Formation of Transparent Nylon Thread with a High Pressure Carbon Dioxide Processed Additive.

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ABSTRACT :

The cause of the formation of transparent Nylon with a small amount of additive that treated by high pressure carbon dioxide was investigated. With the addition of 0.05 wt% of high pressure CO_2 treated dimethyl silicone oil emulsion to the Nylon enhanced the transparency, while untreated and high pressure N_2 treated additive had no effects. Analysis with differential scanning calorimetry and X-ray large angle diffraction revealed that the crystallinity and the size of crystal is almost the same with untreated, N_2 treated and CO_2 treated Nylons, which means the treatment with high pressure CO_2 leads to the homogeneous mixing of Nylon and silicone oil that acts as crystal nuclei during the extrusion process. The cause of the uniform mixing was attributed to the enhanced wettability of the CO_2 treated additive to the Nylon pellets. It could be concluded that with the high pressure CO_2 treatment, nanoscale mixing, or the precision mixing, of polymers could be achieved.

KEYWORDS

Carbon Dioxide, Nylon, Transparent, nanoscale mixing, precision mixing

1. Introduction

Modern technical community and social life could not be retained without polymeric materials. It is due not only to the technological progress in polymer synthesis such as the development of new catalysts and new polymerization processes, but also to the development of additives. Polymers widely used in our world are the mixtures of polymeric raw materials and additives such as antioxidants, light stabilizers, vulcanization agents, anti-scorching agents, and so on. Studies on the polymer additives are the most important area in the polymer engineering [1].

Recently, our research group found that ca. 3-5 ppm (by weight) of additive that processed with carbon dioxide enhances tensile strength, breaking strength, and rupture elongation of PE film up to two fold. Similarly, it was also found that the 500 ppm (by weight) of carbon dioxide processed additive make turbid Nylon transparent. The PE film had already commercialized as an ecological trash bag that the thickness is half compared with the conventional products. The transparent Nylon had also commercialized as a value added fishing thread. Many other commercial applications that use the high pressure carbon dioxide processed additives are now under development in many fields of polymer applications however, the mechanism of improvement in strength and transparency is not clarified yet.

In this article, using the Nylon as a model polymer, the mechanism of these functional improvement of polymers with the high pressure carbon dioxide processed additives are investigated.

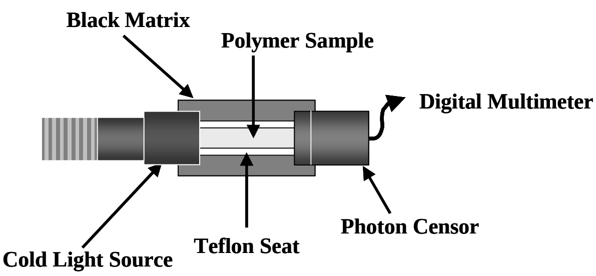
2. Experimantal

Materials: Nylon used in this study is NOVAMID (Mitsubishi Engineering Plastics Co.Ltd.), mixture of Nylon6:Nylon66=4:1. It was supplied from Boron Japan, and used without further treatment. The additive used is a silicone oil emulsion Matsumoto Silicone softener #302(Matsumoto Yushi-Seiyaku Co.Ltd., MS302), and used as received. Water content of the MS302 was 83% by weight. Special grade carbon dioxide (CO_2, 99.99%) was used as the pressurizing medium without further purification. Special grade nitrogen gas (N_2, 99.99) was used in the control experiments.

Procedures: The MS302 is sealed in an autoclave, and processed with CO_2 at 25 and 40 ^oC, 12MPa for 15 minutes. After the depressurization, MS302 is taken out from the autoclave, and mixed with the Nylon pellets. The nylon is then fed into a single screw extruder (IKEGAKI Co. Ltd., PCM30), and extruded to obtain a thread of about 6mm in diameter at 285 ^oC, and cooled in a water bath.

Analysis: Thermal analysis of the extruded Nylon threads with a DSC (SEIKO SSC5200) is conducted to determine the crystallinity. The crystallinity X_C was calculated as follows:

$$X_C = \frac{H_C}{H_{C0}} \times 100 \qquad (1)$$



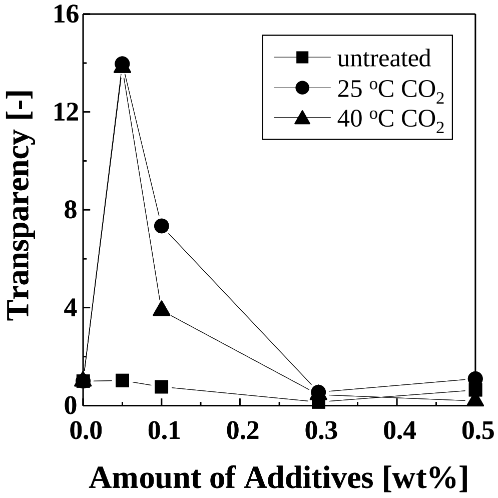


Figure 1. Schematic representation of an apparatus for tranaprency measurements.
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Figure 2. Effects of the amount of additives on the transparency

the Nylon

where H_C the hest of fusion of polymer samples, and H_{C0} the that of perfect crystal.

XRD analysis is also conducted to determine the size of the crystallite of the Nylon with a diffractmeter. Following Scherrer's equation was used for the calculation:

$$D = \frac{K \cdot \lambda}{\beta \cos \theta} \quad \textbf{(2)}$$

where D the size of crystallite, K the Scherrer's constant (=0.9 in this study), λ the wave length of the X-ray, β the half width of the diffraction peak, and θ the diffraction angle.

Figure 1 shows the schematic representation of the apparatus for the transmittance of the light through the sample. The intensity of light transmitted through the thread (6mm in diameter and 20mm in length) is measured by a photon censor, and the transparency is calculated by an equation shown below;

$$\text{Transparency}\,[-] = \frac{\text{Intensity of light through the sample [mA]}}{\text{Intensity of light through the untreated sample [mA]}} \quad \textbf{(3)}$$

Wettability: Wettability of the MS302 was evaluated by the contact angle measurements. Contact angle of the MS302 was measured with a contact angle meter (Drop Master D-701, Kyowa Interface Science co. Ltd.). A PTFE plate was used as substrate.

Viscosity: Viscosity of the MS302 was measured with a oscillating viscometer (SA-1, A and D Co.Ltyd.).

3. Results and Discussion

Optimum mixing ratio: The additives are basically impurities, and too much amount of additives might deteriorate the properties of polymers. Thus, optimum mixing ratio of MS302 to the Nylon was investigated. Figure 2 shows the transparency of various samples

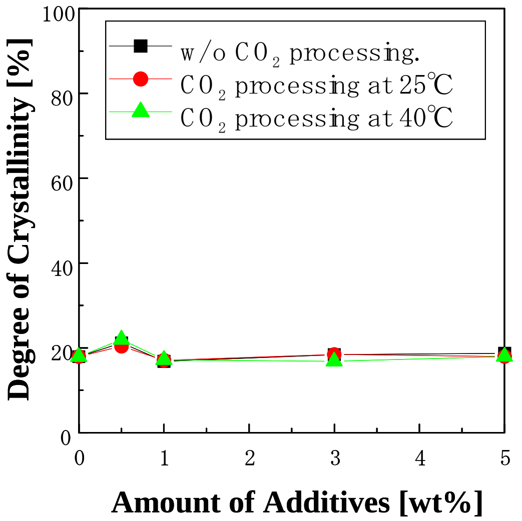

Figure 3. Effects of thenamount of the additives on the degree of crystallinity.

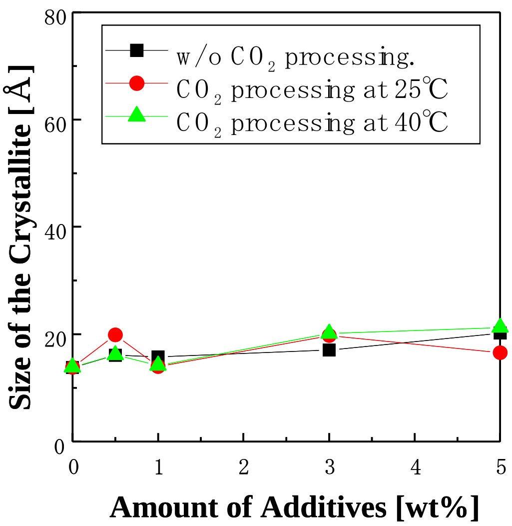

Figure 4. Effects of thenamount of the additives on the size of crystallite.

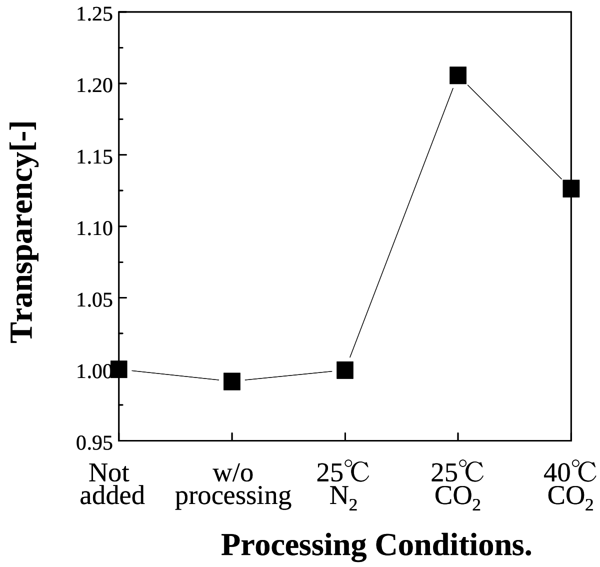

Figure 5. Effects of processing conditions on the transparency.

with different amount of MS302 extruded at 240°C. The figure clearly shows that the addition of the 0.05 wt% of the MS302 treated with CO_2 resulted in high transparency of the Nylon, and the processing at 25°C is more desirable than that at 40°C. Figures 3 and 4 shows the effects of the amount of additives on the degree of the crystallinity and the size of crystallite. The addition of the additives had almost no effects on both the crystallinity and the size of crystallite. From these results, successive experiments were conducted with the additive of 0.05 wt%.

Effects of the processing condition: Figure 5 shows the effects of the processing conditions on the transparency. For a reference, results of processing with N_2 as well as without processing are added in the figure. As could be seen from the figure, processing with CO_2 gave a significant improvement in the transparency, and lower the temperature, higher the transparency.

Mechanism of making the Nylon transparent: It is well known that there are two ways to make the polymers transparent: One is that make the polymer amorphous, and the other is that make the size of crystal small enough not to diffract the incident light. As described above, addition of the CO_2 treated additive gives minute effects on the crystallinity and the size of crystallite but had the significant effect on the transparency. These facts implie that the additive presumably improved the dispersivity of the crystal. Thus, the problem is, why the dispersivity of the additive improved by the processing with the high pressure CO_2 ? We are focused on the wettability of the MS302 processed with the CO_2 on the hypothesis that the silicone oil in the MS302 acts as a nuclei of the polymer crystal, and the processing with the CO_2 improve the dispersibity of the silicone through the wetting of the Nylon pellet.

Figure 6 shows the contact angle of water, silicone oil and the MS302. Viscosities of the water and MS302 are also presented. The contact angle decreases with the processing. Further, the contact angle of all samples treated at 25°C is lower than that treated at 40°C. Figure 7 shows the pressure dependence of the contact angle of water treated with CO_2. From theb figures 6 and 7, it is clear that processing with high pressure CO_2 lowers the contact angle of water, silicone oil and the MS302, and the degree of contact angle depression

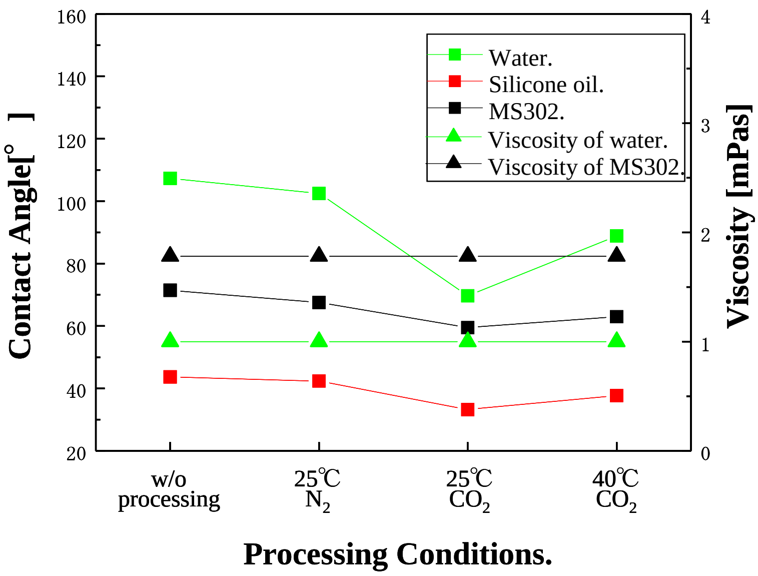

Figure 6. Effects of processing condidions on the contact angle of the samples.

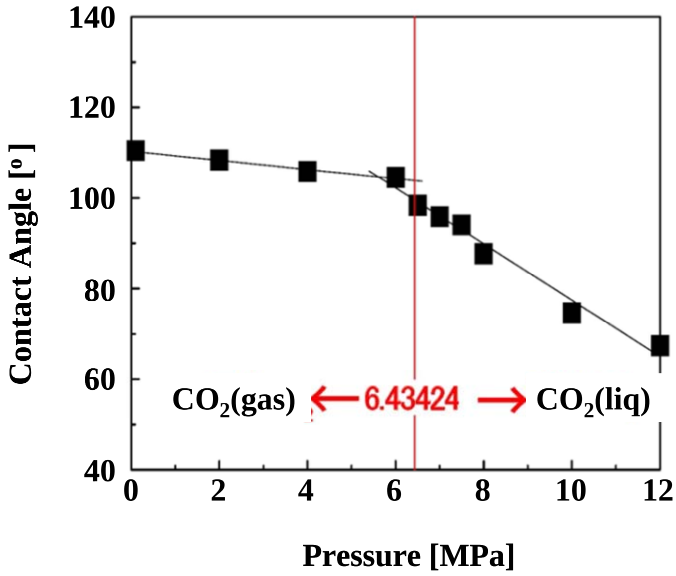

Figure 7. Effect of pressure on the contact angle of water

depends on the pressure of CO_2. Presumable, these effects could be attributed to the CO_2 dissolved in the liquids to act as an impurity.

In this study, it became clear that the Nylon extruded with CO_2 treated MS302 becomes transparent due to its improved wettability to the Nylon pellet surface to achieve the improved dispersion of the additive that acts as a nuclei of the Nylon crystal.

4. Conclusions

In ordinary cases, making of the materials that act as nuclei is very difficult and needs skills for the molecular design of the systems. On the contrary, in this study, it was found that the CO_2 treatment of simple w/o emulsion makes Nylon transparent without any further consideration. It is due to the improved wettability to the Nylon pellet surface to achieve the improved dispersion of the additive that acts as nuclei of the Nylon crystal. This kind of approach will be very useful for the polymer processing. Further study should be conducted for the applicability of this technique.

Literatures Cited.

[1] *Research and Environmental Measure of Polymer Additives (Japanese)*. CMC Publications: Tokyo, 2008.