Supercritical Carbon Dioxide-Induced Epitaxy on the Surface of Nylon1212 Substrate

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(Received July 8, 2002; CL-020570)

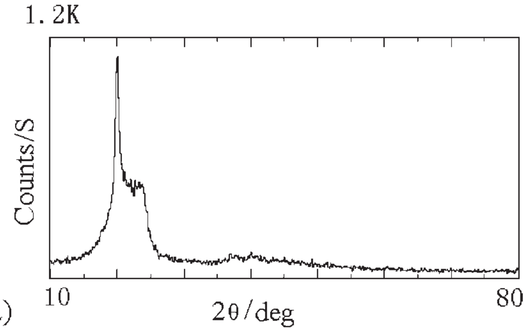
In this study we focus on the influence of the absorbed supercritical (SC) CO_2 on the surface aggregation structure of the substrate polymer, nylon1212. Both virgin and treated nylon1212 were measured or observed with wide-angle X-ray diffraction (WAXD), micropolariscope and SEM. A novel phenomenon, SC CO_2-induced epitaxy (crystalline overgrowth) was discovered and the mechanism is deduced.

It is well known that crystallization of some amorphous and semicrystalline polymers can be induced by solvent as well as by heat and strain. The interaction between polymer and the solvent reduces the effective glass transition temperature (T_g) and, if the reduction of T_g is large enough to put the system in the crystallization temperature region, the polymer chains rearrange themselves into a lower free energy state.[1,2] Chiou,[3] Johnston[4,5] and K. Mizoguchi[6] et. al. have both discovered that supercritical CO_2 also has inducing crystallization effect on polymers.

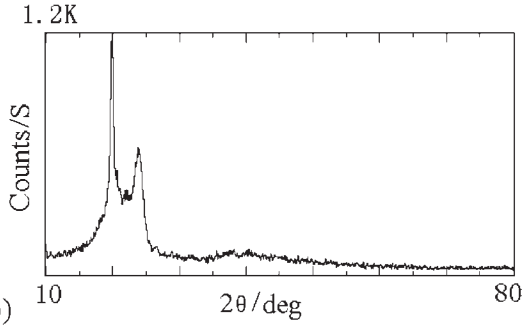
Yet previous work was focused on the study of plasticizing effect of SC CO_2 and the internal crystallization caused by it. In our study a new form of supercritical fluid-induced crystallization, homoepitaxy was observed on the surface of the CO_2-treated nylon1212. Epitaxy is generally defined as a kind of oriented crystallization of a crystalline matter on another crystalline substrate.[7] In other words, it is an oriented crystallization induced on the substrate surface. As the action of the substrate on the overgrown matter causes strict orientation between them, the overgrown matter presents extraordinary morphology and structure. It is sure that this particular epitaxy orientation will cause some distinctive properties of the crystal-overgrown materials.

In the experiments transparent light-yellow nylon1212 pellets were dried and processed to 0.9 ± 0.02 mm-thick sheets on the press vulcanizer. After being sheared into 1.2×3.0 cm samples, they were swollen by pure CO_2 (99.9%) at 8–14 MPa and 40 °C for 4 h. Then WAXD was used to determine the possible change of nylon1212's aggregation structure before and after CO_2 absorption. The results are shown in Figure 1, from which we can see that with CO_2 sorption in the nylon1212 substrate, there appears an apparent crystalline peak at 23.89° besides the former one at 20.01°. This demonstrates that the aggregation structure as well as the partitioning between crystalline and amorphous regions of nylon1212 has changed and it also indicates that the absorbed CO_2 has plasticizing action on the polymer and that may contribute to the percent crystallinity change of nylon1212.

To achieve further evidence, untreated and CO_2-treated thin nylon1212 films were observed through a polarizing microscope. The photographs are given in Figure 2, and it can be seen that there are some arborescent and bacillary structures on the surface of CO_2-treated samples. Subsequent SEM measurements were also carried on, and similar structures were found on the surface of some other CO_2-treated nylon1212 samples, as shown in Figure 3. It is obvious that the arborescent and bacillary structures formed on the polymer surface because of the existence of SC CO_2. When the enlargement factor was changed to ×500 to achieve wider field of vision, the distribution of these structures on the polymer surface was found to have quite high uniformity. Based on these results, a conclusion is preliminarily drawn that epitaxy has taken place on the sample surface.



a)



b)

Figure 1. Results of WAXD measurements of virgin nylon1212 (a) and SC CO_2-treated nylon1212 (b).

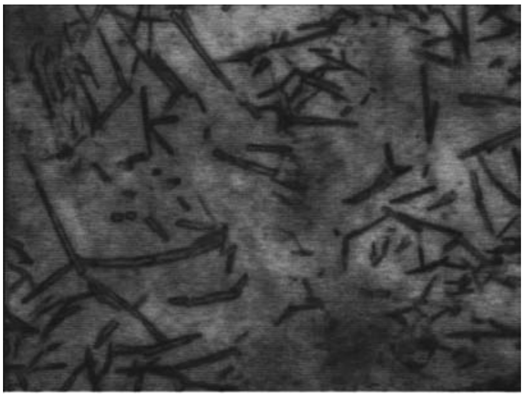
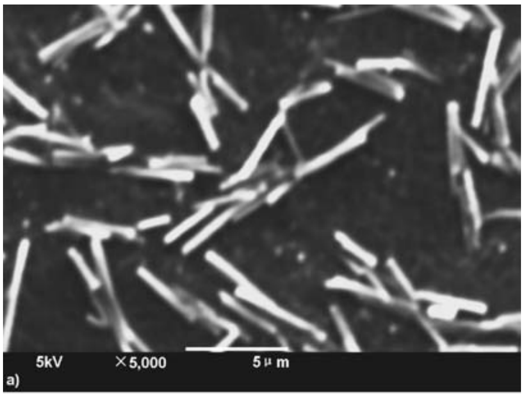


Figure 2. Micropolariscopy photographs (×100× 0.9 × 10) of SC CO_2-treated nylon1212.



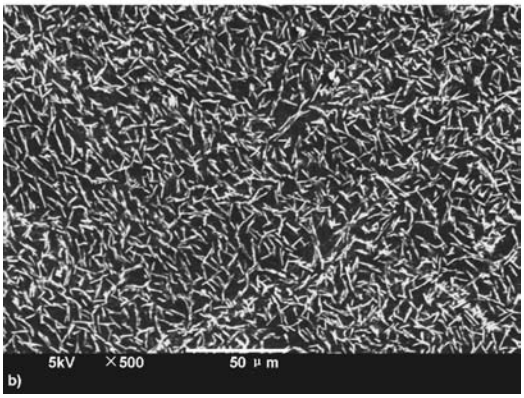


Figure 3. SEM photographs of SC CO_2-treated nylon1212.

L. Royer[8,9] held that happening of epitaxy is based on the structure resemblance between the substrate and the overgrown matter, i.e. it depends on certain geometric matching between the two matters. For example, there is a definition as following:

$$\Delta = 100\% \times (d - d_0)/d_0$$

where d and d_0 stand for the partitioning parameters of the overgrown matter and the substrate, respectively; Δ is the ratio of mismatch. Generally, 10–15% is the upper limit under which an epitaxy can take place. In this study, homoepitaxy described by Wittmann and Lotz[10–13] may have taken place. When nylon1212 was treated in CO_2 above T_c and P_c, a certain amount of macromolecules were dissolved in or highly swollen by the SC CO_2. These dissociated molecules would act as the overgrown matter in the crystallization process. In addition, based on the Bragg equation, it is known from the WAXD data that the *d*-spacing values of the surface crystalline structure have been changed by SC CO_2 treatment. So it is reasonable that this CO_2-induced change caused certain effect on substrate's geometric dimension to change the partitioning parameters of the dissociated nylon1212 and the substrate nylon1212. Then Δ of the system changed, followed by epitaxy happening and crystal forming on the polymer surface.

In summary, we have observed arborescent and bacillary crystalline structures on the surface of supercritical CO_2-treated nylon1212, which are thought to be overgrown crystals induced by SC CO_2. Further studies on the advantages and importance of this SC CO_2-induced homoepitaxy is being carried out now.

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