The Effect of Acrylonitrile Content of Styrene-Acrylonitrile Copolymer on Styrene-Acrylonitrile / Styrene-Butadiene-Styrene Alloy System

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ABSTRACT

As toughening the brittle polymers with the rubber components has been recently drawing attention, the investigation of the characteristics of toughened SAN/SBS polymer blend has been made in this study.

The microphotographs showed the SBS (styrene-butadiene-styrene) domain in the SAN (styrene-acrylonitrile) matrix. This study concentrates on the effect of acrylonitrile content on the mechanical properties and the optical properties of SAN/SBS alloy system. This paper describes the role of the acrylonitrile(AN) in SAN/SBS by comparing SAN only with SAN/SBS blend.

Key Words

toughened polymer, SAN/SBS blend, rubber component, domain, matrix

INTRODUCTION

Styrene/acrylonitrile copolymer(SAN) has been a useful material in the polymer industry. However, because it is so brittle, elastomer particles must be mixed with it for toughening. Rubber toughened polymers have become an important commercial material and much research in this field has been reported [1-4] which indicate that rubber concentration, dispersion state and interaction force between rubber domain and polymer matrix in the influenced variables. In an immiscible alloy system, the interaction between domain and matrix depends on the ratio of each component. In our previous papers [5-6], we described the effect of the blend ratio and the processing method on the properties of the SAN/SBS.

The major focus of this study is to relate the effect of acrylonitrile (AN) content of SAN matrix to blend with SBS. We have studied how the AN content in SAN affects the influenced variables with comparison of the SAN only and SAN/SBS alloy system.

The AN content in SAN induces high value of tensile strength and elongation. By blending SAN with SBS, the increasing rate is decelerated at over 30% of AN in SAN. The softening temperature of the sample increases with increasing AN content. However, the impact resistance is not influenced by AN content.

Generally, SAN is known to be a transparent material. By increasing AN content in SAN the yellow index of the material is increased. When blending SAN with SBS, the material becomes opaque. The haze of the SAN/SBS blend is increased with 32% AN content in SAN.

EXPERIMENTAL

Sample Preparation

The materials used in this study were three SANs of different styrene contents and a SBS. Table 1 shows the manufacturers and the compositions of these materials. The SANs were the commercial products of Cheil Industries, Inc. comprising 76%, 71% and 68% styrene. The SBS was manufactured by Asahi Chemical Industry Corporation. It contained 70% styrene as a block copolymer.

Three samples were prepared by blending the SANs with the SBS at a ratio of 7 to 3 each. Table 2 shows the compositions of these samples. The samples had a butadiene content of 9%, which acts as a rubbery segment in the blend. The AN contents were 17%, 20% and 23% respectively. A co-rotating intermeshing twin screw extruder (D=45mm, L/D=28.5) was used for blending. The extruder was operated at 210 rpm. The cylinder temperature was maintained at 180°C, 210°C, 230°C, 230°C, and 230°C from the hopper to the die.The die temperature was maintained at 220°C during the operation.

Testing Method

Transmission electron micrographs were obtained by scanning the SBS from SBS/SAN blends with osmium tetraoxide (OsO_4) for a morphological study. Sample preparation for measuring the mechanical properties was carried out by injection molding. Tensile strength was determined by universal tensile tester (Instron) at a crosshead speed of 5mm/min. Izod impact strength was measured with 1/4" notched sample by using a pendulum type tester. Yellow index, color difference and transparency were determined by using a color difference meter (SUGA).

RESULTS AND DISCUSSION

Morphology

We compared the morphology of the SAN/SBS

Table 1. Characteristics of raw materials used in this study.

Chemical Name	Model Name	Manufacturer	Styrene Content
Styrene-acrylonitrile	HF5661	Cheil Ind.	76 %
	HR5330	"	71 %
	CR5381	"	68 %
Styrene-butadiene-styrene	ASAFLEX	Asai Chem.	70 %

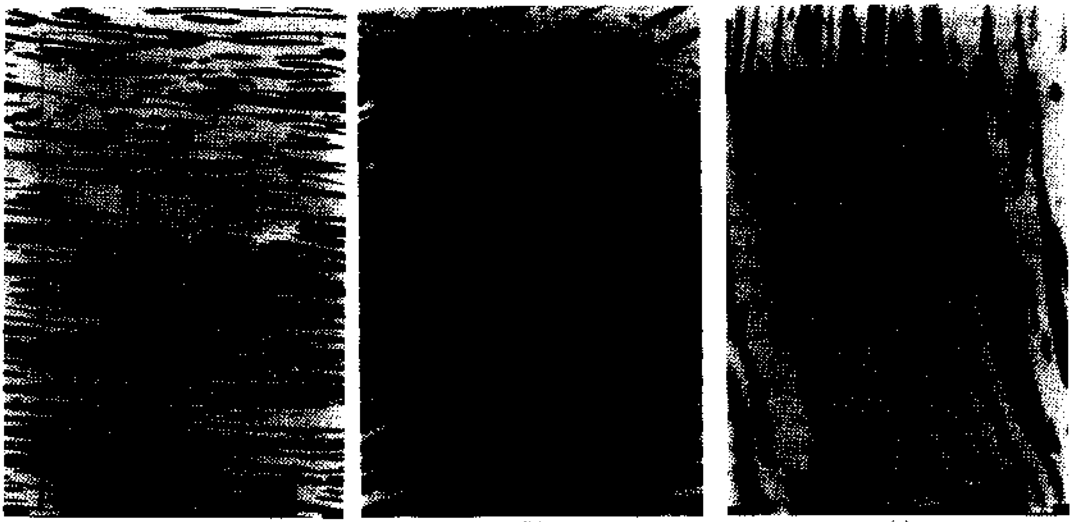


Fig. 1. Transmission electron microphotographs for SAN/SBS blends for various AN content in SAN (a) 24% (b) 29% (c) 32%.

Table 2. Composition of the blend.

Sample No.	Styrene	Butadiene	Acrylonitrile
1	74%	9%	17%
2	71%	9%	20%
3	68%	9%	23%

blends for different AN content at a fixed blend ratio (SAN/SBS=7/3). Figures 1 (a)-(c) show the transmission electron micrographs for the SAN/SBS blends prepared using SANs with different AN contents of 24%, 28% and 32%, respectively. The fraction of the dark area by point counting method approached 37% for all three blends. However, the striation thickness of the dark area in the blends began to broaden as AN content increased. The estimated thicknesses were 0.2 μm for 24%, 0.4 μm for 28% and 0.5 μm for 32% of AN content in SAN. The dark area in the microphotographs were believed to be the rubbery segments in the blend. Some of the styrene components seemed to be diffused through the boundary of domain and matrix.

Effect of AN Content on Mechanical Properties

The behavior of tensile strength versus AN content in SAN for SAN/SBS blend is shown in Figure 2. The results indicate that the tensile strength of the SAN increased with increasing AN content. When SAN was blended with SBS, the tensile strength decreased because of the rubbery segment (butadiene) in SBS. However,the trend of tensile strength of blend differed from that of SAN only. While the tensile strength increases as the AN

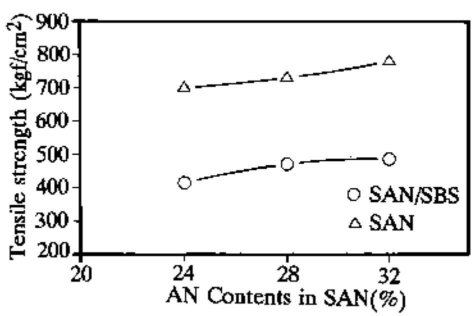


Fig. 2. The effect of AN content in SAN on the tensile strength of SAN/SBS.

content increases with constant slope in case of SAN only, the slope is shifted downward over 28% of AN in the blends. The reason may be explained by the miscibility between SAN and SBS. If SAN and SBS is miscible, the tensile strength may increase with increase of AN content with a constant slope. In an immiscible system, the state of rubber particle dispersion should be influenced by the mechanical properties of blends. Figure 1 shows that the rubber particle of 24% of AN in SAN was better dispersed than that of 32% AN content when mixed in the same ratio of SBS to SAN.

Figure 3 shows the effect of AN content on the elongation behavior of SAN and SAN/SBS blend. The elongation increases with an increased of AN content in SAN. When blending with SBS, the value of elongation increases because of its own rubbery component. The result indicates that the elongation increased exponentially as with increase of AN content in case of SAN only. If it blends with SBS, however, the AN content reduces the increasing rate of the elongation. The reason may be explained by insufficient adhesion between SAN matrix and SBS domain, which will lead to a reduced level of stress transfer yielding across the interference between SAN matrix and localized rubber particle domain resulting in prevention of an increase in the elongation value.

The impact resistances of blend and SAN are shown in Figure 4. The impact resistance of SAN increases by blending with SBS. The rubbery segments make the SAN toughen. However, the AN content in SAN did not affect the impact strength.

The effect of the AN content in SAN on the softening temperature is shown in Figure 5. The softening temperature lowered by blending with SBS, because the rubber segments have a very good chain mobility at lower temperature. The softening temperature slightly increased with increasing AN content in SAN.

Effect of AN Content on Optical Properties

First, we checked the yellow indices of polymers according to AN content in SAN. Figure 6 shows

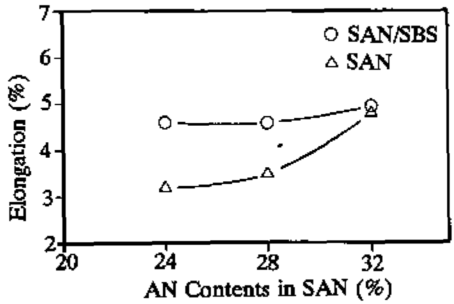


Fig. 3. The effect of AN content in SAN on the elongation of SAN/SBS.

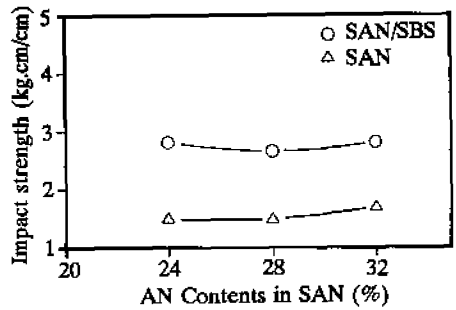


Fig. 4. The effect of AN content in SAN on the impact strength of SAN/SBS.

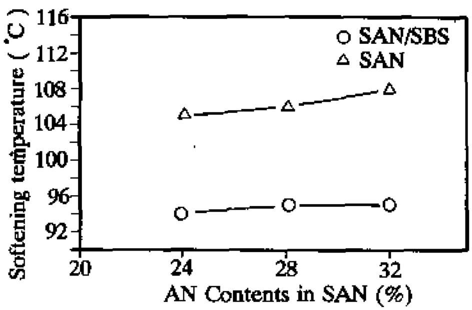


Fig. 5. The effect of AN content in SAN on the softening temperature of SAN/SBS.

the yellow indices of virgin SAN and SAN/SBS

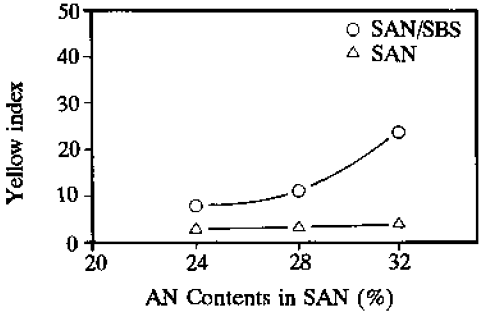
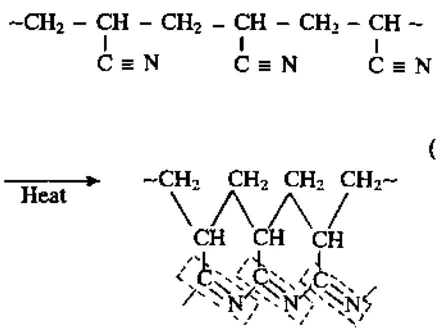


Fig. 6. The effect of AN content in SAN on the yellow index of SAN/SBS.

blend versus AN content in SAN. It is known that the yellow indices increase with increasing AN content in SAN. The reason is explained as follows:



(1)

The dotted line (C=N) of formulation (1) represents the yellow wavelength region. With the addition of SBS to the SAN, the yellow index increased because of the butadiene component in SBS. Butadiene is easily attacked by heat which is mentioned in detail in our previous paper [7]. Figure 6 indicates that butadiene is easily attacked by heat at higher level of AN content (32%) rather than low level of AN content (24%).

Figure 7 shows the color difference according to AN content. The value of color difference from reference, ΔE was calculated by:

$$\Delta E = \sqrt{(\Delta L)^2} + \sqrt{(\Delta a)^2} + \sqrt{(\Delta b)^2} \qquad (2)$$

where, ΔL: lightness
Δa: saturation
Δb: hue

All three kinds of SAN have the similar values according to AN content but the value was changed by increasing AN content with blending SBS.

The transparencies of SAN and blends versus AN content are shown in Figure 8. The transparency decreased in blending in SBS. The reason can be explained by the difference in refractive index between SAN and rubber particle in the SBS, so the light is scattered.

The haze is frequently used for evaluation of the optical property. The value of haze(h) is obtained by the following equation.

$$h = \frac{T_d}{T_t} \times 100 \qquad (3)$$

Where, T_t : total transparency
T_d : transparency by diffusion

The effect of the AN content on the haze is shown in Figure 9 which presents slight changes of the haze for SAN only. When blending it with SBS, the increasing rate was changed sharply at the same AN content. This can be explained by the fact that the rubber particles are more diffused

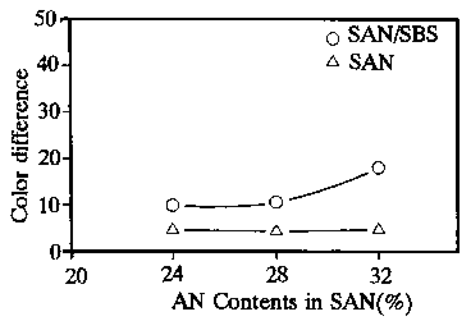


Fig. 7. The effect of AN content in SAN on the color difference of SAN/SBS.

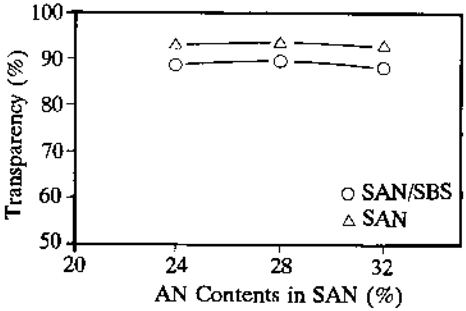


Fig. 8. The effect of AN content in SAN on the transparency of SAN/SBS.

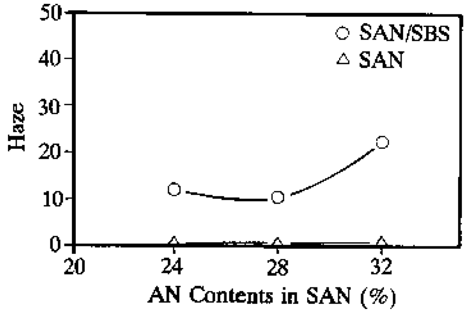


Fig. 9. The effect of AN content in SAN on the haze of SAN/SBS.

with 32% of AN content in SAN and SBS blend than with 24% of AN content blend.

CONCLUSION

We studied SAN/SBS blend system as a rubber toughened polymer. From microphotographs, we found this alloy system to be immiscible. Therefore, the state of interface between rubber and plastic should be considered as well as concentration of rubber in the polymer blend.

According to these points, the role of AN content in SAN was investigated for SAN/SBS alloy system. With increasing of AN content in blends, the boundary between domain and matrix becomes unclear and the striation thickness of the domain are broadened.

From our experimental results, we reached the following conclusions. The tensile strength increased with increasing AN content. But when blending SAN with SBS, the increasing rate decelerated at over 30% of AN content in SAN. The impact resistance increased with addition of SBS. However, the AN content did not influence the impact resistance of the materials. The softening temperature of SAN/SBS blend increased with increasing AN content in SAN.

The yellow index of SAN increased with increasing AN content because of the C≡N component. When blending it with SBS, the butadiene component appears more easily attacked by oxygen at the high level of AN content than the lower level of AN content.

The transparency of SAN is higher than that of SAN/SBS blend, but the AN content in SAN did not influence the total transparency of materials. The value of haze of the blends was increased at over the 32% of AN content in SAN.

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