Enhanced Compatibility of SAN and PC in Their Blends Exposed to Extremely High Shear Field

HIDEROH TAKAHASHI, TAKAAKI MATSUOKA, TAKASHI OHTA, KENZO FUKUMORI, TOSHIO KURAUCHI, and OSAMI KAMIGAITO, *Toyota Central Research and Development Laboratories, Inc., Nagakute-cho, Aichi-gun, Aichi-ken, 480-11, Japan*

Synopsis

Originally incompatible blends of SAN 30% and PC 70% were extruded with extremely high shear rate up to 10^7 s^{-1} as a typical example of the blends. The materials were examined with a scanning electron microscope (SEM), a pulsed NMR, etc. The molecular weight of the blends was also measured with gel permeation chromatography. The blends are of binary systems microscopically in the first run of extruding, in which the minor constituent is present as small spherical particles in the major constituent. The apparent volume fraction of the spherical minor constituent estimated from the microscopic photographs decreases with the shear rate. The fraction is decreased also with the repeated runs. SEM observation reveals that dimple fracture of microsize takes place on SAN sphere dispersed in PC matrix. And at the bottom of the dimple, a small particle, which would be composed of PC, is present. From these, SAN in the blend is thought to be partly ductile even at the temperature of liquid nitrogen. At the fifth run, the blend appears uniform or structureless. Dynamic loss tangent gives two peaks corresponding to that of SAN and that possibly attributed to PC. The latter shifts to lower temperatures with the number of extruding run. These show that some of SAN is mixed with PC in a compatible form. The pulsed NMR analysis supports the conclusion. Furthermore, the analysis suggests that some of SAN is mixed in PC. This result shows the compatibility of SAN with PC is enhanced in extremely high shear rate processing.

INTRODUCTION

An extremely high shear rate processing has been proved to affect the molecular weight of some macromolecules.[1,2] There has been much interest in the properties of the macromolecules exposed to the high shear. The blend composed of SAN and PC is very attractive material from the viewpoint of energy absorbance,[3] and it has a very important position in many macromolecules. Among the blends, some of them are incompatible, and others are partially compatible. The reason for this separation of the compatible blend from the incompatible one is not fully known.[4]

Some studies have been made on the influence of processing on the blend.[5] However, that of the extremely high shear rate above 1×10^4 s^{-1} has not been made yet.

In this work, the extremely high shear rate processing is applied to the incompatible blend, and some typical characters and properties are investigated in relation to the shear rate.
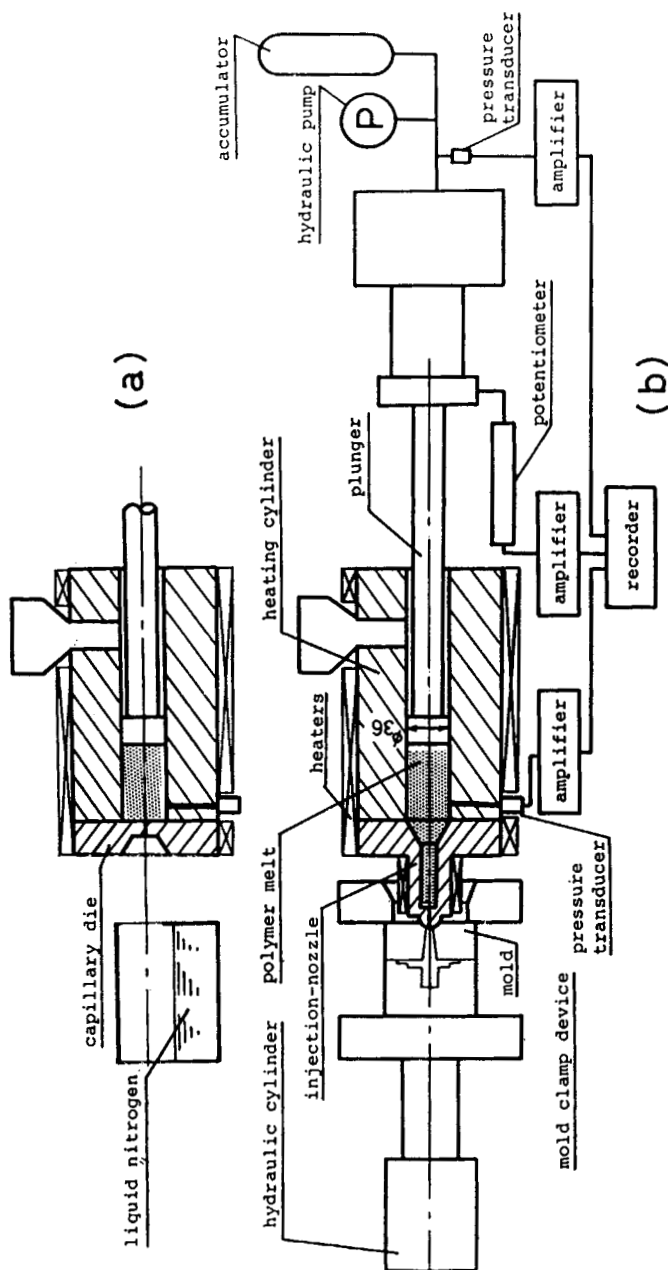
Fig. 1. Outline of the apparatus for extremely high shear rate extrusion and injection molding: (a) high shear rate capillary rheometer; (b) high shear rate injection molding apparatus.

EXPERIMENTAL

The apparatus for extremely high shear rate extrusion and injection molding is shown in Figure 1, schematically. The details of the apparatus have been explained in an earlier article.[1] The capillary of 0.5 mm diameter and 10 mm length was used for the apparatus. A new clamping equipment for molding was attached to the apparatus in order to mold specimens under high shear or pressure. A specially designed injection nozzle with the same size as the capillary for viscosity measurements was set at the barrel in place of a die.

As a typical example of SAN–PC blends, SAN 30%–PC 70% was studied in this experiment. Each constituent is commercially available. Sanrex SAN-H, Mitsubishi Monsanto Chemical, and Iupilon S-3000 (PC), Mitsubishi Gas Chemical, were used. These constituents were mixed with a conventional twin-screw extruder at a temperature of 230°C, and the blend was extruded into a form of bar with a circular cross section of 3 mm diameter. After cooling by dipping into a water bath, the bar was cut into pellets of the length of 3–4 mm. These pellets were used for the high shear rate experiment.

The material was injected into liquid nitrogen as shown in Figure 1(a) for rapid cooling of the material. To get some specimens to measure the dynamic loss tangent of the extruded material, it was molded into a cavity with a rectangular cross section of 10×4 mm. The mold was cooled before molding. The specimen for measuring dynamic loss tangent was prepared by machining the molded bar into a smaller bar of $2 \times 4.5 \times 35$ mm. Most of the experiment was made at the temperatures of 250 and 280°C. The shear rate in the experiment is varied from 1×10^4 to 1×10^7 s^{-1}. Some specimens were exposed repeatedly to the high shear rate of about 3×10^6 s^{-1} to study the influence of repeated shear on the character and property of the blend.

To examine the influence of the molding conditions on the morphology, some specimens were molded with molding temperatures (material temperature) of 240, 260, 280, and 300°C under a shear rate of about 5×10^3 s^{-1} by using a conventional injection-molding machine.

The morphology of the specimen was examined with a scanning electron microscope (SEM). SEM observation was made on the fracture surface of the specimen. The fracture was made by impacting the specimen, which was cooled down to the liquid nitrogen temperature, with a Charpy testing machine. Gold was sputtered on the surface before SEM observation.

Dynamic loss tangent of the specimen was measured with a viscoelastic meter (Iwamoto Manufacture Co.) in the temperature range from 30 to 170°C.

Nuclear spin–spin relaxation time T_2 was measured on the specimens to estimate the degree of the interaction between both constituents, by using pulsed nuclear magnetic resonance method.[6,7] For that, a JEOL-FSE-60Q pulsed nuclear magnetic resonance spectrometer (14 kgauss, resonance frequency of 60 MHz, ^{1}H) was used. The molecular weight distribution of the specimen was measured with gel permeation chromatography (Waters Associates).

RESULTS AND DISCUSSION

SEM images of the fracture surface of the blends are shown in Figures 2 and 3. Figure 2 shows a picture of that injection-molded under the conven-
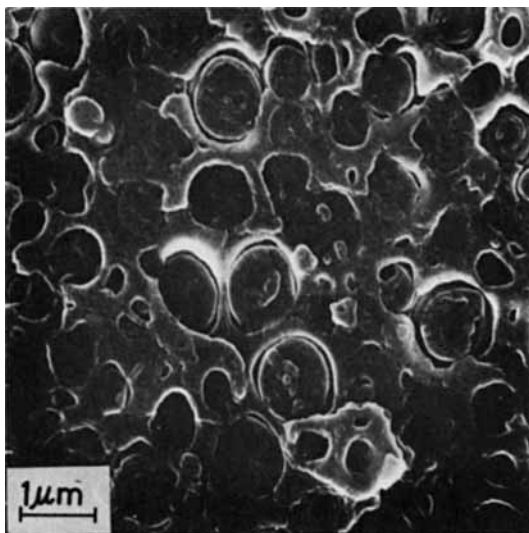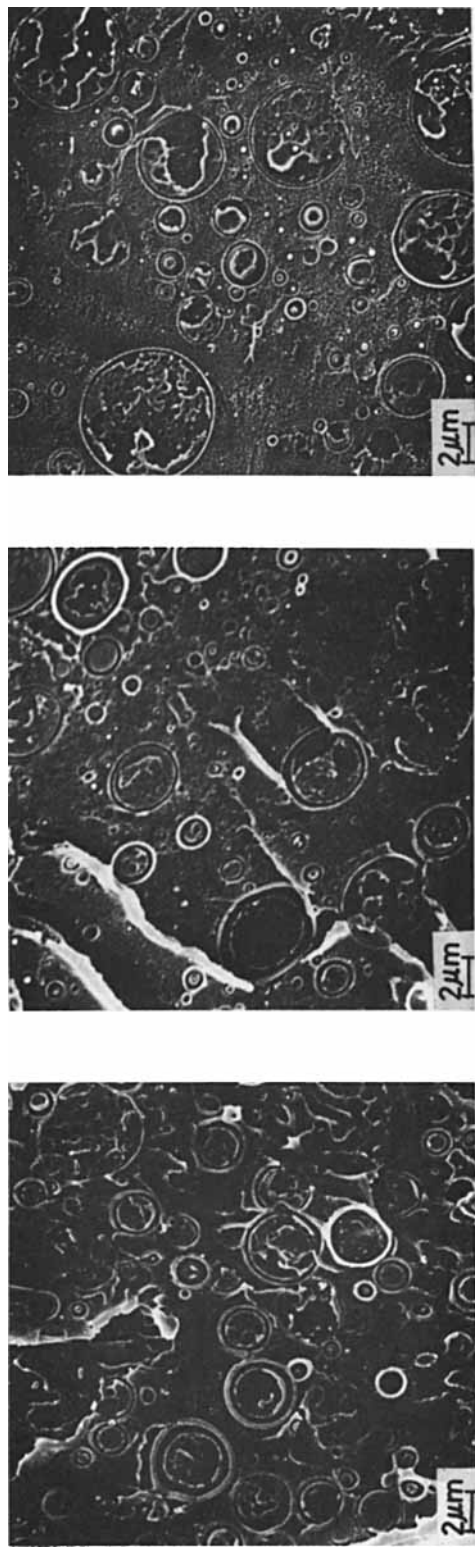
Fig. 2. SEM image of the fracture surface of the SAN 30%–PC 70% blend specimen injection-molded conventionally (molding temperature = 280°C).

tional shear rate of about 5×10^3 s^{-1} by using a conventional injection molding machine (molding temperature: 280°C). Small spheres of 1 μm in diameter are dispersed in PC, shown in Figure 2. The spheres are considered to be composed of SAN.[8] The fractional volume of SAN spheres is estimated as about 30% from the picture in consistence with the mixture composition. The same morphology was observed on the fracture surface of the blend specimens injection-molded conventionally with molding temperature from 240 to 300°C. And any shift was not observed on the dynamic loss tangent–temperature curves for those specimens. Therefore, the blend used in this study is considered to be incompatible essentially in conventional processing.

Figure 3 shows SEM images of the fracture surface of the blend exposed to various shear rate (injected into liquid nitrogen). As the shear rate increased, the volume decreases evidently in Figure 3. It is estimated as about 20% or less at a shear rate of 2.8×10^6 s^{-1}. Some of the spheres are larger in size than that in the blend injected under the conventional shear rate, and others are much smaller than the original ones. The largest size of the spheres appears to increase with the shear rate, and it reaches about 6 μm.

The smallest size appears to decrease with the shear rate. Then the size distribution becomes wider with the shear rate. The formation of smaller spheres means that the extremely high shear breaks the SAN sphere in the blend. A smaller sphere produces a wider interface between the matrix and the spheres, and it increases the chemical instability of the blends. The smaller sphere tends to be absorbed by the larger or original spheres, which would be responsible for the formation of the larger sphere.

The decrease of the fractional volume of SAN means that SAN must be dispersed in PC like a compatible constituent.

Fig. 3.   SEM images of the fracture surface of the SAN 30%–PC 70% blend exposed to various shear rates or shear stress (injected into liquid nitrogen).
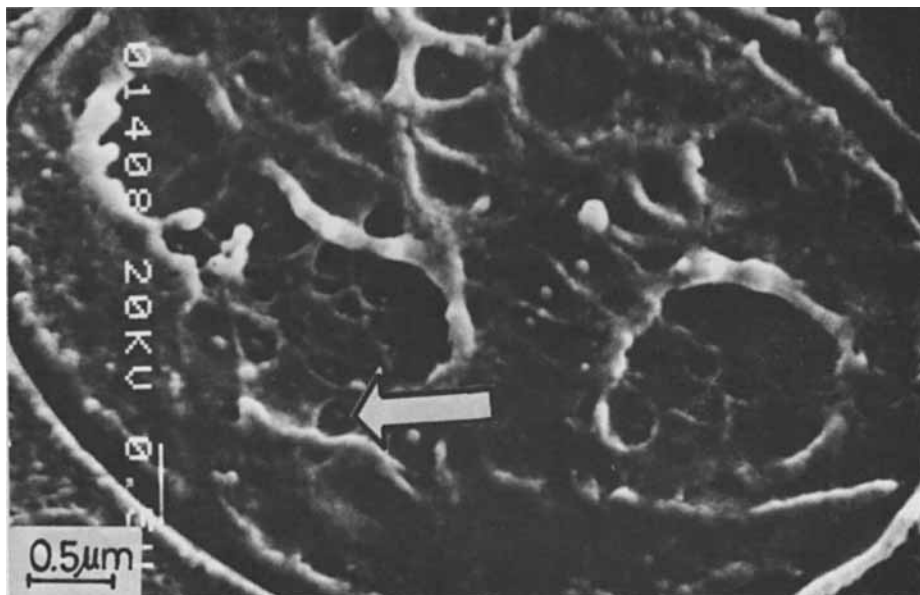
$2.5 \times 10^4 \, \text{sec}^{-1} \, (0.7 \, \text{MPa})$

$2.8 \times 10^6 \, \text{sec}^{-1} \, (4.6 \, \text{MPa})$

$5.0 \times 10^6 \, \text{sec}^{-1} \, (6.7 \, \text{MPa})$

Fig. 4.   SEM images of the SAN sphere in the SAN 30%–PC 70% blend exposed to high shear rate (2.8×10^6 s^{-1}) or high shear stress (4.6 MPa).

The fracture surface appears flat on the matrix or PC area. But the fracture surface of the sphere has a fine structure, and it has a kind of flow pattern. The magnified image of the SAN sphere is shown in Figure 4. The fine structure is composed evidently of so-called dimple patterns. At the bottom of the dimple, a small particle of the size of about 500 nm is present, as indicated by an arrow. The dimple is thought to be generated from the small particle under the tensile force in fracturing. The small particle must be different from the surrounding material in properties; otherwise such a dimple cannot be produced. In the blend, only two constituents are present. One is SAN, and the other is PC. Then the small particle at the dimple bottom must be PC, which suggests that PC is also dispersed in SAN like a compatible constituent in the blend exposed at the extremely high shear rate.

The separation between the PC particles at the bottom of the dimples is about 0.3 μm. From these, the quantity of PC present in SAN is estimated to be about 0.5% at the least. From these observations, formation of mutual compatibility among SAN and PC is suggested.

The presence of the dimple patterns shows that SAN in the blend is ductile microscopically, even at the temperature of liquid nitrogen.

In Figures 2 and 3, a separation of SAN sphere from PC matrix can be seen. The separation or the gap between the sphere and the matrix is thought to be caused by the difference in volume shrinkages of SAN sphere and PC matrix in solidification of the materials from molten state.

The surface morphology of the blend exposed to the extremely high shear repeatedly is shown in Figure 5. The sphere size is nearly the same until three runs are repeated. After five exposures to the high shear, the fine structure on the surface disappeared. This suggests that the constituents become mutually compatible.
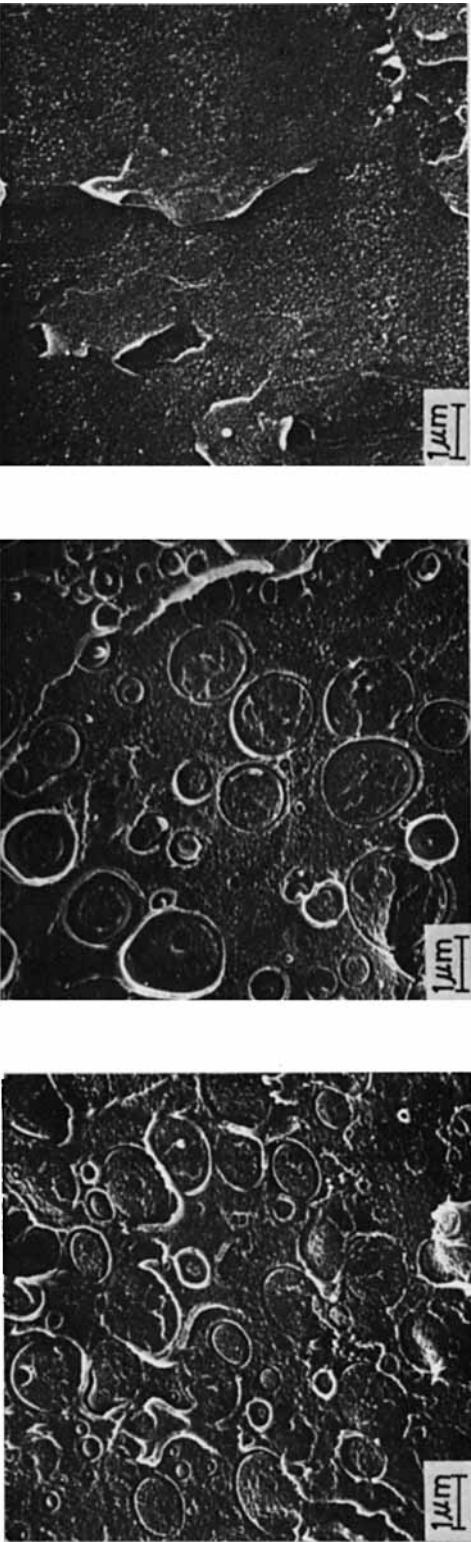
Fig. 5. SEM images of the fracture surface of the SAN 30%–PC 70% blend exposed repeatedly to the shear rate of 2.8×10^6 s^{-1} at 250°C (N = number of repeatedly exposing time).
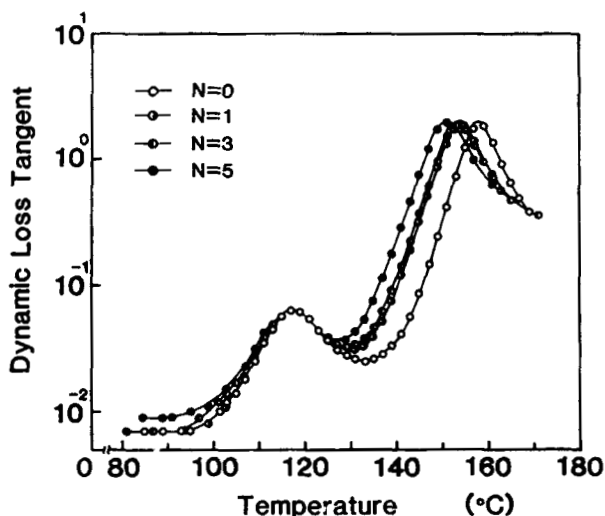
Fig. 6. Dynamic loss tangent of the SAN 30%–PC 70% blend exposed repeatedly to the high shear rate of 2.8×10^6 s^{-1} at 250°C N = number of repeatedly exposing time: (O) 0; (◑) 1; (◐) 3; (●) 5.

Dynamic loss tangent is shown in Figure 6 taking the repeated number N as a parameter. The curves have two peaks. One takes place at 117°C, which corresponds to the glass transition temperature of SAN. Then the curve shows that some part of SAN is present in the blend in an unmodified form. The curve around the peak at 117°C becomes dull with the repeated time, which shows that some of the SAN is modified by PC. The other takes place at about 155°C, depending on the repeated time. The temperature giving the peak shifts gradually with the repeated time from 158°C at $N = 0$, which corresponds to that of PC, to 151°C at $N = 5$. These shifts are thought to be caused by the modification of PC with the other constituent, SAN.
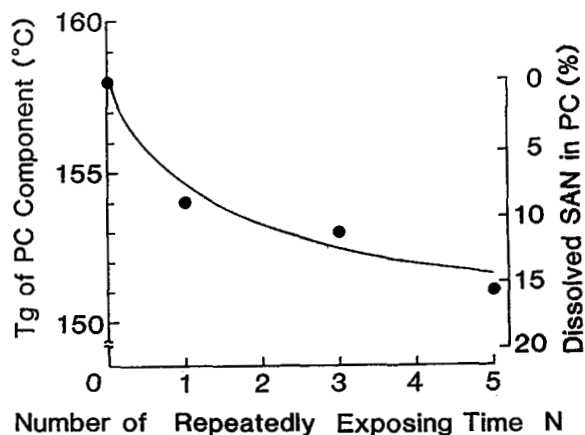

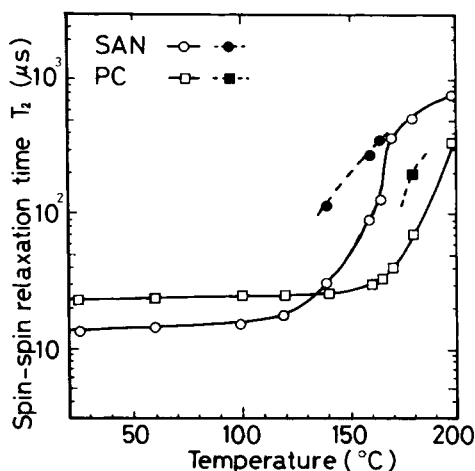Fig. 7. Change of glass transition temperature for PC component.

Fig. 8.   Spin–spin relaxation time T_2 of SAN (○, ●) and PC (□, ■).

Applying Fox's analysis with T_g shift to the results,[3,9] the concentration of dissolved SAN in PC is estimated as shown in Figure 7. According to the figure, 9% of SAN dissolves in PC at $N = 1$, and it reaches 15% at $N = 5$. This result is consistent with the SEM observation result that some amount of SAN starts to disperse in the PC matrix by exposure to high shear.

As shown in the SEM image, some of the PC in the SAN sphere is present as very small particles of 50 nm, which corresponds to the molecular size of PC. SAN near the PC particles will be modified by the particles, but SAN far from the particles will hardly be affected by the particles. Then SAN lying near the PC particles would be responsible for the occurrence of the dull peak of SAN in the dynamic loss tangent, and SAN lying far from PC particles would be responsible for the unmodified peak of the SAN in the loss tangent.
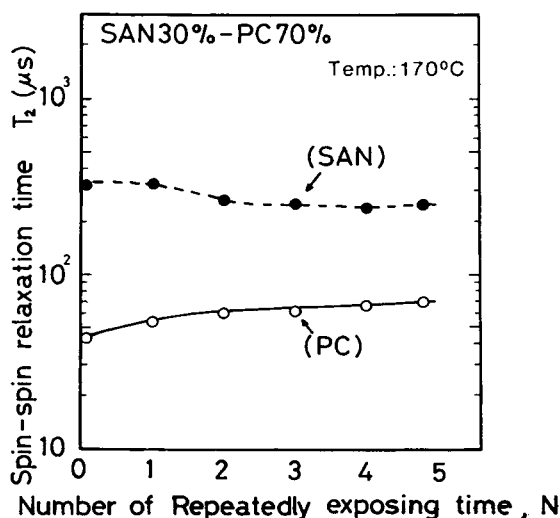

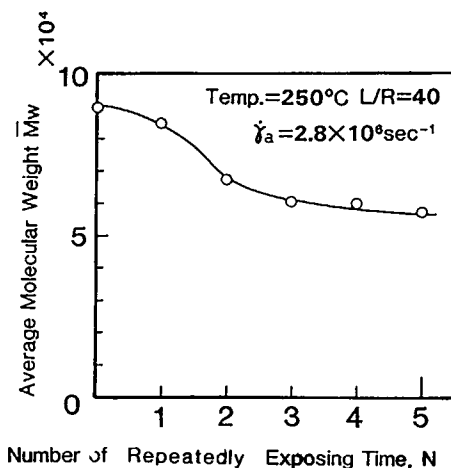Fig. 9.   Spin–spin relaxation time T_2 vs. number of repeatedly exposing time, N.

Fig. 10. Weight-averaged molecular weight $\overline{M}_w$ versus number of repeatedly exposing time, N.

Spin–spin relaxation time T_2 of SAN as well as that of PC is shown in Figure 8. Both T_2's have two components, shorter T_2 and longer T_2 in different temperature ranges as shown in Figure 8.[10] Outside the ranges, the two T_2's turn into one. At 170°C, SAN gives one T_2 of about 400 μs, and PC, a T_2 of 40 μs. Therefore, at this temperature the two materials give their own T_2's separately. The blend gives two T_2's. Both T_2's are plotted as a function of N in Figure 9. The values of T_2 depend on the repeated number N. The shorter one is less than 70 μs, and is thought to have originated from PC. The longer one is about 250 μs, and is thought to be originated from SAN. The variation of each T_2 with N means that both materials, SAN and PC, are modified by each other, which also means that the blends are forced to be compatible to each other by the high shear.[6] This result is consistent with the results obtained through SEM observation and dynamic loss tangent measurement.

The weight-averaged molecular weight ($\overline{M}_w$) of the blend is shown in Figure 10 as a function of N. It decreases slightly with N until $N = 2$, followed by near saturation. The decrease of molecular weight results generally in the decrease of T_g, which might appear to be responsible for the decrease of that of PC in Figure 10. But the decrease of T_g calculated by the application of the following formula[11] to the results gives only about 2.2°C or less for $N = 5$ on the assumption that the molecular weight decrease is entirely caused by the decrease in PC:

$$T_g = 154 - 3.6 \times 10^5 / \overline{M}_w \tag{1}$$

In eq. (1), T_g was determined by measuring the variation of specific volume as a function of temperature according to a buoyancy procedure.[11]

This result is too small to account for the actual decrease of 7°C, as shown in Figure 7. Therefore, the decrease results from the dissolving of SAN into PC, as mentioned before.

CONCLUSIONS

1. Originally incompatible blends of SAN 30% and PC 70% were extruded with an extremely high shear rate up to 10^7 s^{-1}. The blends were of binary systems microscopically in the first run of extruding, in which the minor constituent was present as small spherical particles in the major constituent.

2. The apparent volume fraction of the spherical minor constituent estimated from the microscopic photographs decreases with shear rate. The decrease of the fractional volume of SAN means that SAN must be dispersed in PC like a compatible constituent. SEM observation revealed that dimple fracture of microsize took place on the SAN sphere dispersed in PC matrix. And at the bottom of the dimple, a small particle ($\sim$ 50 nm), which would be composed of PC, was present. This suggests that also PC is dispersed in SAN like a compatible constituent in the blend exposed to the extremely high shear rate. The presence of the dimple patterns shows that SAN in the blend is ductile microscopically at least even at the temperature of liquid nitrogen.

3. The fraction of the spherical minor constituent was decreased also with the repeated runs. At the fifth run, the blend appeared uniform or structureless. This also suggests that the constituents are forced to be mutually compatible.

4. The dynamic loss tangent gave two peaks corresponding to that of SAN and that possibly attributed to PC. The latter shifted to lower temperature with number of extruding run. These show that some of SAN is mixed with PC in a compatible form.

5. Pulsed NMR analysis supported the above-mentioned consideration.

6. It is concluded by this study that compatibility of SAN with PC is enhanced in extremely high shear rate processing.

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