The Role of Rubber Modification in Improving High Rate Impact Resistance

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Prediction of response of a material to high rate impact involving wave propagation effects such as spallation requires computer analysis utilizing accurate mechanical property data. The rate sensitivity of these properties is significant in polymeric materials and must be characterized in an accurate model. Since rubber modification can suppress spallation, markedly improving high rate impact resistance, the rate and temperature sensitivity of the yield stress of a promising series of rubber modified acrylics was characterized as a function of rubber content. Apparent activation parameters were determined to elucidate the nature of the flow process. The yield criteria obtained help to explain the occurrence of a maximum in impact resistance with increasing rubber content and may be used in computer analysis to predict detailed response to impact.

The use of polymeric materials to protect against high rate particle and projectile impacts is extensive and increasing rapidly. Since polymeric materials combine light weight with actual or potential transparency, their use in these applications is natural. However, the detailed nature of the response of polymeric materials to this type of impact (*i.e.*, impact conditions involving microsecond interaction times as compared with second interaction times in quasistatic loading or millisecond interaction time in conventional Izod impact loading) is not well understood. These differences arise from two sources. The first is the general rate sensitivity

of the mechanical properties of polymers, and the quantification of this rate sensitivity could explain several observed differences between Izod impact and high rate projectile impact (*1*). Another factor is the influence of such wave propagation effects as spallation which become important as the velocity of impact becomes comparable with the velocity of propagation of stress waves through the material. Spallation is discussed later in greater detail.

Analysis of these effects is difficult and time consuming. Much recent work has utilized two-dimensional, finite-difference computer codes which require as input extensive material properties, *e.g.*, yield and failure criteria, and constitutive laws. These codes solve the equations of motion for boundary conditions corresponding to given impact geometry and velocities. They have been widely and successfully used to predict the response of metals to high rate impact (*2*), but extension of this technique to polymeric materials has not been totally successful, partly because of the necessity to incorporate rate effects into the material properties. In this work we examined the strain rate and temperature sensitivity of the yield and fracture behavior of a series of rubber-modified acrylic materials. These materials have commercial and military importance for impact protection since as much as a twofold improvement in high rate impact resistance can be achieved with the proper rubber content. The objective of the study was to develop rate-sensitive yield and failure criteria in a form which could be incorporated into the computer codes. Other material properties (such as the influence of a hydrostatic pressure component on yield and failure and the relaxation spectra necessary to define viscoelastic wave propagation) are necssary before the material description is complete, but these areas will be left for later papers.

Experimental

Materials. This study was directed primarily toward a series of American Cyanamid materials (*3*) with a terpolymer matrix of methyl methacrylate, styrene, and acrylonitrile modified by particles of butadiene rubber with a graft layer of matrix material to ensure good bonding between matrix and rubber. These particles were approximately 1000 A (100 nm) in diameter but exhibited considerable agglomeration with diameters of particle clumps up to 5000 A (*see* Figure 1). The American Cyanamid materials studied contained 0, 4, 10, and 13% rubber. Also included in the study for comparison purposes was a Goodyear Research material (*4*) also containing 13% rubber with the smaller rubber particles approximately 500 A in diameter well dispersed in the matrix (*see* Figure 2). The matrix in the Goodyear material was also a glassy terpolymer.

At quasi-static rates of loading the effect of the rubber particle is twofold. First, the stress concentrations near the rubber particles induce

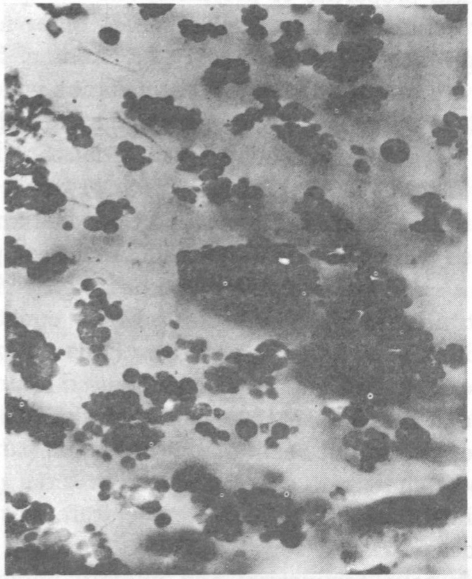

Figure 1. Transmission electron micrograph (22,050×) of American Cyanamid rubber-modified acrylic with 16% butadiene rubber

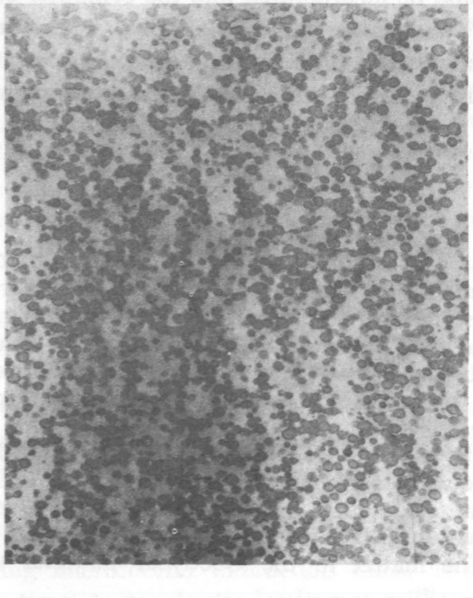

Figure 2. Transmission electron micrograph (20,250×) of Goodyear rubber-modified acrylic with 13% butadiene rubber

the material to yield locally. This yielding can be either dilational (crazing) or distortional (shear yielding). In these materials crazing predominates, but the occurrence of shear yielding cannot be ruled out, especially near the small rubber particles. The second effect of the rubber particles is to stabilize the crazes once they have initiated and thus prevent the formation of flaws which could propagate catastrophically to produce brittle fracture. This craze–crack mechanism is the process by which brittle fracture occurs in the unmodified matrix materials.

Procedures. The specimens were tested in an Instron Universal testing machine at 0°, 23°, 50°, and 75°C and at crosshead extension rates of 0.02, 0.2, 2.0, and 10.0 inches/min. Clip-on strain gage extensometers were used to record sample strain, and testing was done in an environmental chamber capable of maintaining the selected temperature to within ±0.5°C. All samples were soaked at temperature for at least 30 min before testing.

The Role of Spallation in High Rate Impact

At high rates of loading the brittle nature of the unmodified material is manifested by the occurrence of spallation (*see* Figure 3). Spallation is fracture away from the impact point caused by dynamic tensile stresses which arise from interactions of the intial, compressive stress pulse with unloading waves from the free surfaces. Spallation results in particles with fairly high velocities being ejected from the rear surface, and it also decreases the effective thickness of the material resisting the impact. Occurrence of spallation significantly decreases the impact resistance of a polymeric material, and conversely, suppression of spallation by various

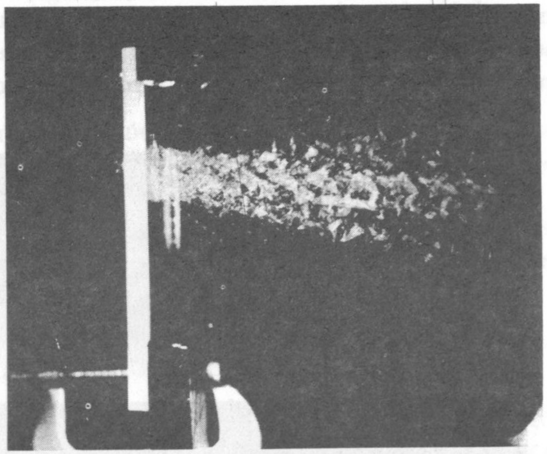

Figure 3. Multiflash photograph of ¼ inch plexiglas under ballistic impact. Projectile is moving from right to left.

means is a very powerful method of enhancing impact resistance. If the material can be induced to yield rather than to fracture, spallation can be eliminated, and plug-like failure at the projectile occurs instead.

As is shown in Figure 4, spallation is suppressed by rubber modification. On the left are front and rear views of an unmodified matrix material which has been subjected to partial penetration by a metal projectile. Extensive spallation and radial cracking are apparent. The material on the right is the same matrix material modified by incorporating 16% rubber (*see* Figure 1). Figure 4 illustrates the response of this modified material to both partial and complete penetration. At a given rate of loading as the rubber content of the system is increased, spallation is eventually eliminated, and a maximum in impact resistance as a function of rubber content is achieved. Stress whitening replaces spall fracture. In these materials stress whitening accompanies crazing at quasi-static rates of loading. A measurable decrease in density in impacted samples indicates that crazing also occurs at high loading rates.

Additional evidence of crazing at high loading rates can be seen in Figure 5 which is a transmission electron micrograph of a section obtained from the stress-whitened area shown in the previous figure. The section was obtained using an ultramicrotome at liquid nitrogen temperature and subsequent staining with osmium tetroxide. This micrograph shows crazes that propagated outward into the glassy matrix from points of initiation at the particle–matrix interface. This provides experimental evidence that craze yielding is an important factor in the response of these materials to high rate impact. To quantify this response, especially in regard to spallation, one must quantify the rate dependence of yield by crazing in these materials.

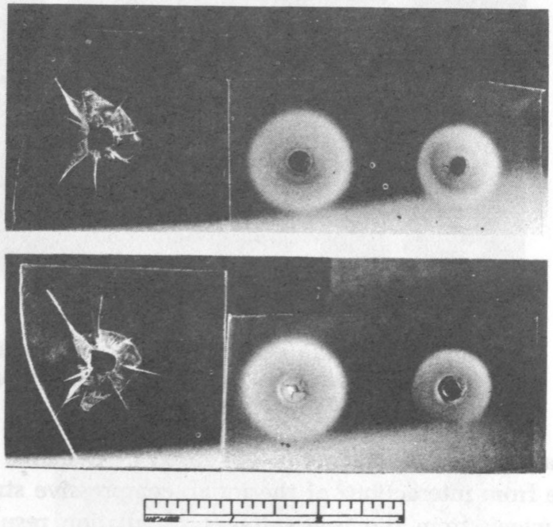

Figure 4. Front and rear views of American Cyanamid materials subjected to ballistic impact. Material on left is unmodified; material on right contains 16% rubber.

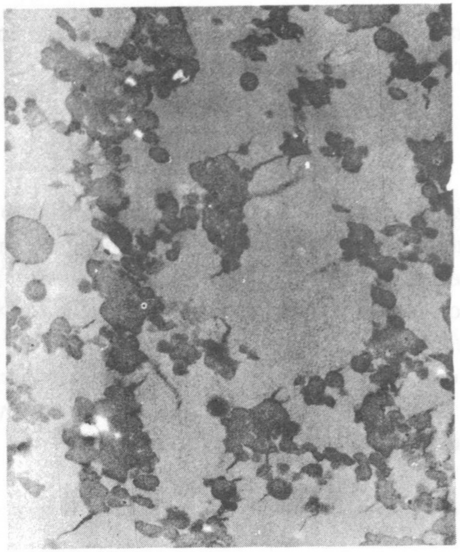

Figure 5. Transmission electron micrograph (21,600×) of craze material produced by ballistic impact in American Cyanamid material with 16% rubber

Choice of an Analytical Yield Criterion

Simplicity is highly desirable in a yield criterion used in a wave propagation code since the numerical schemes are often only conditionally stable and since ease of implementation is desirable in any case. Simplicity is attained by assuming that the yield process is controlled by a single, thermally activated mechanism which can be described by the Eyring rate theory. Given $d\sigma/dt = 0$, satisfied during yield (σ is stress), a viscous flow process can be assumed to be occurring, produced under the action of an applied shear stress along a series of parallel layers in the stress direction. The basic process is a jump of a molecular patch from one equilibrium position to another; in glassy polymers this flow patch is a molecular segment. Assuming a symmetrical energy barrier of height E_0 (attributed to the energy required to open a new equilibrium position for the flow unit) which can be biased in the forward direction by the applied stress, the Eyring theory gives

$$\dot{\gamma} = \dot{\gamma}_0 \exp\left[-(E_0 - v\tau)/RT\right] \qquad (1)$$

where $\dot{\gamma}$ is the shear strain rate, $\dot{\gamma}_0$ is a pre-exponential, v is an activation volume, τ is the molecular shear stress, R is the gas constant, and T is the absolute temperature (*5*).

Since spallation is controlled by the response to tensile stress pulses, the measurements of yield behavior were performed in uniaxial tension rather than in shear, and a tensile yield stress criterion was required. Bouwens–Crowet *et al.* (*6*) rearranged Equation 1 to give an expression for the uniaxial-tension yield stress σ_y as follows:

$$(\sigma_y/T) = A\left[\ln \dot{\epsilon} + \ln B + (E_0/RT)\right] \qquad (2)$$

where A and B are modified constants related to the molecular parameters v and $\dot{\gamma}_0$, and $\dot{\epsilon}$ is the tensile strain rate. Yield data can be fit to this equation to give values of the apparent activation energy E_0, although A and B cannot be used directly to determine the activation volume and the pre-exponential. Although more complex forms of this equation are available, including for example the influence of multiple yielding mechanisms, we determined the applicability of this simple equation as a yield criterion by performing quasistatic tensile tests as a function of strain rate and temperature and by fitting these data to Equation 2.

Results and Discussion

Representative stress–strain curves for the various materials, rates, and temperatures are shown in Figure 6. Tests were replicated from two to five times; in general these replications had very high reproducibility in yield values. Values at fracture, especially fracture strain, showed much more scatter. Accordingly the yield values of the unmodified material, which are really fracture values, also contained more scatter. (In the plots of yield values to follow, the data symbols lie over all of the replication values unless the values are sufficiently spaced to permit another symbol.)

Figure 6a shows the effect of rubber content on the stress–strain behavior of these materials. All the rubber-modified materials exhibited a load maximum under all testing conditions. In most tests the unmodified material failed before it exhibited a yield maximum, although the data were reduced in the same manner used for the other samples. In all cases the yield stress decreased as the rubber content was increased, but the

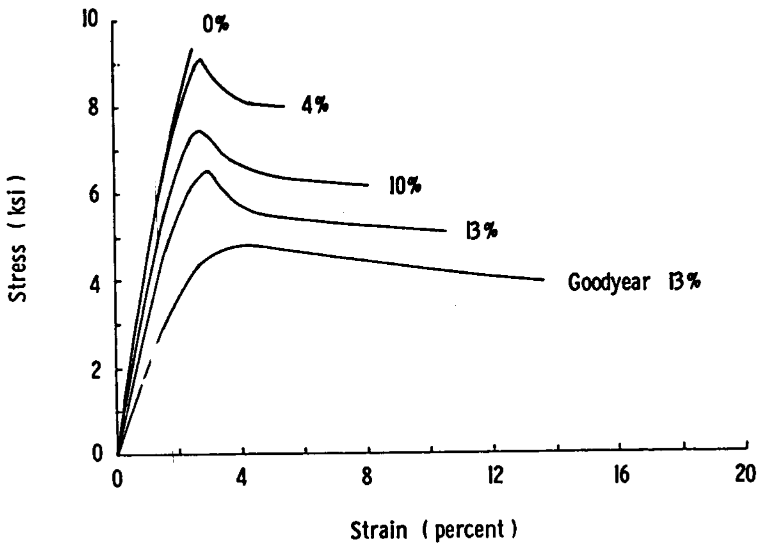

Figure 6a. Stress–strain curves for various rubber-modified acrylics at 0.2 inch/min and 23°C

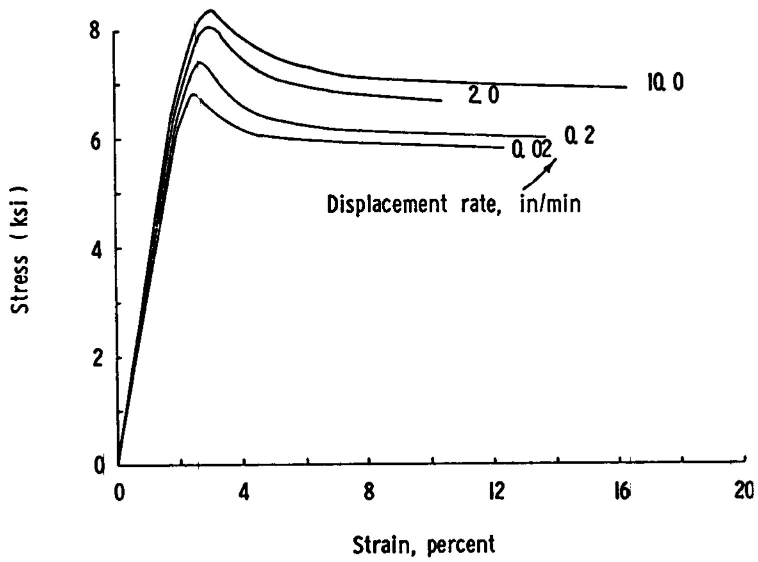

Figure 6b. Stress–strain curves for 10% American Cyanamid material at 23°C and various displacement rates

Goodyear material with the same rubber content as the 13% American Cyanamid material exhibited more ductile stress–strain behavior. Possible reasons for this difference will be discussed later in the paper. Figure 6b shows the effect of rate on the behavior of the 13% American Cyanamid material. The yield stress increases with strain rate as was the case in all materials tested. Figure 6c shows the effect of temperature on the behavior of the same material. Again, as was the case in all materials tested, the yield stress decreases as the temperature is increased.

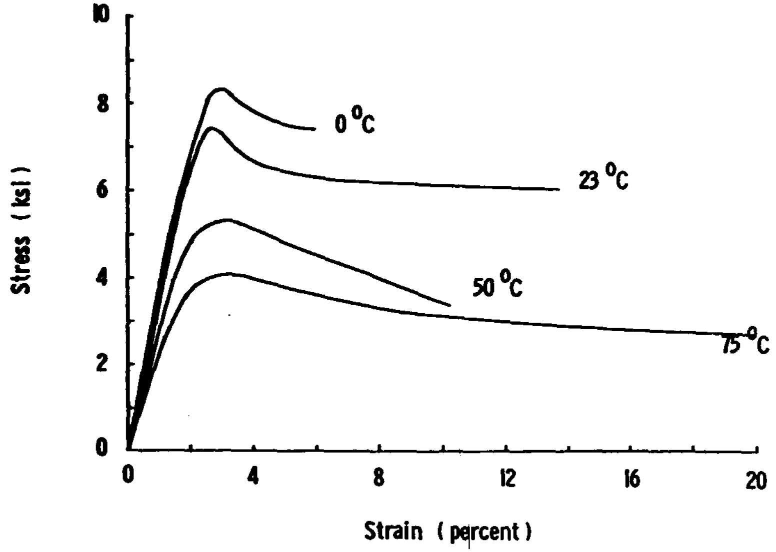

Figure 6c. Stress–strain curves for 10% American Cyanamid material at 0.2 inch/min and various temperatures

To determine the applicability of the Bauwens–Crowet criterion, these these data were plotted as σ_y/T *vs.* log $\dot{\epsilon}$ and $1/T$. Figure 7 shows the results for the 13% American Cyanamid material. As seen in Figure 7a, the behavior is linear at each temperature, and the slopes are the same except at 75°C. At 75°C yielding becomes localized, stress whitening diminishes, and the material appears to undergo a transition in its yield behavior. Since we were interested only in the high effective strain rate behavior, we used only the data obtained at 0°, room temperature, and 50°C to calculate the slope. A good least-squares linear fit was obtained from the data, and the slope obtained in these calculations can be used to determine the value of the constant *A* in the Bauwens–Crowet equation. As Figure 7b indicates, the yield behavior of the material is more sensitive to temperature than to strain rate. This illustrates the advantage of low temperature testing. If an equivalence between low temperature and high rate conditions can be established, details of the mechanical behavior can be studied much more easily at low temperatures than at high rates. The slope obtained by least-squares fit to the σ_y/T *vs.* $1/T$ data, can be used along with the value of *A* to determine E_o.

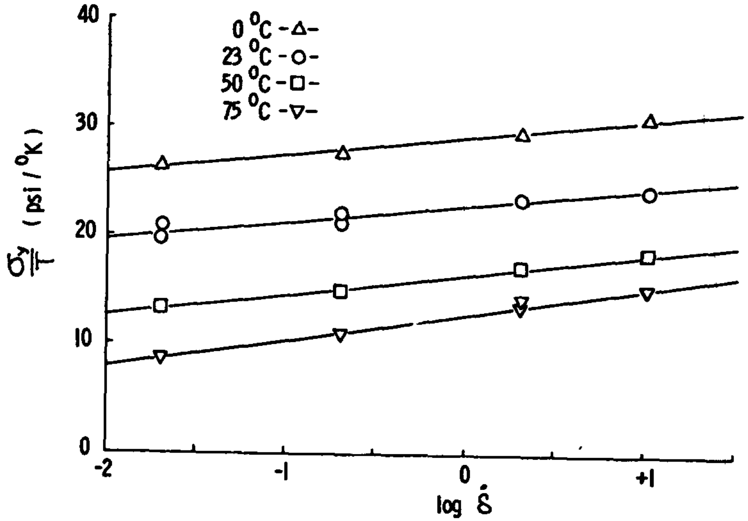

Figure 7a. σ_y/T vs. *log* δ *for 13% material*

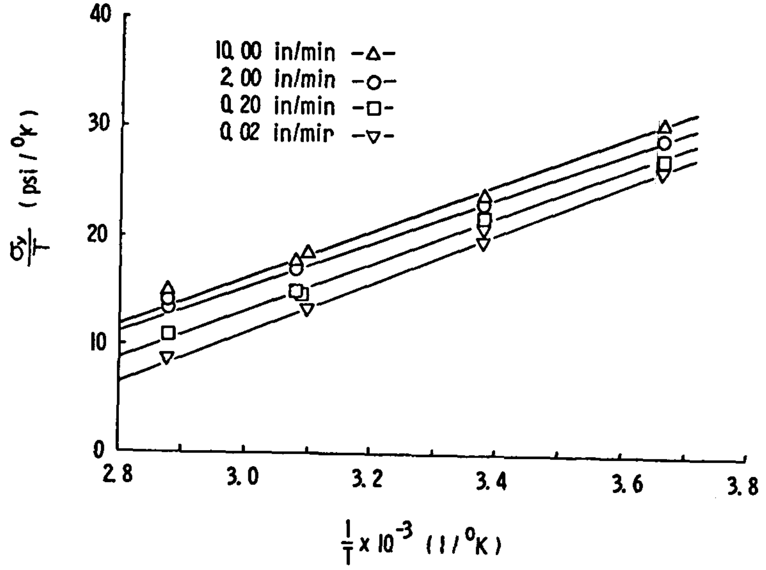

Figure 7b. σ_y/T vs. 1/T *for 13% material*

Table I. Constants from Bauwens–Crowet Equation for Various Materials

Material	A	*ln* B	E_0
American Cyanamid 0%	1.25	29.6	40.2
American Cyanamid 4%	.98	36.2	63.6
American Cyanamid 10%	.90	30.1	56.0
American Cyanamid 13%	.75	32.5	59.3
Goodyear 13%	1.12	19.2	39.5

Table I shows the values of these activation parameters for the materials tested. A time–temperature superposition shift factor (Δ) can be calculated from Equation 2 as follows:

$$\Delta = \log a_T = E_0/R\,[(1/T) - (1/T_{\text{ref}})] \qquad (3)$$

and this value of Δ can be used to obtain master curves of σ_y/T against log effective strain rate. The fit of these shifted data to the Bauwens–Crowet equation is another test of the applicability of the Bauwens–Crowet criterion to these materials.

Using room temperature as a reference the shifted data for the American Cyanamid 13% material is shown in Figure 8. The fit to the Bauwens–Crowet equation represented by the solid line is excellent especially at high effective strain rates. The data obtained at 75°C are included in this figure but were not used to calculate the contents for the Bauwens–Crowet equation. The fit to the Bauwens–Crowet equation was good at the high effective strain rate for all American Cyanamid materials tested, even the unmodified material.

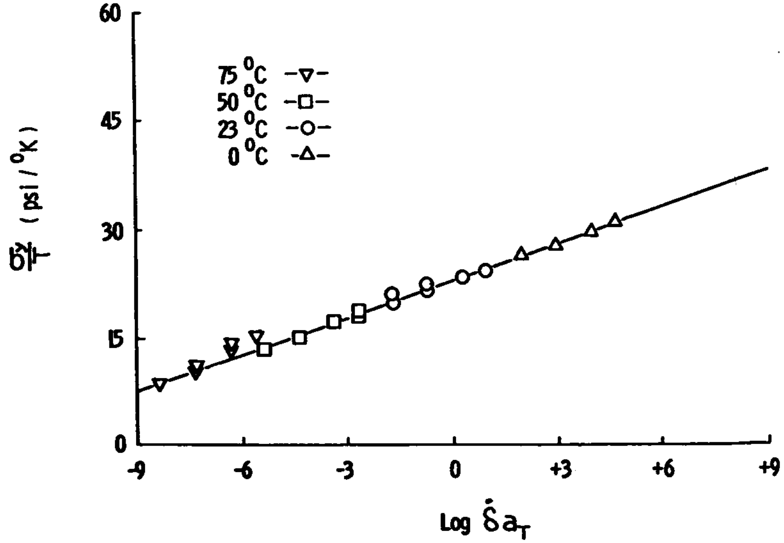

Figure 8. σ_y/T vs. *log* δa_T *for 13% material.* $T_{ref} = 23°C$

Turning to Table I, values of the parameter *B* are essentially the same for all the American Cyanamid materials but differ for the Goodyear material. These values are calculated from the intercept of the σ_y/T *vs.* log effective strain rate curve. This value reflects the pre-exponential in the Eyring equation and therefore depends on the basic frequncy of the flow unit as modeling by Eyring. This value should be characteristic of the matrix since the actual flow process occurs in the matrix material. Therefore differences in matrix formulation between the American Cyanamid and Goodyear materials are indicated by the data. This conclusion is borne out by the fact that the Goodyear material undergoes a gradual transition in the effective strain rate range of the study manifested by an upward curvature in the data points around the line representing the Bauwens–Crowet equation. Roetling (7) reported yield data for pure PMMA which exhibits this same curvature. Analysis of data in a transition region requires the use of the more sophisticated Ree–Eyring model however, and activation parameters obtained from the simple Bauwens–Crowet equation are essentially meaningless. Since the simple Bauwens–Crowet equation seems a good model for the American Cyanamid materials, information about the basic nature of the yielding process in these materials may be obtained from examining the Bauwens–Crowet activation parameters. The values of E_0, apparent activation energy, are essentially the same for all the rubber modified American Cyanamid materials. Under all test conditions all these materials exhibited whitening at yield accompanied by a decrease in density. This indicates that crazing occurs extensively in all these materials and that *ca.* 60 kcal/mole is the appropriate apparent activation energy for this process; 40 kcal/mole, which is observed in the unmodified American Cyanamid material, represents the apparent activation energy for craze fracture and not that for craze yielding. Even though a yield point was not observed, the data were included in the analysis since crazing would still be involved in the fracture process. Although there is considerable scatter in the fracture data, it still behaves in a linear fashion describable by the Bauwens–Crowet equation indicating the thermally activated nature of this fracture process. The values of *A* listed in Table I are a measure of the sensitivity of the yield stress of each material to the applied strain rate. Also the Bauwens–Crowet constant *A* is inversely proportional to the apparent activation volume *v* in the Eyring equation. It can be seen from Table I that the rate sensitivity becomes less pronounced and the apparent activation volume increases as the rubber content increases. This may reflect the fact that increasing the amount of rubber induces a larger volume of matrix to undergo yield.

Figure 9 compares the master curves obtained for all the materials tested. At a given effective strain rate, which would correspond to a given impact velocity, the material with the lowest rubber content gives the highest yield stress. Barring spallation, the highest yield stress should correspond to the highest impact resistance since high speed photography of high rate impact indicates that strains during plug-flow under impact are essentially the same for all these materials. However if spallation occurs because of the material's inability to yield under dynamic tensile stresses, the impact resistance of the material is drastically reduced.

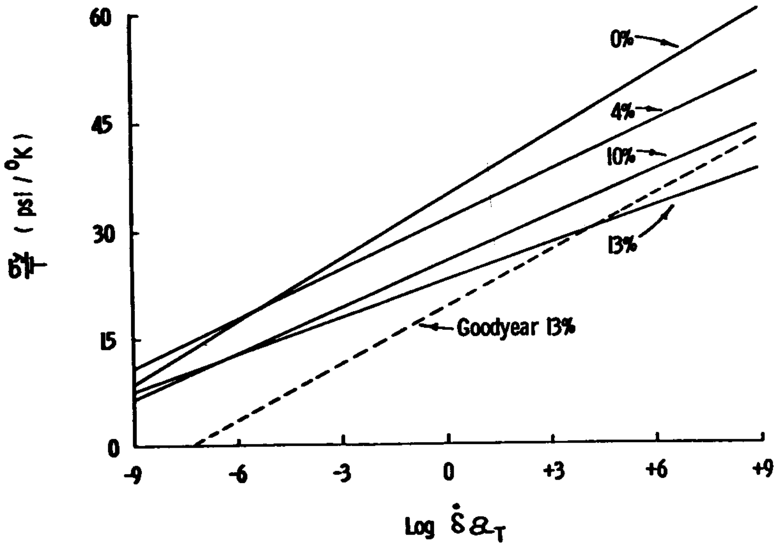

Figure 9. Comparison of shifted curves for various materials

Thus at a given rate the lowest rubber content which can induce ductility and suppress spallation will result in maximum energy absorption under impact. If this yield–spall transition coincides with the ductile–brittle transition which occurs in these tensile tests, the effective strain rate of the onset of spallation could be predicted by tests of this type. This ductile–brittle transition occurs at low effective strain rates for the unmodified material since it is brittle through the range of conditions used in these tests. For the 4% material at the highest effective strain rates achieved in these tests, the load maximum is just beginning to disappear. Thus, if rate–temperature equivalence holds, extension of these test to lower temperatures should allow prediction of both yield stress and the occurrence of spallation as a function of rubber content and rate. By this means the optimum rubber content for a given strain rate or impact velocity could be predicted.

Conclusions

First, the role of rubber modification in high rate impact is to suppress spallation by inducing the material to yield in the presence of dynamic tensile stresses arising from impact. Second, this yield–spall transition occurs at different strain rates for different rubber contents and may be predictable using quasistatic, low temperature tests of this type. These tests can also provide information concerning the basic nature of the yield process in these materials through the activation parameters which are obtained. Third, the Bauwens–Crowet equation seems to be a good model for the rate and temperature sensitive behavior of the American Cyanamid materials and is therefore a likely candidate for a yield criterion to use in the analytical code work on these materials which we hope to perform as a continuation of this work.

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RECEIVED October 18, 1974.