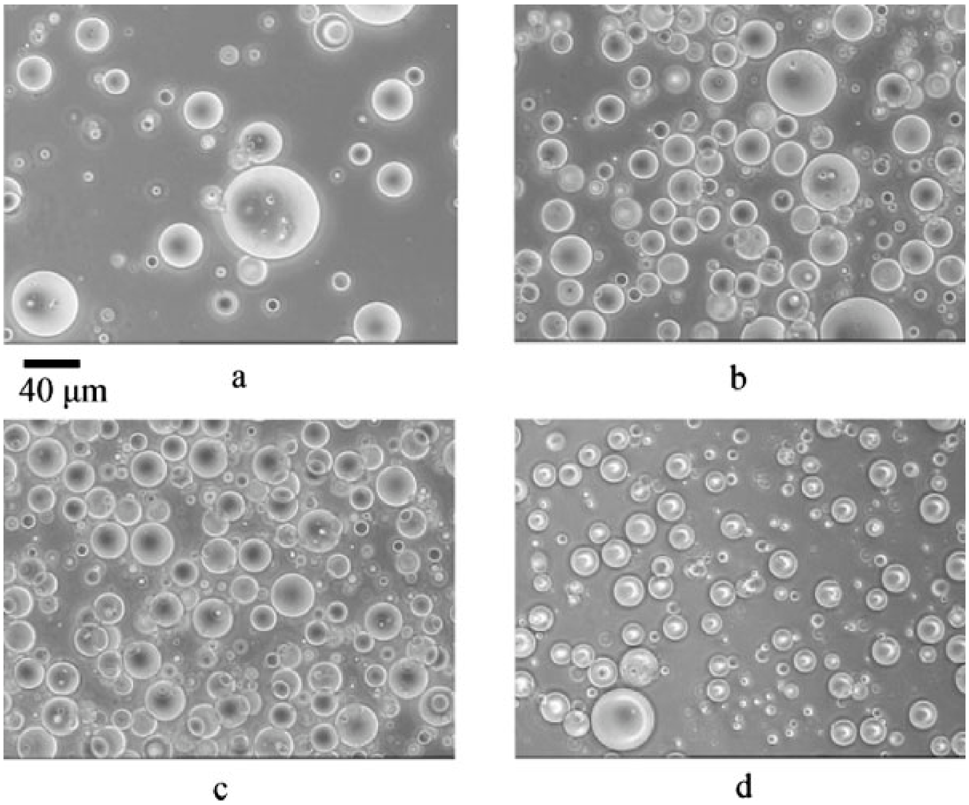

**Figure 8** Micrographs showing the micrographs of the PA6/PP blends for $\dot{\gamma} = 20\ \text{s}^{-1}$ at 250°C. Shearing time: (a) 80 s; (b) 120 s; (c) 160 s; and (d) 200 s.

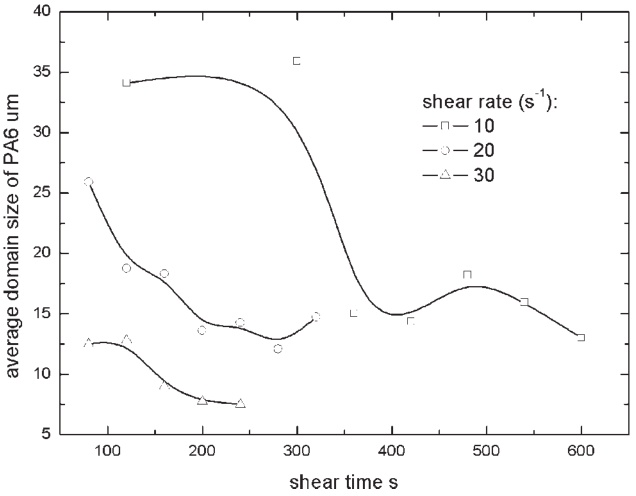

**Figure 9** Variation of average PA6 domain size with shearing time for various shear rates.

spheres considerably decreased with increasing shear time.

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