

Hard Rubber Polyblends: Shear Modulus-Temperature Relationships

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Synopsis

Polyblends which undergo two distinct modulus transitions between glassy and rubbery behavior have been made from sulfur-vulcanized diene rubbers. In these blends butyl rubber or polyisobutylene is used to form the rubbery phase of a mixture in which an appropriate diene polymer is converted to resinous hard rubber by sulfur vulcanization. Data are given to illustrate the modification of modulus produced in polyblends based on hard rubber mixtures and to show the importance of marginal compatibility in determining the properties of the product.

Introduction

Polymer mixtures in which a rubbery phase is finely but not molecularly dispersed through a hard or glassy plastic phase are called polyblends.^{1,2} A well-known example is the impact-resistant polystyrenes, in which butadiene-styrene rubbery copolymers are the rubbery phase and polystyrene is the glassy plastic phase. The words rubbery and glassy refer to the properties of these phases at room temperature.

The modulus temperature curves of polyblends of amorphous polymers frequently show two transition regions, one corresponding to the rubbery phase and one to the glassy phase.¹⁻³ In a polyblend one achieves high impact strength and high modulus in the temperature region bracketed by the glass transition temperatures of each phase.

To obtain a proper polyblend from two amorphous polymers it is desirable that the polymers should be on the border line of compatibility-incompatibility. If the polymers are completely mutually soluble, the polymers can become molecularly dispersed during the mixing operation. Such a polymer mixture behaves as if it had a single intermediate glass transition temperature. Indeed it is very similar in behavior to the random copolymer of the same gross composition, namely the temperature region in which high modulus and high impact strength are both present is very narrow.

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If the two polymers are very incompatible they tend not to wet each other, and it is very difficult to get a fine dispersion of one polymer in the other by the usual mixing techniques.

Most frequently polyblends are formed from two linear (thermoplastic) polymers. It is therefore interesting to consider the possibilities of polyblending in a crosslinked thermosetting system.

An interesting possibility arises in the case of hard rubber systems. These are formed by reacting natural rubber or butadiene-styrene rubber or butadiene-acrylonitrile rubber with large amounts of sulfur. The sulfur acts to crosslink these rubbers and also reacts intramolecularly. With increasing amounts of sulfur one raises the T_g of these polymers very substantially, and at the same time one increases the crosslink density.^{4,5}

If polyisobutylene or butyl polymer are thoroughly mixed with the diene polymer and with sulfur before the vulcanization process, we create a situation in which thermoset polyblends may be formed after vulcanization.

Experimental Results and Discussion

SBR-1000 and Hycar 1042 (registered trademark of B. F. Goodrich Chemical Co. for a "medium high" acrylonitrile-butadiene copolymer)

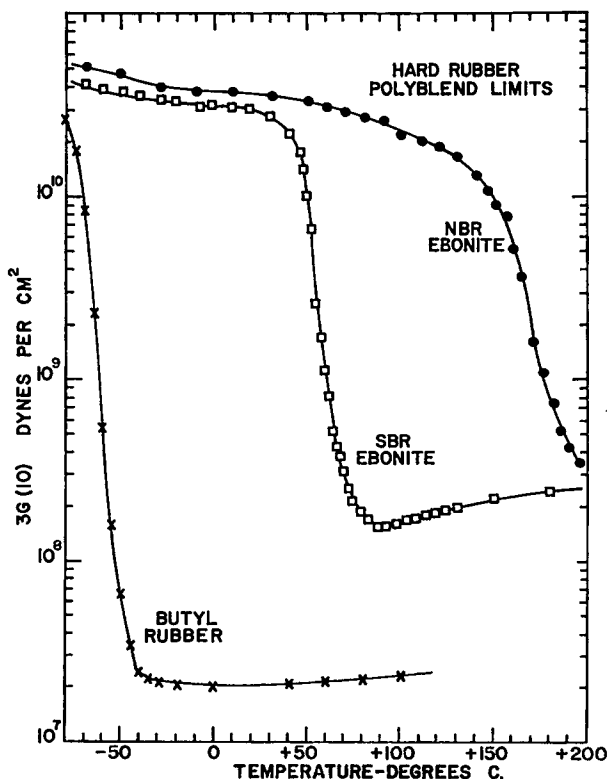


Figure 1.

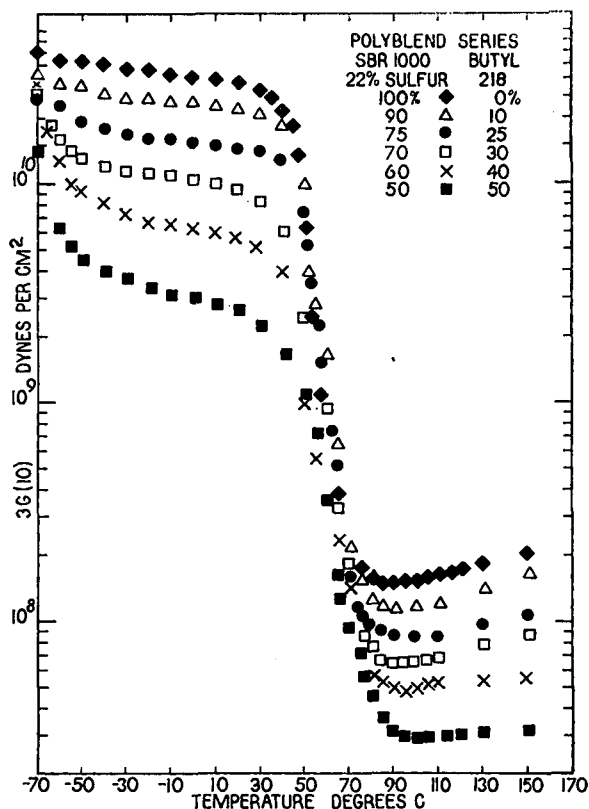


Figure 2.

are respectively representative of butadiene-styrene and butadiene-acrylonitrile general-purpose copolymer rubbers containing enough unsaturation to permit vulcanization to hard rubber. Butyl 218 (registered trademark of Enjay Chemical Co. for isobutylene-isoprene copolymer containing 1.5-2.0 mole-% unsaturation) and Vistanex MD 333 polyisobutylene (registered trademark of Enjay Chemical Co. for polyisobutylene of 300,000 Staudinger molecular weight) are too highly saturated to be converted to hard rubber by sulfur vulcanization. Blends of either of these isobutylene polymers with one of the butadiene copolymers can be made on conventional rubber mixing equipment and, after vulcanizing the highly unsaturated copolymer to hard rubber, modulus-temperature measurements can be made to determine whether the mixture has resulted in a polyblend.

We prepared sulfur master batches from both SBR-1000 and Hycar 1042 NBR polymers by adding butyraldehyde-amine accelerator (du Pont Accelerator No. 808) in the proportion of 4 parts by weight of accelerator to each 100 parts of the unvulcanized rubber. Sulfur was then added to obtain an SBR mixture containing 22 wt.-% sulfur and an NBR mixture

containing 27.15 wt.-% sulfur. The remainder of each sulfur master batch consisted of the previously prepared accelerator-rubber mixture. The proportions of sulfur used in each case were calculated to allow enough sulfur in the master batch to combine with most of the unsaturation in the polymers. The sulfur master batches were cured 2 hrs. at 165°C., and modulus-temperature curves were obtained for each by measuring the shear modulus at 10 sec. stress on a Gehman torsional wire apparatus⁶ modified to take a specimen 6.35 mm. (0.250 in.) wide and 63.5 mm.

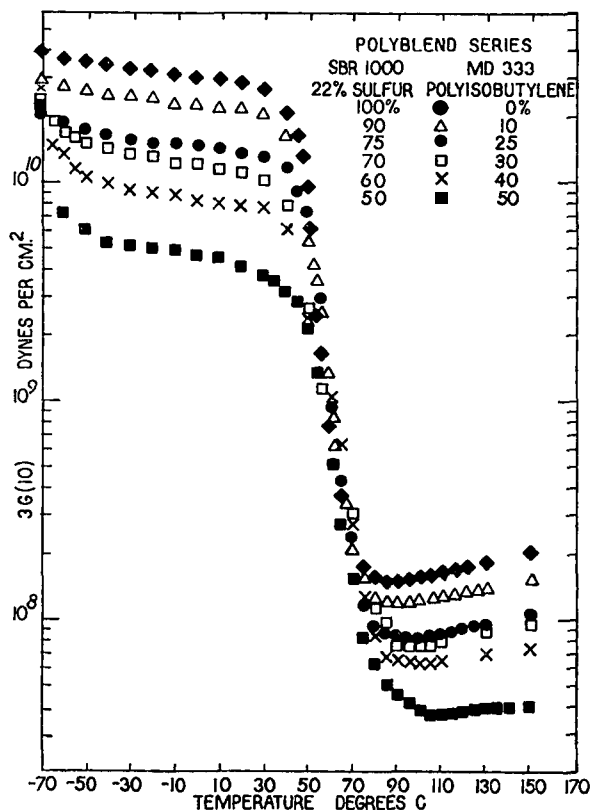


Figure 3.

(2.50 in.) long. Thrice the shear modulus, G , was plotted versus temperature (approximately the Young's modulus) to obtain the curves for the vulcanized hard rubber mixtures shown in Figure 1. The curve for butyl rubber is also shown.

Blends of the SBR-1000 sulfur master batch with Butyl 218 were prepared by banding a small quantity of butyl on tight rolls on a laboratory rubber mixing mill and then adding small portions of SBR-sulfur master batch until a well-blended mixture of the desired composition was obtained. Slabs of material from each batch were cured 2 hr. at 165°C., and modulus

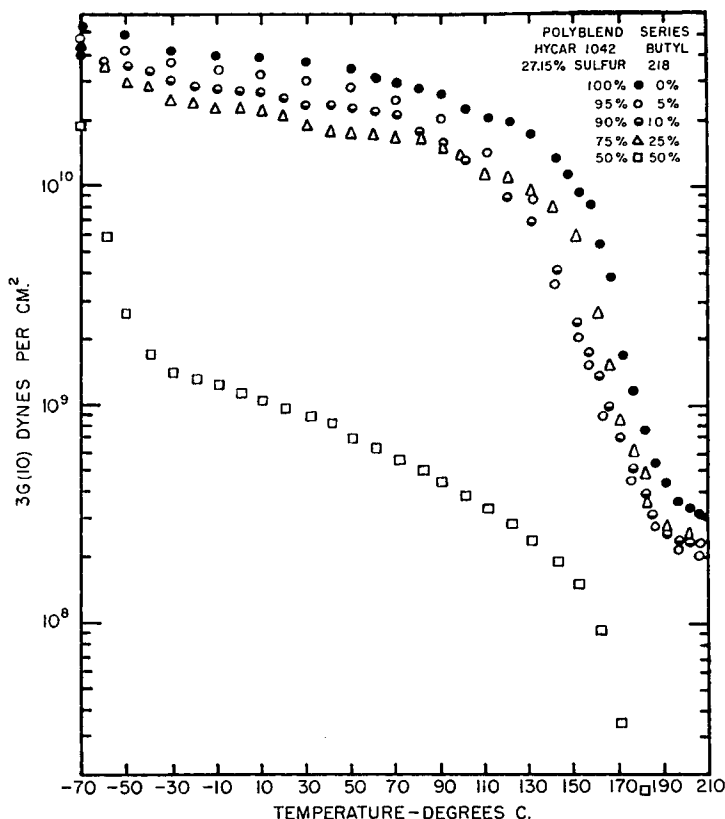


Figure 4.

measurements were made in the same way as had been done for the cured sulfur master batches.

Figure 2 shows that each of these mixtures is characterized by a modulus plateau below the glassy modulus level of the SBR master batch and between the -80 to -50°C . transition temperature range of the butyl and the 40 to 70°C . transition temperature range of the vulcanized 22% sulfur SBR. It is interesting to note that, although the complete transition to glassy behavior below -70°C . is not shown, there is a pronounced inflection of the modulus curves for all of the blends below -50°C . corresponding to the temperature range for the transition of the butyl between rubbery and glassy behavior. A second transition to lower modulus takes place in the 40 – 70°C . transition range of the unblended 22% sulfur hard rubber. The modulus plateau between these two transitions characterizes these mixtures as polyblends. The level of the polyblend modulus plateau is indicative of the degree to which the physical properties of the hard rubber have been modified by the addition of butyl.

In Figure 3, polyisobutylene is shown to produce a series of polyblends with SBR hard rubber similar to those made with butyl rubber but dis-

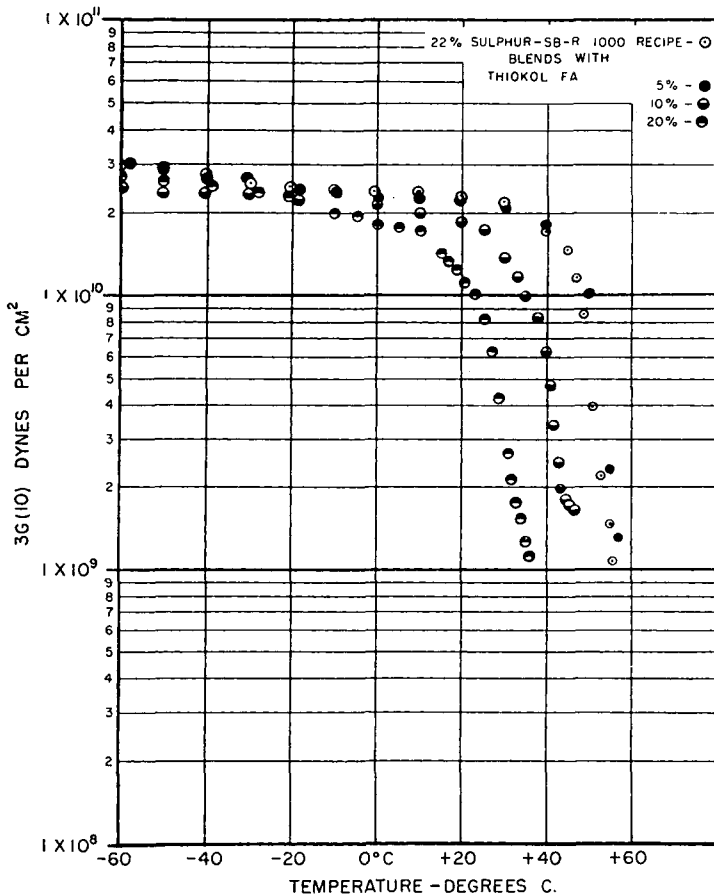


Figure 5.

playing even more abrupt transitions in identical temperature ranges beyond either end of the polyblend modulus plateau. The modulus plateau between the glassy to polyblend transition and polyblend to rubbery transition is both flatter and higher for the polyisobutylene blends than for the corresponding butyl blends. These differences may result from the comparatively higher molecular weight of the polyisobutylene.

Hard rubber polyblends are not confined to SBR-butyl or SBR-polyisobutylene mixtures. Figure 4 shows the modulus-temperature behavior of a series of polyblends prepared by blending butyl rubber with the NBR-sulfur master batch depicted in Figure 1. The NBR-butyl mixtures are also polyblends as shown by the lowering of the modulus plateau between the T_g of the butyl and the T_g of the unblended hard rubber. These blends are quite close to the margin of incompatibility because we found it impractical to prepare the complete series we had intended. Lack of compatibility prevented us from molding satisfactory pieces for blend pro-

portions between 50 and 25% butyl. Even the proportions which were prepared and tested were very difficult to mix and to mold without gross defects. These mixtures provide good illustrations of the effects of inadequate compatibility.

In Figure 5 we show the results of blending a hard rubber mixture with a too compatible material. The data in this figure were obtained by measurements of shear modulus at 10 sec. stress made on a Clash-Berg torsion stiffness tester.⁷ Because of the greater yield resulting from the higher stress level applied by the Clash-Berg instrument, the numerical values of modulus are lower than those in the preceding figures. The modulus curves also terminate in the glass transition region, because the specimens break before measurements of modulus can be made in the rubbery region. The curves for the SBR hard rubber-polysulfide rubber mixtures in Figure 5 are sufficiently complete to show that the glassy modulus of the hard rubber is virtually unchanged by additions of Thiokol FA (registered trademark of Thiokol Chemical Corp. for polysulfide polymers). The changes which are produced by blending result in a series of mechanically equivalent materials which differ only in T_g according to the law of corresponding viscoelastic states.² We have seen that analogous effects are produced by varying the ratio of monomers combined in a copolymer¹ or the amount of sulfur combined with a diene rubber during vulcanization.^{4,5}

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Résumé

Il a été fait à partir d'un caoutchouc diénique vulcanisé au soufre des polyblends, qui subissent deux transitions distinctes entre les comportements vitreux et caoutchouteux. Le caoutchouc butylique ou le polyisobutylène est employé dans ces mélanges pour former la phase caoutchouteuse du mélange, dans lequel un polymère diène approprié est transformé en un caoutchouc dur et résineux par vulcanisation au soufre. Des chiffres montrent le changement du module produit dans les polyblends basés sur des mélanges de caoutchouc dur. Ils montrent l'importance de la comptabilité marginale dans la détermination des propriétés du produit.

Zusammenfassung

Polymermischungen aus schwefelvulkanisierten Dienkautschuken mit zwei verschiedenen Modul-Umwandlungen zwischen glasartigem und kautschukartigem Verhalten wurden dargestellt. Bei diesen Mischungen wird Butylkautschuk oder Polyisobutylen als Kautschukphase benützt, in welcher ein geeignetes Dienpolymeres durch Schwefelvulkanisation in einen harzartigen Hartgummi umgewandelt wird. Ergebnisse, welche die in Mischungen auf Hartgummigrundlage erzeugte Modifizierung des Moduls erkennen lassen und die Bedeutung der Verträglichkeitsgrenzen für die Eigenschaften des Produktes zeigen, werden mitgeteilt.

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