

## Structure-Property Relationships in Elastomer-Modified Terpolymer Systems

EDWARD M. HAGERMAN, *General Motors Research Laboratories,  
Warren, Michigan 48090*

### Synopsis

A number of terpolymers, incorporating as the elastomer phase polybutadiene, polyisoprene, poly-2,3-dimethylbutadiene, poly(butadiene-co-styrene), and poly(butadiene-co-2-methyl-5-vinylpyridine), were studied. Matrices were composed of poly(styrene-co-acrylonitrile) (SAN), poly( $\alpha$ -methylstyrene-co-acrylonitrile), and poly(styrene-co-acenaphthylene). At constant elastomer content and elastomer molecular weight in systems employing a SAN matrix, Izod impact resistance was found to vary inversely with rising elastomer-glass transition temperature. In systems of various matrix composition, using a polybutadiene elastomer, heat deflection temperatures were found to vary directly and impact resistance inversely with rising matrix-glass transition temperature. In acrylonitrile-butadiene-styrene (ABS), systems of constant matrix composition and elastomer content, varying the elastomer molecular weight from 0.6 to  $2.6 \times 10^5$  resulted in increasing the Izod impact resistance from 0.67 to 12.8 ft-lb/in. of notch.

### INTRODUCTION

The elastomer-modified terpolymer systems have been shown to be two-phased,<sup>1,2</sup> with a rigid exterior phase or matrix and a dispersed elastomer phase. The dispersed phase is in the form of spheres. The mechanism of the formation of the dispersed phase has recently been described by Molau and Keskkula.<sup>3</sup> One of the characteristics of these materials is that their interphase adhesion is achieved through covalent linkages between the two phases. The interphase linkages are established during the synthesis by polymerizing the matrix forming monomers in the presence of the preformed elastomer.

The single property which is enhanced as a result of the elastomer modification is impact resistance; i.e., tensile strength, modulus, deflection temperature, etc., are all reduced. For example, poly(styrene-co-acrylonitrile) has an Izod impact resistance of 0.3 to 0.5 ft-lb/in. of notch, while acrylonitrile-butadiene-styrene materials with Izod impacts of up to 7 ft-lb/in. are available. A very early explanation of the mechanism of the impact enhancement was proposed by Merz et al.<sup>4</sup> These authors suggested that the elastomer is stretched across a propagating crack with large amounts of energy being absorbed in the tensile failure of the elastomer. The requirements of the Merz theory are that the dispersed phase be above

its glass transition temperature ( $T_g$ ), that good interphase adhesion exists, and that the dispersed phase be uniformly distributed throughout the mass.

A second treatment of the same problem has been presented by Bucknall and Smith.<sup>5</sup> These investigators proposed that the formation and propagation of crazes are responsible for the improved energy absorption in these modified polymeric systems. Crazes or stress whitening are flat, reflecting dislocations formed at right angles to applied stress. They consist of 40 to 60% voids and 60 to 40% highly oriented matrix material.<sup>6</sup> The function of the elastomer, according to the theory, is to act as stress concentration points so that numerous crazes form without formation and propagation of major cracks. The requirements of the Bucknall-Smith theory are essentially the same as for the Merz theory.

On the other hand, the theory proposed by Neuman and Strella<sup>7</sup> more fully describes the requirements of the matrix and elastomer phases. These authors<sup>7</sup> have suggested that the elastomer acting under triaxial stress initiates a dilation of the matrix structure and allows cold drawing to occur in the vicinity of the elastomer particles. The energy-absorbing mechanism is then the cold drawing of the matrix. In a more recent paper,<sup>8</sup> Strella has presented a mathematical expression relating the degree of expected cubical dilation in terms of the physicomaterial properties of the matrix and dispersed phase materials. The Strella expression is based on an early paper by Goodier.<sup>9</sup> Maximum impact enhancement, from the equation, would result from both the matrix and elastomer moduli tending to zero.

The present paper has as its premise the assumption that stepwise variations in the physicomaterial properties of the independent phases of these modified polymers should result in stepwise variations in the overall properties of the total system, the existing theories of the mechanism of impact enhancement, with the exception of the Strella treatment, require only that the elastomer be above its glass transition temperature.

In this study, terpolymers were prepared in which the type and molecular weight of the elastomer, as well as the matrix composition, were varied. The terpolymers were tested for impact resistance and deflection temperature in an effort to demonstrate the structure-property interrelationships.

## EXPERIMENTAL

### Materials

Butadiene (Matheson Instrument Grade) was distilled from the shipping container and used as such. Isoprene and 2,3-dimethylbutadiene (Monomer-Polymer) were distilled through an 18-in. packed column and the center 50% fraction used. Styrene, acrylonitrile (Eastman), and 5-vinyl-2-methylpyridine (Monomer-Polymer) were distilled prior to use with center 50% fraction used. Acenaphthylene (Monomer-Polymer) was recrystal-

lized from ethyl ether. *tert*-Dodecyl mercaptan (Eastman), sodium oleate (Baker), and potassium persulfate (Baker) were used as received. Water was distilled and deoxygenated by boiling under a stream of nitrogen for 30 min. Nitrogen from Matheson or Airco, prepurified grade, was used as received.

### Synthesis Procedure

Emulsion graft polymerization technique was used throughout this study. Pop bottle reactors were used. The two-step synthesis consisted of purging the pop bottle with nitrogen, introducing the emulsifier (sodium oleate), modifier (*tert*-dodecyl mercaptan), initiator (potassium persulfate), water, and monomer and sealing with a bottle cap. The bottle was then shaken for 18 hr at 50°C. Residual monomer was removed by steam distillation. In step two, the above elastomer latex was introduced into a purged pop bottle along with the matrix-forming monomers and additional initiator, modifier and emulsifier. The graft reaction was run for 6 hr at 50°C with continuous shaking. Monomer residues were again removed by steam distillation. Care was taken to provide a nitrogen blanket, wherever possible, in all steps of the synthesis. The latex was broken by creaming with 5% NaCl and coagulating with 5% acetic acid solution. The coagulation step was carried out under high-speed mixing conditions. The product was washed repeatedly with water and finally with methanol before vacuum drying at 60°C. The dried solids were blended with 1% to 1.5% *N*-phenyl-2-naphthylamine for protection against oxidation during subsequent processing.

### Molecular Weight Determinations

Elastomer molecular weights were estimated from limiting viscosity number (LVN) determinations and osmometry in benzene at 30°C. Elastomer molecular weights were controlled through variations in the initiator and/or modifier concentrations.

### Physical Testing

The polymers were milled on a two-roll mill and compression-molded into  $1/8 \times 1/2 \times 2 1/2$ /in. Izod impact specimen and  $1/2 \times 1/2 \times 5$ /in. deflection bars. Actual testing was carried out in accordance with ASTM specifications D-256-56 and D-648-56 at 264 psi.

## RESULTS AND DISCUSSION

One of the clearest methods of relating chemical structure and mechanical properties stems from the work of Tobolsky and others dealing with the corresponding states theory.<sup>10</sup> The theory infers that the chemical structure, along with interchain interactions, define the glass transition temperature (*T<sub>g</sub>*) of a polymer. Knowing the *T<sub>g</sub>* of a polymer, the mechanical properties, such as modulus and tensile strength, are thus defined. Fur-

thermore, the theory states that linear, amorphous materials, regardless of chemical components, possessing similar  $T_g$ 's will show similar mechanical behavior.

The present study involved the synthesis of a series of elastomer-modified terpolymers in which elastomers of varying  $T_g$  were used. The molecular weights of the various elastomers were controlled to fall in the 1 to  $1.2 \times 10^5$  range. Elastomers used were polybutadiene, polyisoprene, poly(butadiene-co-styrene) 75/25, poly(butadiene-co-2-methyl-5-vinylpyridine) 75/25, and poly-2,3-dimethylbutadiene. Each elastomer was grafted with poly(styrene-co-acrylonitrile) 76/24 (SAN), using identical recipes, and the elastomer content was maintained in the 20 to 25 wt-% range. Glass transition temperatures for the series ranged from  $-85^\circ\text{C}$  ( $-121^\circ\text{F}$ ) to  $-20^\circ\text{C}$  ( $-4^\circ\text{F}$ ). The effect of elastomer  $T_g$  on terpolymer impact strength is shown in Figure 1. The data clearly show an interrelationship between

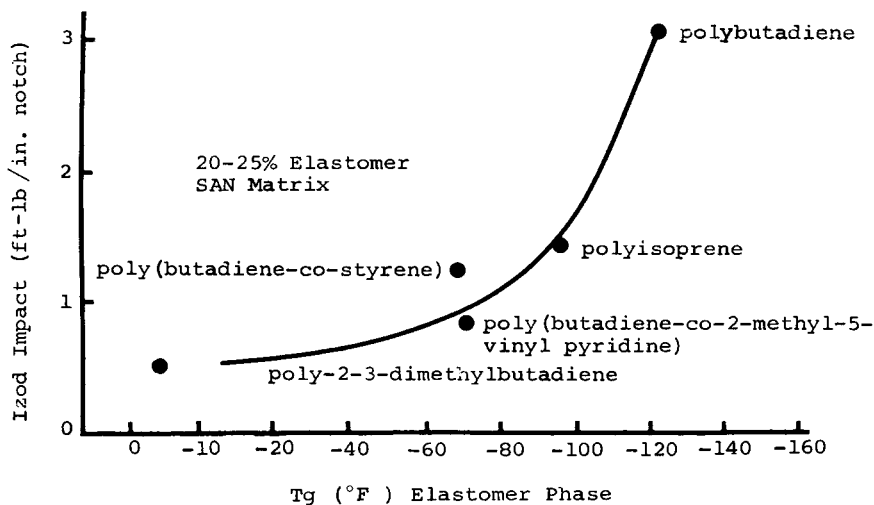


Fig. 1. The effect of decreasing  $T_g$ (elastomer) on impact resistance.

elastomer  $T_g$  and terpolymer impact resistance. Furthermore, the relationship shows maximum impact enhancement from elastomers of lower  $T_g$ , i.e., lower modulus, a result predicted from the Strella-Goodier<sup>8,9</sup> treatment. It is also suspected that elastomers of any chemical structure exhibiting a  $T_g$  in the  $-85^\circ\text{C}$  ( $-121^\circ\text{F}$ ) to  $-20^\circ\text{C}$  ( $-4^\circ\text{F}$ ) range are defined as terpolymer components by Figure 1.

#### Effect of Elastomer Molecular Weight

In order to further define the effect of component mechanical properties on terpolymer properties, the effect of varying elastomer molecular weight was also investigated. A direct relationship between dispersed-phase molecular weight and particle size was shown by Bender.<sup>11</sup> The existence of

an optimum dispersed particle size has been suggested in the works of both Bender<sup>11</sup> and Merz.<sup>4</sup> The herein described method of study did not allow the differentiation between slight variations in elastomer mechanical properties due to molecular weight variation and elastomer particle size variations. However, a definite trend in impact strength was found due to variations in elastomer molecular weight. Referring again to the Stella-Goodier treatment, maximum impact enhancement would be realized from largest possible dispersed particle size. The mathematical equation is

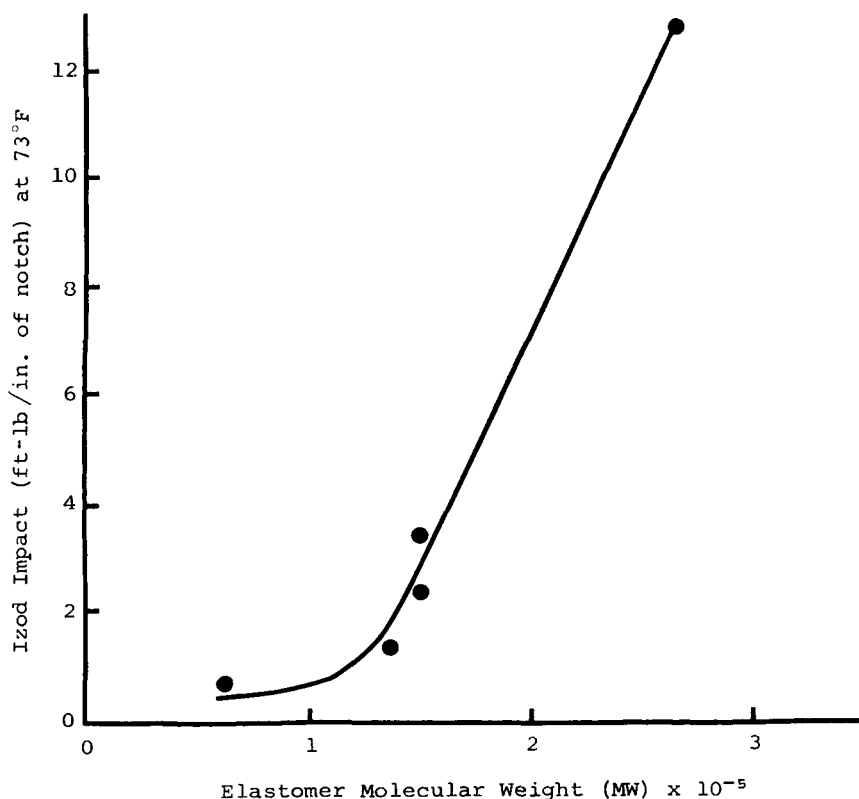
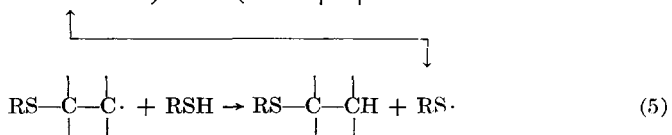
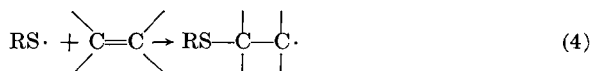
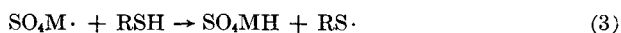


Fig. 2. The effect of elastomer molecular weight on impact resistance.

valid only for a sphere dispersed in an infinite matrix and would have to be tempered by the facts that in real terpolymer systems a limit is placed on the amount of elastomer to be present and that the elastomer must be uniformly distributed throughout the mass. In this investigation, the system acrylonitrile-butadiene-styrene was used. The polybutadiene molecular weight was controlled by variation in the chain-transfer agent concentration. The molecular weights shown are viscosity average values developed from limiting viscosity numbers (LVN) via the Mark-Houwink relationship. Grafting was carried out using identical recipes with the

styrene-acrylonitrile ratio at the 76/24 wt-% composition. Elastomer content in the final terpolymer was in the 24 to 27 wt-% range. The effect of elastomer molecular weight on impact resistance is shown in Figure 2. On a change in elastomer molecular weight from 0.6 to  $2.6 \times 10^5$ , a variation in Izod impact resistance from 0.67 to 12.8 ft-lb/in. of notch was noted in the final terpolymer.

In light of the very large apparent effect of elastomer molecular weight on the properties of the terpolymers it was considered a possibility that the variations in the *tert*-dodecyl mercaptan concentration had resulted in changes in addition to the change in molecular weight. One possible change which could occur would be in the basic elastomeric nature of the elastomer proper. An examination of the mechanisms of the chain-transfer process shows the following reactions<sup>12</sup>:



where RSH = *t*-dodecyl mercaptan.

In this series, eqs. (1) and (2) are included to show the initiation stage. Equations (3), (4), and (5) are the actual chain-transfer steps, while eq. (6) shows transfer agent loss through radical recombination yielding disulfides. The overall effect, as shown in the equations, is only the incorporation of RS endgroups. Since the degree of polymerization in the elastomers used in the present experiments are sufficiently high to negate endgroup effects, it has been assumed that no basic changes have been incurred in the basic elastomeric nature of the elastomers. In addition to the incorporation of RS endgroups, it has also been suggested<sup>13</sup> that mercaptans may chemically add to unsaturation in the formed polymer. This effect is also considered sufficiently small so as not to cause noticeable variation in the basic nature of the elastomers.

Another source of possible difficulty lies in unreacted *tert*-dodecyl mercaptan carrying through to the graft reaction step. The result of such an occurrence would be variations in the matrix molecular weight. This could result in changes in the mechanical properties of the terpolymers. This effect has been negated in light of mercaptan disappearance curves found in the literature.<sup>13</sup> The data indicate that mercaptan consumption

is proportional to monomer conversion and is 95+ % reacted at monomer conversions in the 65 to 70% range.

In addition, a steam distillation step was included in the synthesis at the end of butadiene polymerization. From the above facts, it appears clear that the large variation in terpolymer impact resistance is, in fact, due to variation in the elastomer-component molecular weight. Attempts to further increase the elastomer molecular weight led to crosslinking but to no further increase in impact resistance.

### Effect of Matrix-Glass Transition Temperature

Continuing the development of data relating component physico-mechanical properties with terpolymer properties, a series of experiments was carried out in which matrices of varying  $T_g$  were used along with a polybutadiene elastomer phase of constant molecular weight. Elastomer content was maintained in the 22 to 25 wt-% range. Matrix monomer combinations used were styrene-acrylonitrile,  $\alpha$ -methylstyrene-acrylonitrile, and styrene-acenaphthylene. The  $T_g$ 's for these matrices are 204, 246, and 266°F, respectively. As expected, the terpolymers incorporating

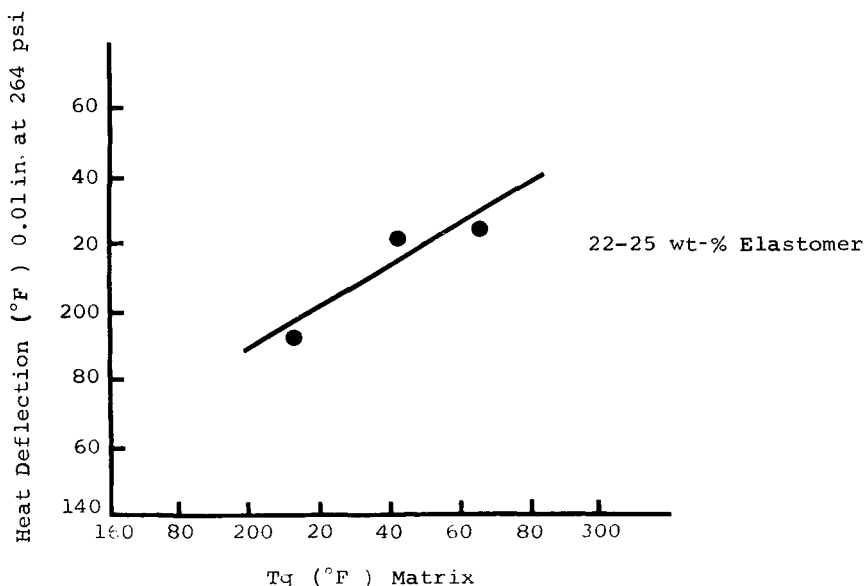


Fig. 3. The effect of increasing  $T_g$  (matrix) on heat deflection temperature.

these matrices showed an increasing trend in deflection temperatures (Fig. 3). Deflection temperatures of 194, 224, and 226°F were recorded.

On the other hand, the impact resistance showed a definite decreasing trend, falling from a high of 3.1 to a low of 0.4 ft-lb/in. of notch (Fig. 4). These results may be interpreted theoretically from the viewpoint that the

higher  $T_g$  matrices require a greater input of thermal energy to increase the free or unoccupied volume to the point where deformation under load can occur. These same factors, e.g., more rigid chains, etc., make it increasingly more difficult for the forces, in the Stella concept, to dilate the

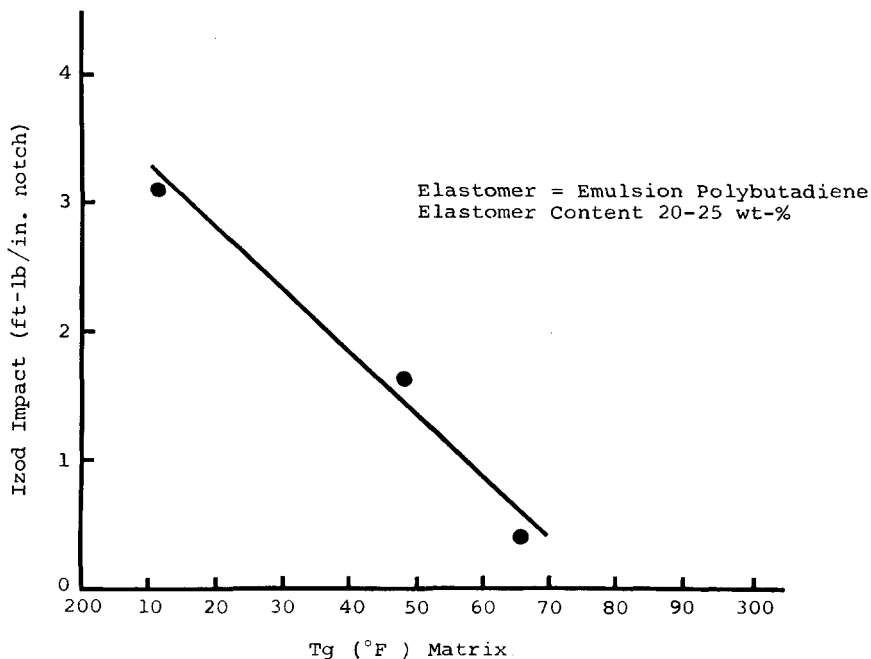


Fig. 4. Effect of increasing  $T_g$  (matrix) on impact resistance.

matrices allowing cold drawing to take place. Substantiating evidence for this concept may be found in the recent papers by Litt and Tobolsky<sup>14</sup> and Litt, Tobolsky, and Koch.<sup>15</sup>

In order to more fully define these systems, another series of experiments was conducted in which the most rigid matrix (styrene: acenaphthylene, 70:30) was utilized with a dispersed elastomer phase composed of emulsion polybutadiene ( $T_g = 85^\circ\text{C}$  or  $-121^\circ\text{F}$ ) with the elastomer content variable. Literature data<sup>16</sup> have shown that increased elastomer content leads to increased impact resistance with a lowering of deflection temperature. It was considered a possibility that the more rigid matrices would tolerate larger elastomer loadings and the resultant compromise would yield a terpolymer with both higher impact resistance and higher deflection temperature as compared with existing terpolymer materials. Experimental results did not support this hypothesis. Elastomer contents used were 24, 35, and 45 wt-%. Impact resistance (notched Izod) for the series showed increasing values (0.4, 1.4, and 2.3 ft-lb/in. notch, respectively) and decreasing heat deflection temperatures (226, 212, and  $138^\circ\text{F}$ ). The results are shown graphically in Figure 5.



## CONCLUSIONS

In this study, a number of new interrelationships existing in elastomer-modified terpolymer systems were developed. Impact resistance was found to increase with decreasing elastomer-glass transition temperatures.

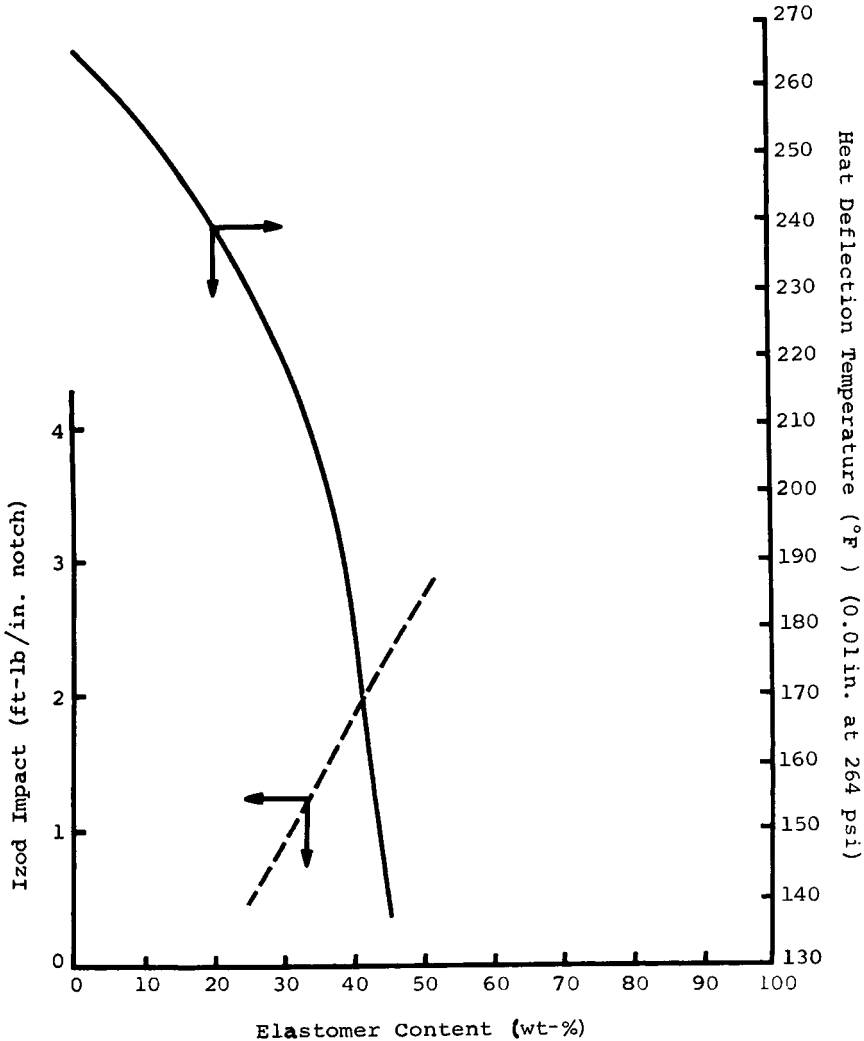


Fig. 5. The effect of variable elastomer content on the acenaphthylene-styrene-butadiene terpolymer.

Increasing elastomer molecular weights also resulted in greater impact resistance. Use of matrices of higher  $T_g$ 's reduced impact resistance; however, higher deflection temperatures were recorded.

The data is consistent with the Stella equation describing the cold draw

theory of impact enhancement in these elastomer-modified terpolymer systems.

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