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SAN BLENDS WITH A PHENOXY POLYMER: MORPHOLOGY AND PROPERTIES

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Abstract—Styrene-acrylonitrile copolymer (SAN) and a phenoxy polymer having practically identical melt viscosities were blended using a single screw extruder. A two phase morphology was seen from scanning electron microscopy. The phase boundary was sharp and gaps formed upon debonding were noticeable when the phenoxy polymer formed the dispersed domain, while the phase boundary was blurred and fracture left no gaps when SAN was the dispersed phase. The glass transition temperature (T_g) of the SAN phase was almost unchanged or marginally increased in the blends, while the T_g of the phenoxy polymer increased by about $4 \sim 5°$. A positive deviation from linearity in modulus and strength was generally obtained in phenoxy-rich blends, while melt viscosity showed a negative deviation in SAN-rich blends and a positive deviation in phenoxy-rich blends.

INTRODUCTION

Polymer blends became more important since they can meet specific performance requirements not possible with a single type of commodity polymer. Blends of brittle thermoplastics with ductile polymers, especially with rubbers [1–5] have received broad attention. Styrene–acrylonitrile copolymer (SAN) is a brittle polymer which is conventionally toughened by rubber, resulting in a most successful thermoplastic material called ABS (acrylonitrile–butadiene–styrene) [6, 7].

Phenoxy polymer, which is a poly(hydroxy ether of bisphenol A), is a tough and ductile thermoplastic with an excellent oxygen barrier property, and it forms miscible blends with highly polar materials such as poly(butylene terephthalate) [8, 9], polycaprolactone [10] and poly(ethylene oxide) [11]. This miscibility is mainly due to strong hydrogen bonding. That is, the hydroxyl group of the phenoxy polymer acts as a proton donor while the ester or ether group of the other polymer acts as a proton acceptor, which results in thermodynamically miscible blends. Recently, the interchange reactions between polyesters and a phenoxy polymer have also been observed in melt processing. It is well known that graft or cross-linking occurs in these reactions.

We consider melt blends of SAN with a phenoxy polymer. To the best knowledge of the authors, the phase behavior of SAN/phenoxy blends has not been reported in the open literature. These blends should be important with regard to performance/cost improvement. This paper considers the morphological, thermal, mechanical and rheological properties of these blends.

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EXPERIMENTAL PROCEDURES

Materials and blending

Commercial grades of SAN(Hyosung BASF, M_n = 34,000, M_w = 55,000, acrylonitrile content = 35%) and phenoxy polymer (PKHH, Union Carbide) after drying for 3 days at 80° *in vacuo* were used for blending. Blending was performed using a single screw extruder (Brabender plasticorder), $L/D = 30$, at rpm = 50, and with a temperature profile of 230, 235, 240, 235° (die). Tensile (specimen type IV, ASTM D-638), flexural, and impact specimens were prepared by injection moulding (BOY 22SVV Dipronic), using the same temperature profile as extrusion. The cycle time was 50 sec and the mould temperature was 40°.

Morphology

The morphology of the blends was examined using a scanning electron microscope (SEM, JSM820). SEM micrographs were taken from cryogenically fractured surfaces in liquid nitrogen of injection-molded tensile specimens. The fractured surfaces were sputtered with gold before viewing. Transverse views of the samples with respect to the flow direction in mold cavity were examined.

Thermal properties

Thermal properties were evaluated using a DSC (differential scanning calorimeter, Du Pont 9900) following the enthalpy relaxation method [12–14]. Extrudates were sealed in the DSC pan using a crimping and welding press (Du Pont). Samples were kept for 5 min at 180°, followed by quenching in liquid nitrogen, and aged for 15 days at 75°. The DSC thermograms were taken from room temperature to 150° at a heating rate of 10°/min.

Mechanical properties

Tensile (ASTM D-638) and flexural (ASTM D-790) tests were done using an Instron (Model 6021), with a crosshead speed of 5 mm/min (tensile) and 2.8 mm/min (flexural). Impact tests were carried out with a notched specimen on a Izod impact tester (ASTM D-256). Tests were made at room temperature, and at least five runs were made to report the average.

Rheological properties

Rheological properties of the blends were measured using an RDS (Rheometrics Dynamics Spectrometer, type II) with parallel plate fixture. Discs measuring 12.5 mm (radius) × 1.2 mm (height) were compression molded, and measurements were carried out isothermally at 220°, 15% strain level. The strain level was determined from a strain sweep which gives maximum torque value within the linear viscoelastic limit.

RESULTS AND DISCUSSION

Morphology

Figure 1 shows the SEM micrographs of SAN/phenoxy blends. The dominant morphology is particle-in-matrix (90/10 and 10/90) and a cocontinuous one (50/50). When the phenoxy polymer forms the dispersed domains (a and b), the SAN/phenoxy phase boundary is clean and leaves gaps or crevices around

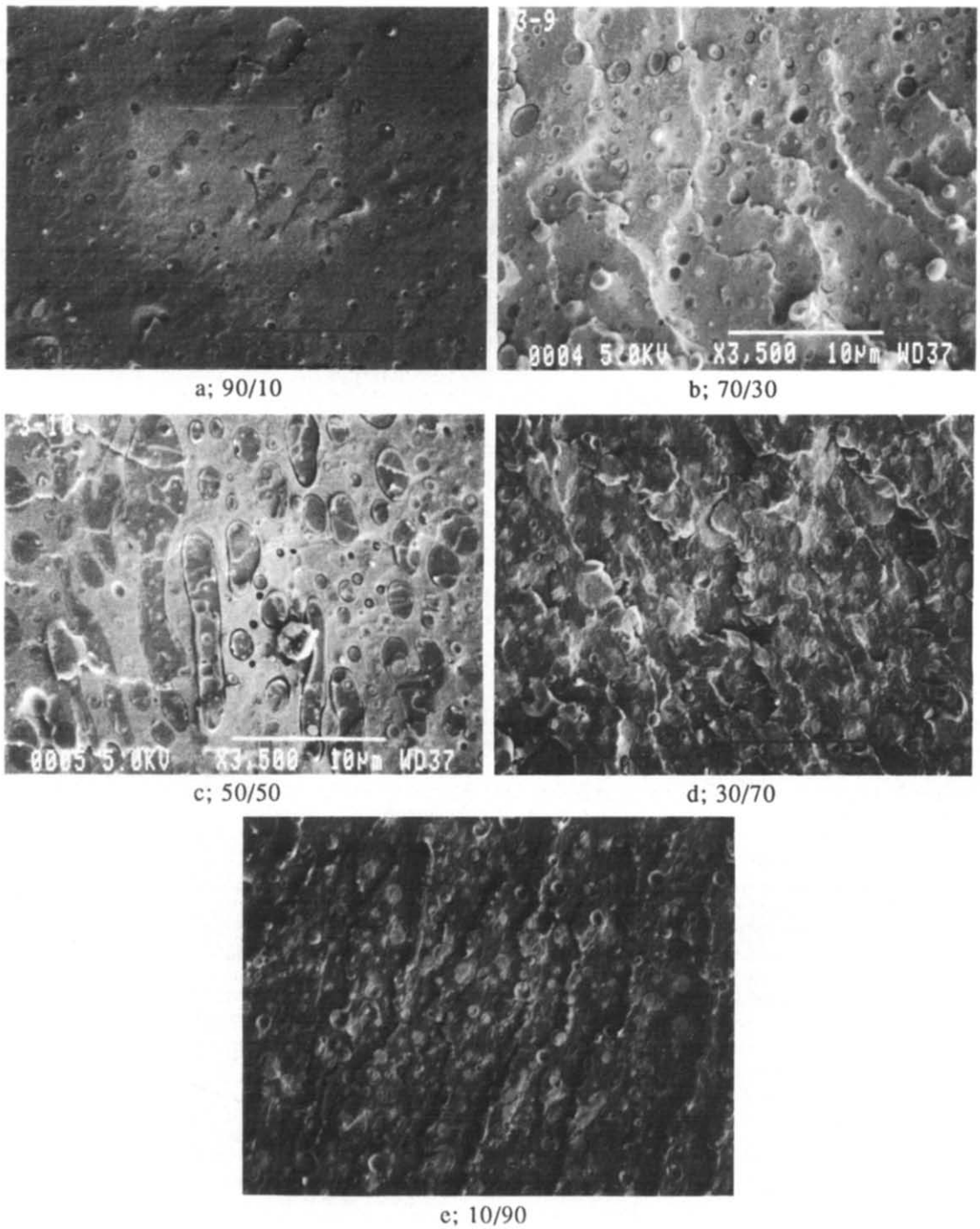

Fig. 1. SEM micrographs of SAN/phenoxy polymer blends fractured transversely to the flow direction: (a) 90/10, (b) 70/30, (c) 50/50, (d) 30/70, (e) 10/90.

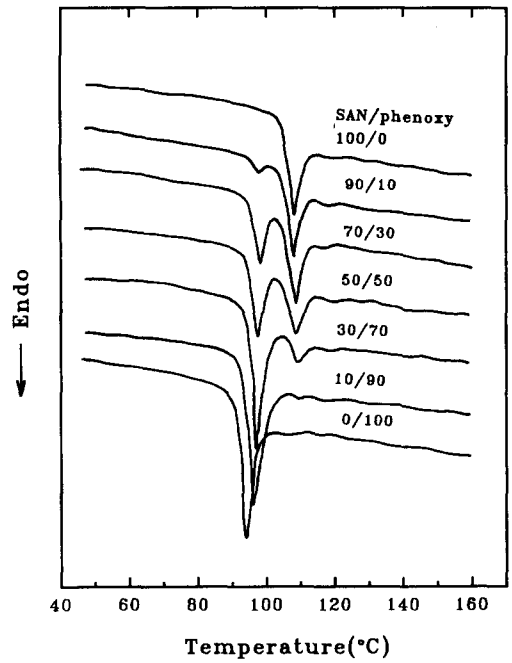

Fig. 2. DSC thermograms of SAN/phenoxy polymer blends.

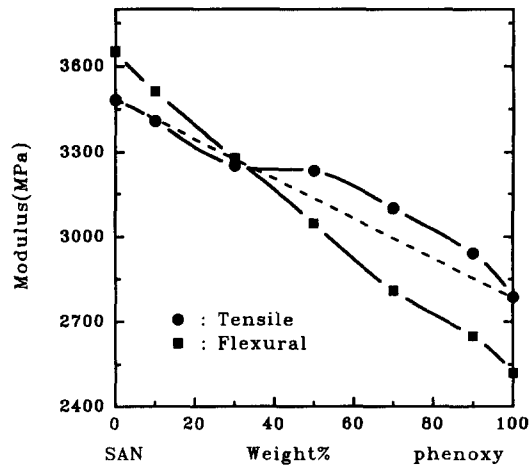

Fig. 3. Tensile and flexural modulus of SAN/phenoxy polymer blends.

the particle upon fracture. On the other hand, the interfacial boundary is blurred and the dispersed domains were broken right through the fracture surface, without showing any sign of pull-out or crevices around the droplets. This implies that the interfacial adhesion is stronger when SAN forms the dispersed phase than for the phenoxy polymer as dispersed phase. It is also seen that, for symmetric compositions, i.e. 10/90 vs 90/10, and 70/30 vs 30/70, the total area of dispersed domain is larger when SAN forms the dispersed phase than for the phenoxy polymer, as dispersed phase indicating that the cracks preferentially propagate through the SAN domain since SAN is much more brittle than the phenoxy polymer.

Thermal properties

DSC measurements of the SAN/phenoxy blends (Fig. 2) reveal two glass transitions (T_g) which proves immiscibility of these blends. The T_g of SAN is almost unchanged or marginally increased in the blends, but that of the phenoxy polymer is increased by $4 \sim 5^\circ$ in the blends. The change in T_g of the blend relative to that of parent polymer indicates some miscibility of the polymers. The composition of a conjugate phase can be calculated from the difference in T_g between the parent polymer and the conjugate phase [15, 16].

According to the Fox equation [17], the T_g of blend is:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}. \tag{1}$$

For conjugate phases,

$$w_2' = \frac{T_{g2}(T_{g1} - T_{g1,b})}{T_{g1,b}(T_{g1} - T_{g2})} \tag{2a}$$

$$w_1'' = \frac{T_{g1}(T_{g2,b} - T_{g2})}{T_{g2,b}(T_{g1} - T_{g2})} \tag{2b}$$

where, w_i is the weight fraction of component i in blend (1 and 2 designate SAN and phenoxy polymer, respectively), and w_i', w_i'' are the weight fractions of i in the SAN-rich and phenoxy-rich phases, respectively. The results (Table 1) show that the solubility of SAN in the phenoxy polymer is much greater than the phenoxy polymer in SAN. From morphology and T_g measurements, it may be said that when the dispersed phase is slightly dissolved in the matrix, the phase boundary becomes blurred, and a strong interfacial adhesion results.

Mechanical properties

The modulus (Fig. 3) and strength (Fig. 4) (tensile and flexural) show a positive deviation in phenoxy-rich blends, and a small negative deviation is generally seen in SAN-rich blends. In phenoxy-rich blends, SAN should act as an effective reinforcement, especially when the loading direction is the direction of

Table 1. Glass transition temperature and composition of conjugate phases of SAN/phenoxy blends from DSC

SAN/phenoxy	100/0	90/10	70/30	50/50	30/70	10/90	0/100
$T_{g1,b}$[a]	381.81	381.59	382.00	381.63	382.06	382.91	—
$T_{g2,b}$[b]	—	371.96	372.51	372.00	371.89	371.28	367.28
w_2'[c]	—	0.01	<0.01	0.01	<0.01	<0.01	—
w_1''[d]	—	0.33	0.37	0.33	0.33	0.28	—

[a]SAN in the blends.
[b]Phenoxy in the blends.
[c]Apparent weight fraction of phenoxy in the SAN rich phase.
[d]Apparent weight fraction of SAN in the phenoxy rich phase.

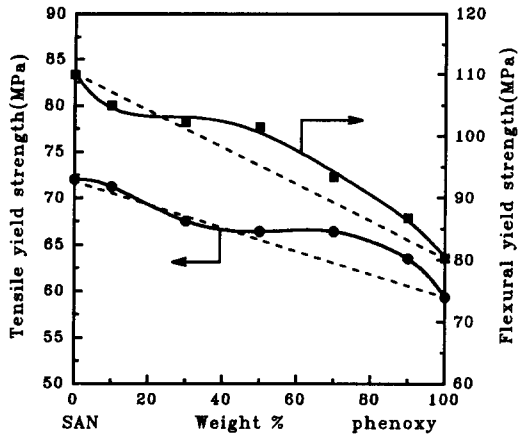

Fig. 4. Tensile yield and flexural strength of SAN/phenoxy polymer blends.

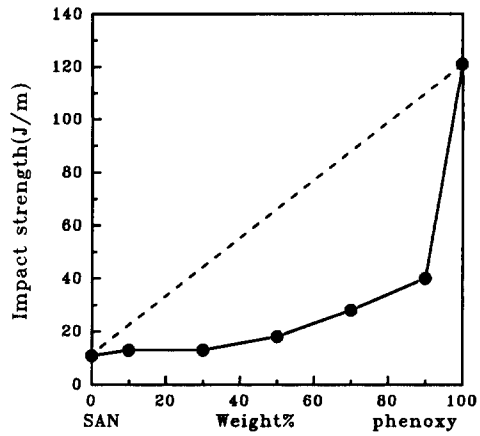

Fig. 6. Notched Izod impact strength of SAN/phenoxy polymer blends at room temperature.

flow in the mould, the case encountered here. In such a case, the modulus and strength of the dispersed SAN should be higher than the isotropic value because of the residual orientation. In addition, strong interfacial adhesion (Fig. 1) should support the interfacial stress transfer, leading to the positive deviation in phenoxy-rich blends.

The elongation at break (Fig. 5) for the blends remains at the level of SAN up to 50/50, and an abrupt increase is obtained at >50 wt% phenoxy polymer. Notably, the ultimate elongation of the 10/90 (SAN/phenoxy) blend is rather higher than the phenoxy polymer. Improvements in ductility of blends are obtained when dispersed domains are oriented along the direction of test with high surface areas [18]. In a separate experiment, we took SEM photographs from a surface fractured parallel to the flow direction in the mould and saw that fibrils were much finer and well developed in phenoxy-rich blends than in SAN-rich blends, and this should contribute to the ductility [15]. On the other hand, the plastic deformation of SAN in a phenoxy polymer matrix should also be accounted for the enhanced ductility of a 10/90 blend as follows. It has been observed that a small amount of brittle materials added to a ductile matrix could augment the ductility above the level of the matrix [15, 18]. For example, for polycarbonate a drastic increase of ultimate elongation from 21 to 63% was reported by adding 10% polymethylmethacrylate to polycarbonate [15]. It is believed that the plastic deformation of brittle particles contributed to this improvement.

Impact strength of a phenoxy polymer is dramatically reduced upon adding a small amount (10 wt%) of SAN (Fig. 6). This implies that the added SAN acts as stress concentrators and thus provides the heterogeneous blends with potential sites for crack growth [19, 20].

Rheological properties

The complex viscosity (η^*) as a function of frequency is shown in Fig. 7. At low frequencies the phenoxy polymer shows a viscosity slightly higher than SAN and the order is reversed at about $\omega = 4$ rad/sec. However, the magnitude of the viscosity difference is insufficient to exert any rheology effect. Following Wu [21], the size of dispersed domain is minimum when the viscosities of the components match each other. In this regard, the morphology of Fig. 1 would be the optimum.

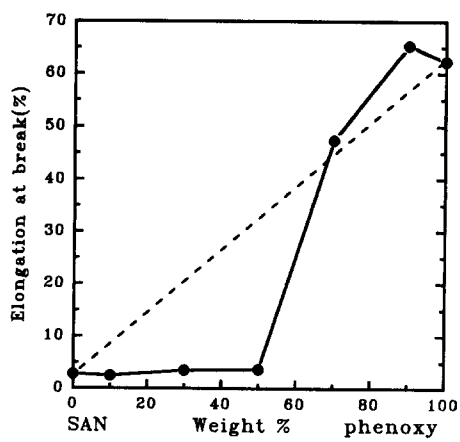

Fig. 5. Elongation at break of SAN/phenoxy polymer blends.

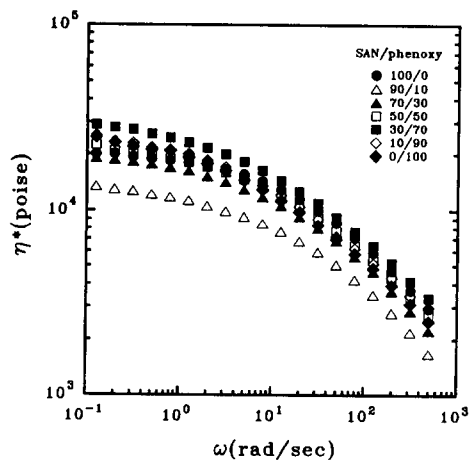

Fig. 7. Complex viscosities of SAN/phenoxy polymer blends at 220°.

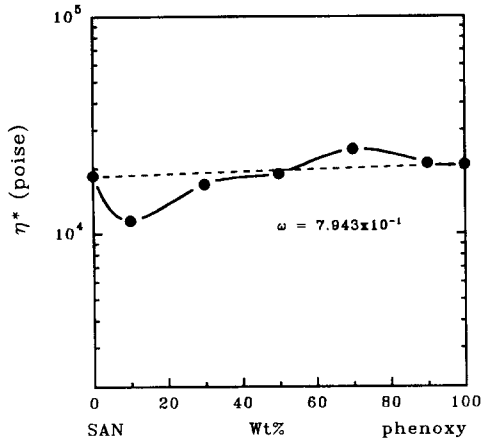

Fig. 8. Complex viscosity as a function of blend composition.

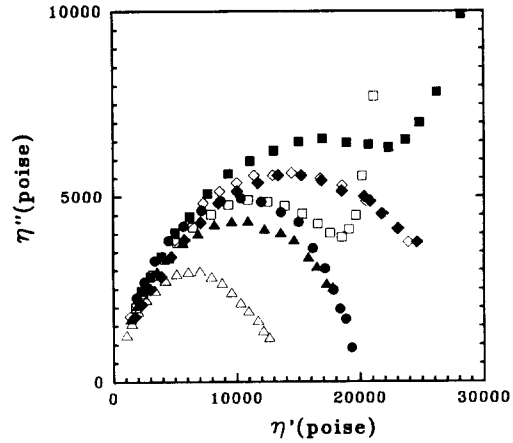

Fig. 10. Cole–Cole plot of SAN/phenoxy polymer blends. Same caption with Fig. 7.

The viscosity–composition relationship (Fig. 8) shows a relatively sharp minimum in SAN-rich, and maximum in phenoxy-rich blends and a crossover point with the additivity (dotted line in the figure) is seen at 50/50 due to the similar magnitude of component viscosity. In immiscible blends, phase inversion is generally observed at viscosity ratio given by [22, 23]:

$$\frac{\eta_1}{\eta_2} \simeq \frac{\phi_1}{\phi_2}$$

where η and ϕ are the viscosity and volume fraction of each component.

In immiscible polymer blends, negative and positive deviation of viscosity is generally related to the morphology [24]. SEM micrographs showed simple particle-in-matrix morphology and poor SAN-phenoxy interfacial adhesion when the phenoxy polymer formed dispersed domains. This would lead to interfacial slip, leading to the reduction in viscosity. On the other hand, in phenoxy-rich blends, significant interdiffusion of dispersed SAN into continuous phenoxy polymer induced strong interfacial adhesion and this morphological intimacy should give viscosity rise over the additivity.

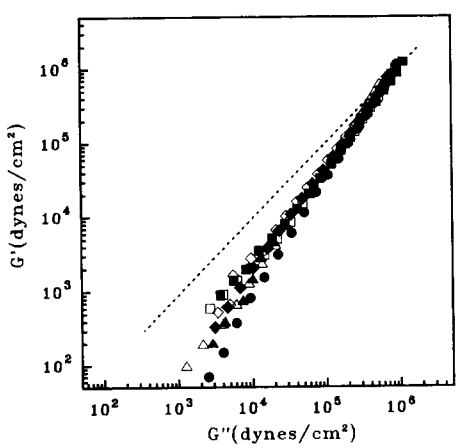

Fig. 9. G' vs G'' of SAN/phenoxy polymer blends. Same caption with Fig. 7.

When the storage modulus (G') is plotted against the loss modulus (G''), generally a temperature independent master curve is obtained [25] (Fig. 9). In this plot, the width across the composition is often an indication of rheological miscibility. Immiscible nature of SAN/phenoxy blend is seen by the broad band in the figure.

A Cole–Cole plot could also be a criterion for rheological miscibility [26, 27]. A well defined semicircle is a necessary condition for a miscible blend, where a drift from the semicircle indicates immiscibility. In a SAN/phenoxy blend, the plot (Fig. 10) shows drift for 50/50 and 30/70 compositions, and this should imply double relaxation mechanism of these blends. The longer relaxation corresponding to the drift should be related to the phase morphology, i.e. phase separated structure, since the relaxation of microstructure takes longer time than molecular relaxations.

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