Structure–Property Relationships in Crosslinked Networks from *cis*-1,4-Polybutadiene and Methacrylic Acid.   Preliminary Results

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Synopsis

In this paper we report preliminary results obtained analyzing structural data and mechanical properties of a composite system prepared vulcanizing mixtures of *cis* polybutadiene and methacrylic acid with different acid amount. The structure was investigated by the small angle x-ray scattering, while the physicomechanical properties were analyzed carrying out stress and birefringence measurements as function of the strain at constant temperature.

INTRODUCTION

As reported in previous papers,[1,2,3] interesting results were obtained by studying the relations between mechanical and structural properties for vulcanized mixtures of rubbery polymers and magnesium methacrylate. The x-ray data indicate for such systems a phase separation with clustering of the polymerized organic salt.   This structural feature plays an important role at level of the physical properties, in particular for the presence of ionic bonds.   The analysis of the experimental data has given some interesting information related to the problem of the rubber elasticity and to the deviations from the Gaussian theory.[4,5]   In the present paper, we report preliminary results obtained carrying on the same kind of investigation on a new class of composite systems, prepared by vulcanization of mixtures of *cis*-polybutadiene and methacrylic acid.   There are two main differences between these systems and the salt vulcanizates[1,2,3]:   an amorphous liquid, methacrylic acid, is used instead of a crystalline powder, magnesium methacrylate; and, moreover, the strong ionic bonds are substituted by the weak hydrogen bonds.   The structural properties were analyzed by using the x-ray low-angle technique, while the physicomechanical properties were analyzed carrying on stress and birefringence measurements as functions of the strain at constant temperature.

EXPERIMENTAL

Materials

cis-1,4-Polybutadiene ANIC, supplied by the SNAM Laboratories of Milan, was used. The methacrylic acid was a Schuchardt, München, product.

Five samples with different amounts of acid, 0, 10, 20, 30, and 40%, were prepared. The five samples were designated as PBMA 0, PBMA 10, PBMA 20, PBMA 30, and PBMA 40, respectively. The mixtures were prepared using a rubber mill of the Werner & Pfleiderer Company, Stuttgart. Dicumyl peroxide was used as initiator; the amount was 0.3% of the polymer weight. The vulcanization was carried out at 145°C for 45 min.

Extraction with benzene for 10 hr does not give evidence of the presence of an unvulcanized fraction.

Methods

Low-angle x-ray diffusion spectra were obtained using a Rigaku-Denki SA camera (resolving power up to 800 Å) by counter technique; CuK_α radiation was used. Other conditions were: 40 kV, 20 mA; time constant, 4; scanning rate, 2′/min. Background diagrams were detected, and only background-corrected scattering values were reported. The angle range was 75′–5′ min. The stress–strain isotherms were carried on using the Tensilon UTM-II of the Toyo Measuring Instruments Co. Ltd.

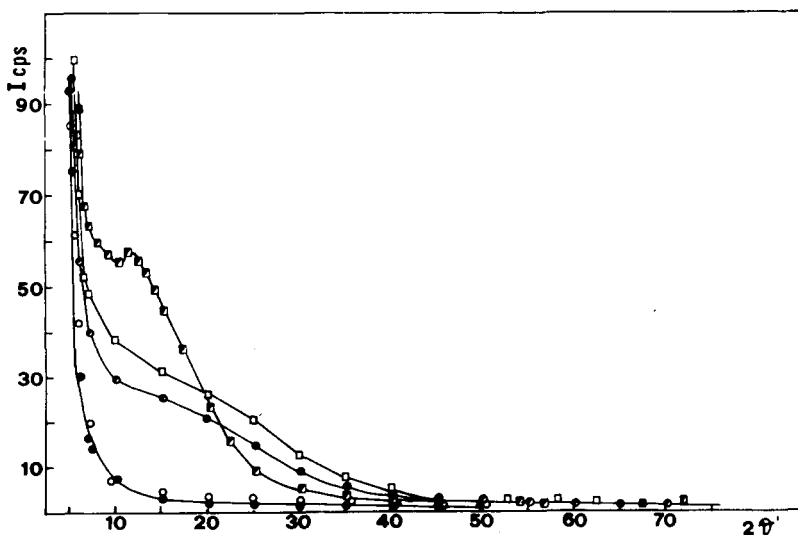The strain was increased step by step and the stress detected at 10-min intervals.

Fig. 1. X-Ray diffusion spectra reported as intensity (counts/sec) vs. diffusion angle: (●) PBMA 0; (○) PBMA 10; (◐) PBMA 20; (□) PBMA 30; (◪) PBMA 40.

The birefringence measurements were done using the system described by other authors,[6] and the Senarmont method[7] was used to evaluate the phase retardation of the polarized beam. The radiation used was the 5891 Å of a sodium lamp and selected by a monochromator. All the elements of the optical system were made by the Spindler-Hoyer, Göttingen.

As for the stress–strain measurements, the birefringence was measured step by step detecting the retardation angle at 10-min intervals. Mechanical and birefringence data were obtained in a room thermostated at 20°C.

RESULTS AND DISCUSSION

The x-ray data are reported in Figure 1. For the samples PBMA 20, PBMA 30, and PBMA 40, the diffusion spectra give evidence of regions with different electronic density, in other words, they indicate that a phase separation takes place in the examined samples. This result suggests that in spite of the substantial differences mentioned in the introduction, as for the salt vulcanizates[2,3] are concerned, the different polarity between the
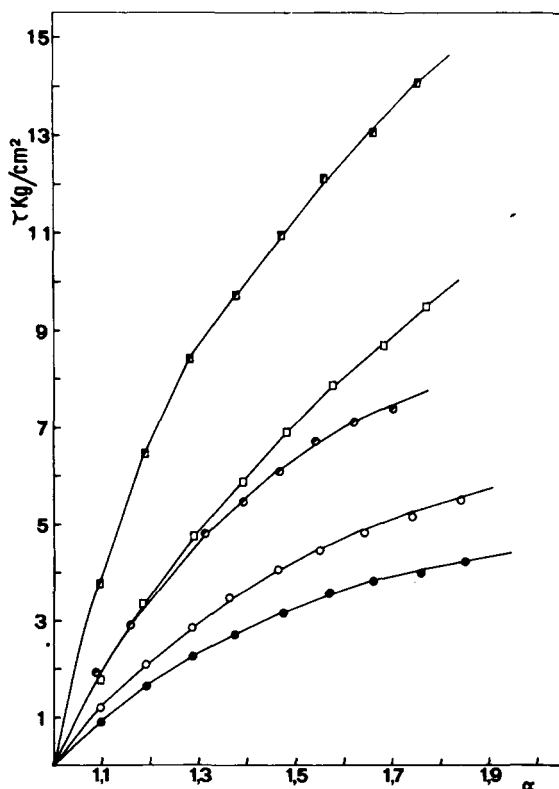

Fig. 2. Stress–strain isotherms. Tensile force on the undeformed section is reported vs. strain ratio: (●) PBMA 0; (○) PBMA 10; (◐) PBMA 20; (□) PBMA 30; (▨) PBMA 40.
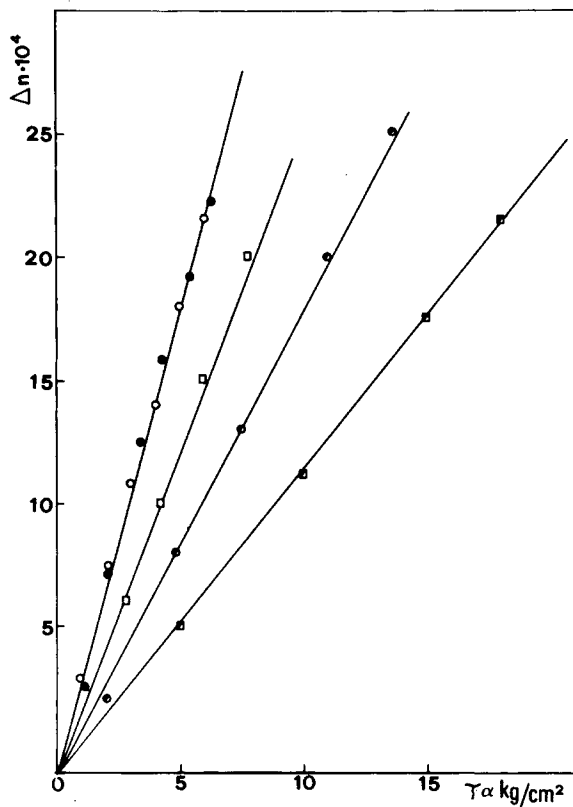
Fig. 3. Birefringence as a function of true stress: (●) PBMA 0; (○) PBMA 10;
(◐) PBMA 20; (□) PBMA 30; (◪) PBMA 40.

polymer and the acid can play a role in determining the phase microsepara-
tion in the samples.

We are, therefore, in the presence of a composite system.   The structural
work is now in progress to obtain informations on the dimensions of the
scattering regions and on their chemical nature and, moreover, to explain
the maximum observed in the PBMA 40 diffusion spectrum.

In Figure 2 we report the stress–strain isotherms obtained on the five
samples.   In Figure 2 at the mechanical level an effect due to the phase
separation is evident.   Namely, we can observe an increase in the elastic
modulus on increasing the acid content.   In other words, the scattering
regions seem to behave as filling agents in the elastomeric network.
Another important factor that can affect the strengthening phenomenon
could be the presence of hydrogen bridges.   On the other hand, the bi-
refringence behavior shows that on increasing the acid content, the in-
crease in the optical anisotropy is not sensitive and not regular.   This is
at variance with the mechanical behavior.   In Figure 3 we report birefrin-
gence versus true stress.   The slope of these straight lines gives the photo-

TABLE I
Photoelastic Coefficients (PC)

Sample	PC, $(kg/cm^2)^{-1} \times 10^4$
PBMA 0	3.62
PBMA 10	3.57
PBMA 20	1.96
PBMA 30	2.50
PBMA 40	1.18

elastic coefficient. Values are reported in Table I. The strong decrease observed in the photoelastic coefficient indicates that, while the phase separation is operative at level of the mechanical properties, the effect on the birefringence is small.

In conclusion, on the basis of these preliminary data, it seems possible to observe that while the mechanical behavior is affected by supramolecular phenomena, at least in this case and in this strain range, the optical anisotropy is governed only by a molecular mechanism. Work is in progress to give a complete picture of the relations between structure and physical behavior for this new class of composite systems.

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