

# Interface-Induced Coarsening Process in Polymer Blends

Xu-Ming Xie,<sup>\*1</sup> Xiang-Ming Kong,<sup>\*</sup> Tian-Jing Xiao,<sup>\*</sup> Yong Yang,<sup>\*</sup> Ning Gao,<sup>\*</sup> and Akihiko Tanioka<sup>†</sup>

*Institute of Polymer Science and Engineering, \*Department of Chemical Engineering, Tsinghua University, Beijing 100084 China; and †Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1, Ookayama, Meguro-ku, Tokyo, Japan*

Received December 9, 1999; accepted October 23, 2000

**The coarsening process of the droplets in a two-phase polymer blend (PP/EVAc) was studied under two-dimensional and three-dimensional conditions using a phase contrast microscope and computer image analyzer. The results showed that under three-dimensional conditions the growth of the droplet's radius with time follows  $r^3 \sim t^{1.01}$ , corresponding to the evaporation–condensation theory of Lifshitz–Slyozov,  $r^3 \sim t$ , while under two-dimensional conditions the growth law is  $r^3 \sim t^{1.31}$ . The growth rate of the droplets under two-dimensional conditions is faster than that under three-dimensional conditions. This difference is caused by an interfacial interaction (wetting effects) between the substrates and polymer blend. The existence of the interface promoted the coarsening process of the polymer blend under two-dimensional conditions.**

© 2001 Academic Press

**Key Words:** polypropylene; ethyl vinyl acetate copolymer; coarsening; substrate; interface; wetting effect.

## INTRODUCTION

The properties of a polymer blend depend on its morphology, and its morphology is closely related to the phase separation process and the subsequent coarsening process. Recently, some studies showed that the substrates have a significant influence on the early stage of phase separation of low molecular blends and miscible polymer blends. In 1977, Cahn (1, 2) observed critical wetting phenomena. Next, Tanaka (3, 4) experimented on low molecular blends and blends with such materials as glass beads, and found that the separation process of these blends had significantly changed in a confined geometry. Wiltz (5) studied polyisoprene (PI) and poly(ethylene–propylene) blends in a 1-mm-thick quartz container. He found that in this system, two kinds of growth modes existed: a fast mode and a slow mode. In the region near the quartz surface, the phase separation followed the fast mode, and the relationship between the dominant length  $L$  and the separation time  $t$  was  $L \sim t^{3/2}$ , while in the bulk region, the relationship changed to  $L \sim t$ . Wiltz stated that the long-distance van der Waals force between the surface and blends caused the difference between these two regions. However, the late stage phenomenon of coalescence coarsening, which also controlled the resulting morphology, and thus

the end performance of materials has been overlooked. We are now concerned with the effect of the substrate on the coarsening process of immiscible polymer blends.

In this research, blend samples with thicknesses of 3 mm and about 15  $\mu\text{m}$  were prepared to study the effects of the substrate on the coarsening process of an immiscible polymer blend system. The formal sample was viewed as a three-dimensional (3D) sample, the latter was seen as a two-dimensional (2D) sample. It can be imaged that during the annealing process the interaction (wetting effects) between the substrates and polymer blends may influence the coarsening process of all the 2D samples. The substrates can influence only the surface region of the 3D samples for a limited annealing time, and had little effect on the entire sample.

In this study, a phase contrast microscope was used to observe the 2D and 3D polymer samples. Comparing the growth law of the dispersed droplets under these two conditions, we determined the effects of the substrate on the coarsening of immiscible polymer blends.

## EXPERIMENT

### Materials

The polypropylene (FA410) used was produced by the Showa Denko Co., and its melt flow rate (MFR) is 7.2 g/10 min. Ethylene vinyl acetate (EV523) containing 33 wt% VAc with an MFR of 14 g/10 min was made by the Mitsui-Du Pont Co.

### Preparation of 2D and 3D Samples

PP/EVAc(70/30) samples were first thoroughly blended at 170°C in a Brabender until the torque reached a constant value. The blended samples were then cut into films about 10  $\mu\text{m}$  thick with an ultramicrotome. These films were expanded between two cover glasses (substrates) and then placed on a 220°C heating stage. After annealing for a certain time, these samples were quenched. Thus, the two-dimensional (2D) samples were prepared.

The above-obtained PP/EVAc blends were put into a 3-mm-thick mold, and then annealed at 220°C after being preheated for 5 min. After being annealed for a certain time, the samples were quickly quenched into ice water. Thus, a series of 3-mm-thick

<sup>1</sup> To whom correspondence should be addressed.

PP/EVAc blended samples of different annealing times were obtained. An ultramicrotome was then used to cut the center section of these 3-mm-thick samples into films. These 3-mm-thick samples and the films were viewed as three-dimensional (3D) samples whose coarsening process during annealing occurred under 3D conditions.

2D samples can be also prepared as below (indicated as 2D\*): PP/EVAc blend (70/30) was dissolved in xylene at 110–120°C and precipitated in methanol. The recovered material was then dried at room temperature. A bit of these materials was sandwiched between two glasses (substrates) and pressed to about 10  $\mu\text{m}$  thickness after being heated for 5 s. The samples were annealed for a specified period of time at 220°C, and then quenched for microscopic observation. No dispersed particles were observed in the 2D\* samples at the initial state, implying the mixture of PP/EVAc was homogeneous.

The morphologies of both samples were then observed using a phase contrast microscope, and a computer image analyzer was used to obtain the radius of the dispersed droplets in the blend samples under different annealing conditions.

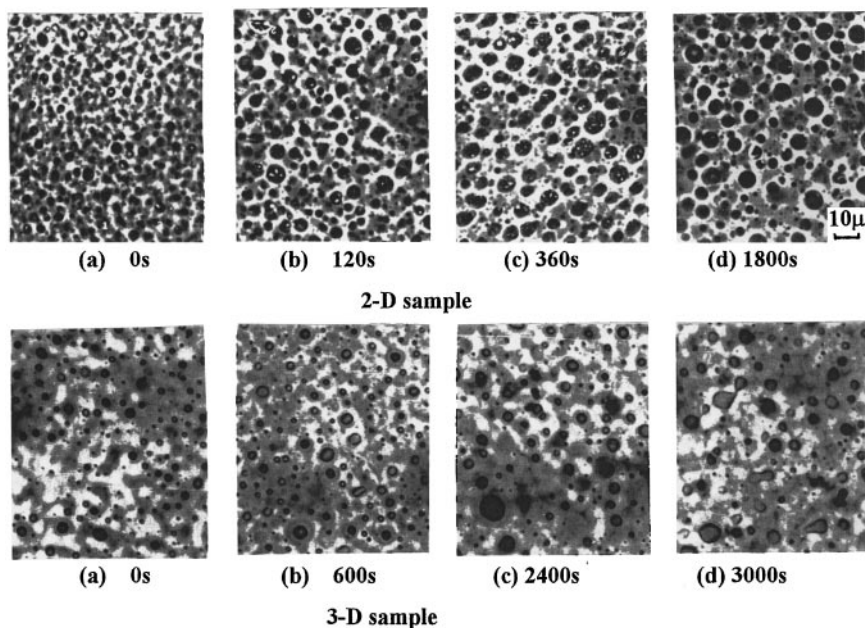
## RESULTS AND DISCUSSION

Figure 1 shows the phase contrast microscope photographs of the 2D and 3D PP/EVAc blend samples at 220°C for different annealing times. Glass was used as the substrate of the 2D samples in this research. From these photographs, it can be seen that the longer the annealing time, the larger the EVAc droplets in the blends. This means that the EVAc droplets gradually grew during annealing. Under 3D conditions, the EVAc droplets changed in a way similar to that of the 2D samples. Comparing the 2D

and 3D samples, the growth of the dispersed EVAc droplets under 2D conditions was faster than that under 3D conditions. The growth of the dispersed droplets under 3D conditions was much slower.

During the observations, it was found that almost all the droplets were round under the 2D conditions. Even when two droplets bumped into each other, there was no apparent deformation. Only at the contacting boundary of the two droplets did a deformation take place to form one larger droplet. However, things are different for the 3D samples. Although most of the droplets were round, a few irregular droplets, attraction between droplets, deformations, and combinations were frequently seen. We postulate that these differences between the 2D and 3D samples were caused by the substrate. 2D samples were significantly influenced by the interfacial interaction between the substrate and polymer blend sample, making the droplets very active, and energetic enough to move and quickly collide. For the 3D samples, the motion of the droplets in the middle of the samples was mainly a Brownian motion. The droplets had less opportunity to come in contact with each other. When the droplets were near each other, due to gravitation, the droplets changed their shapes in order to connect with other droplets, and combined into a new droplet. Therefore, deformed droplets were often seen in the 3D samples. However, the coalescence of the droplets is caused by an evaporation–condensation mechanism for most of the droplets under the 3D conditions. These details will be discussed below.

With the computer image analyzer, data on the radius of the droplets under different conditions were obtained (6, 7). Figure 2 is a plot of the average radius of the droplets  $r$  versus the annealing time  $t$  for the 2D and 3D samples. From this plot,



**FIG. 1.** Phase contrast microscopy photographs of PP/EVAc(70/30) blend under 2D and 3D conditions for various annealing times  $t$ .

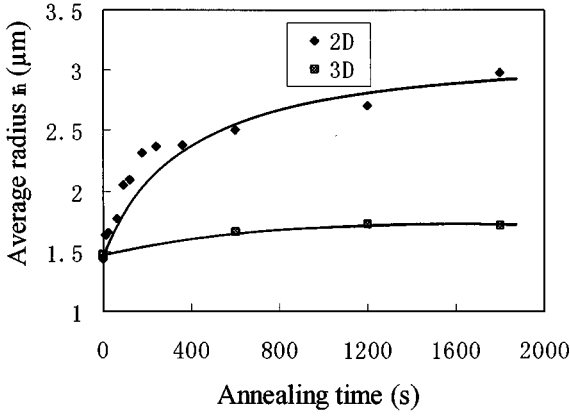


FIG. 2. Plot of the average radius  $r$  of the dispersed droplets versus the annealing time  $t$  in 2D and 3D samples.

we can see that under both sets of conditions, the radii increased with the annealing time: the longer the annealing time, the larger the radii. Also, the radii changed faster during the initial stage, and the growth of the droplets became slower and should approach a different equilibrium with increasing annealing time in both the 2D and 3D samples in the last stage. Comparing the 2D and 3D samples, it is obvious that the growth in the 2D samples was faster than that in the 3D samples.

Based on the evaporation–condensation mechanism and the Brownian collision and coalescence mechanism (9), the coalescence was predicted to have the same general time dependence of coarsening rate,

$$r^3(t) = r^3(0) + Kt, \quad [1]$$

where  $r(t)$  and  $r(0)$  are average particle radii at times  $t$  and 0, and  $K$  is the rate constant of coarsening. Equation [1] has been reviewed adequately in polymer–polymer liquid systems.

Equation [1] can be changed into

$$\Delta r^3 = K \Delta t. \quad [2]$$

Thus, it can be seen that  $\ln \Delta r^3 \sim \ln \Delta t$  will be a linear relation, and its slope must be 1.

Figure 3 shows plots of  $\ln \Delta r^3$  versus  $\ln \Delta t$  for 2D and 3D samples. Here,  $r^3$  was obtained from  $r_n r_w r_z$  where  $r_n$ ,  $r_w$ , and  $r_z$  are number-average radius, weight-average radius, and Z-average radius of dispersed droplets, respectively (10). Fitting two plots as straight lines, it is found that the slope for the 3D sample is 1.01 and that for 2D sample is greater than 1.01. That is to say, the coarsening rate follows Eq. [1] or [2] under 3D condition while it does not under 2D condition. The growing rate of droplets in 2D samples is faster than that in 3D samples. This hints that the coarsening process has an essential difference under 2D conditions and under 3D conditions, but not a quantitative difference.

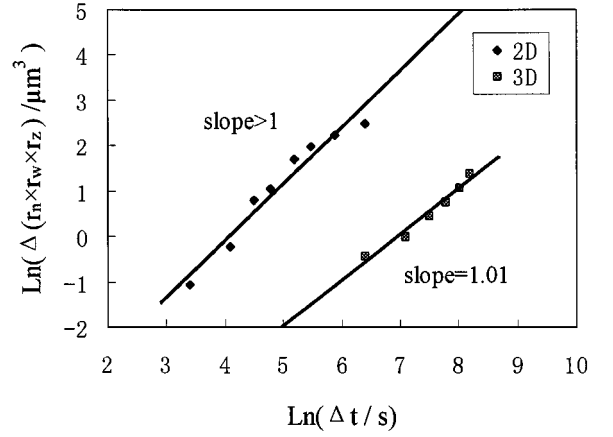


FIG. 3. Plot of the logarithm of  $\Delta r^3$  of the dispersed droplets versus the logarithm of the annealing time  $t$  in 2D and 3D samples.

In order to understand the coarsening rule under 2D conditions, we assume the following equation by which the 2D sample abided:

$$r^3(t) = r^3(0) + Kt^\alpha. \quad [3]$$

Figure 4 is plot of  $\ln r^3$  versus  $\ln t$  for 2D\* samples. Here,  $r^3$  was calculated as described above. In 2D\* samples, the particles radii of the dispersed phase can be assumed to be zero at time  $t = 0$ , i.e.,  $r(0) = 0$ . The plot appears as a straight line and the slope is 1.31. This is in agreement with Eq. [3] and  $\alpha = 1.31$ .

There may be two reasons for the difference between the 2D and 3D samples: the temperature gradient in the samples during annealing or interfacial interaction between the 2D sample and substrate, which induces development of the coarsening. Since both the 2D and 3D samples were thin and the annealing temperature was quite high, the temperature gradient in the samples should vanish in a short time. Moreover, as shown in Fig. 2,

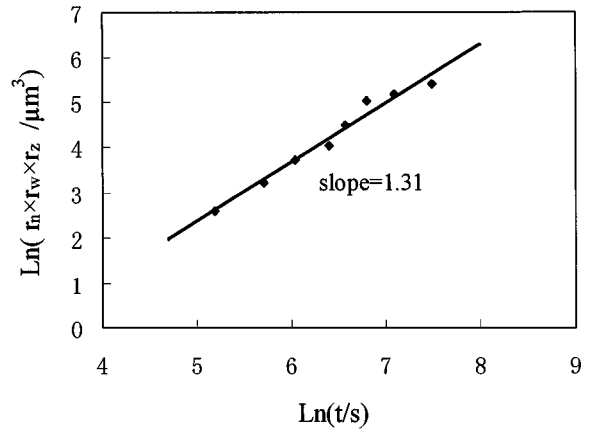


FIG. 4. Plot of the logarithm of  $r^3$  of the dispersed droplets versus the logarithm of the annealing time  $t$  in 2D\* samples.

despite lengthening the annealing time, the growth of the droplets became slower and then should stop with increasing annealing time in both the 2D and 3D samples. This implies that the growth of the droplets in the 3D samples is intrinsically slower than that in the 2D samples. Therefore, the temperature gradient was not the main cause of the difference. The difference was mainly caused by the interfacial interaction between the substrate and blend samples (6–8).

This essential difference implied the substrate greatly influenced the coarsening process, i.e., substrate-induced coarsening in the 2D sample. The substrate has a significant influence on the coarsening of the immiscible polymer blends. It is considered that there is a long-distance van der Waals interaction between the substrate and the polymer blend. It may be possible to suppose that the EVAc molecules in the blend sample near the sample surface in contact with the glass substrate are active mainly because of the effect of minimization of the interfacial energy. During annealing, if the thermal energy of the molecules is sufficiently high to overcome a barrier to diffusion, the diffusion must occur in the blend system and consequently the EVAc droplets will coarsen. The nearer to the surface, the more coalescence takes places easily.

Since the effect between the substrate and the polymer blend only exists in a very shallow region, in the very thin 2D samples, the substrate could significantly influence the motion of almost all the droplets. The droplets were very active and energetic enough to quickly move and contact each other as mentioned above, so the growth of the droplets was quite fast. While the substrate can have an effect on the region near the surface of the 3D samples, it had little influence on the whole sample. The coalescence of the droplets is mainly caused by an evaporation–condensation mechanism for the 3D blend samples, so the coarsening speed of the 2D sample is much faster than that of the 3D samples. For these reasons, we can see that under 3D conditions the relation of the radius of the droplets  $r$  and the annealing time  $t$  was  $\Delta r^3 \sim t^{1.01}$ , corresponding to the Lifshitz–Slyozov theory (11) and under the 2D conditions the relation changed to  $\Delta r^3 \sim t^{1.31}$ . The substrate plays an important role in the coarsening of the polymer blend.

## CONCLUSIONS

1. Under both 2D and 3D conditions, the longer the annealing time, the larger the EVAc droplets in the blends. This means that the EVAc droplets gradually coarsen during annealing. Comparing the 2D and 3D samples, the growth of the dispersed EVAc droplets under 2D conditions was faster than that under 3D conditions.

2. The plots of  $\ln \Delta r^3$  versus  $\ln \Delta t$  for both the 2D and 3D polymer blend samples indicated a linear tendency, i.e.,  $\Delta r^3 \sim t^\alpha$ ,  $\alpha$  being the slope of the fitting line. The slopes were 1.32 and 1.01 for the 2D and 3D samples, respectively; i.e., for the 3D sample, the growth of dispersed droplets is nearly  $\Delta r^3 \sim t^{1.01}$ , corresponding to the evaporation–condensation mechanism suggested by Lifshitz–Slyozov. The difference in the 2D and 3D samples was mainly caused by the interfacial interaction between the substrate and the blend samples, implying that the interfacial interaction could induce a coarsening of the polymer blends.

## ACKNOWLEDGMENTS

We are indebted to the National Natural Science Foundation of China (Grant No. 29604004) and to the Excellent Young Teacher Foundation of State Education Commission of China for their financial support.

## REFERENCES

1. Siggia, E. D., *Phys. Rev. A* **20**, 595 (1979).
2. Cahn, J. W., *J. Chem. Phys.* **66**, 3667 (1977).
3. Tanaka, H., *Phys. Rev. Lett.* **70**, 53 (1993).
4. Tanaka, H., *Phys. Rev. Lett.* **70**, 2770 (1993).
5. Wiltzus, P., *et al.*, *Phys. Rev. Lett.* **66**, 3000 (1991).
6. Xie, X.-M., *Polymer* **33**, 1996 (1992).
7. Xie, X.-M., Xiao, T.-J., and Zhang, Z.-M., *J. Colloid Interface Sci.* **206**, 189 (1998).
8. Xie, X.-M., Chen, Y., Zhang, Z.-M., *et al.*, *Macromolecules* **32**, 4424 (1999).
9. Crest, B., and Nesarikar, A. R., *Macromolecules* **28**, 890 (1995).
10. Mirabella, F. M., *et al.*, *J. Polym. Sci. B* **32**, 2187 (1994).
11. Lifshitz, M., *et al.*, *J. Phys. Chem. Solids* **19**, 35 (1961).