HIGH ELONGATION ELASTOMERS[1]

V. L. Brady, R. Reed, L. Merwin, and R. Nissan
Naval Air Warfare Center Weapons Division
China Lake, CA 93555-6001

ABSTRACT

A new class of liquid curable elastomers with unusual strength and elasticity has been developed at the Naval Air Warfare Center Weapons Division, China Lake. Over the years, studies have been conducted on polymer structure and its influence on the mechanical properties of the ensuing composites. Different tools, including nuclear magnetic resonance, have been used.

This paper presents a summary of the factors controlling the mechanical behavior of composites produced with the new liquid curable elastomers, including the effects of plasticizers. It also provides an overview of the nuclear magnetic resonance study on polymer structure, the composition and properties of some live and inert formulations produced at China Lake, and some possible peace-time applications for these new elastomeric materials.

INTRODUCTION

In the recent past, composites having unusual toughness were developed for use as explosives, propellants, and inert simulants. This advance comes after several years of investigating the effect of polymer structure on mechanical properties. A new class of liquid curable elastomers has emerged from this work. These elastomers display unusual strength and elasticity and are attained by converting solutions of polyether polyols high in functionality (F4) and in molecular weight (18,000 to 27,000 daltons) in plasticizers to lightly cross-linked polyurethanes. Typically, fillers are added to enhance both energy and mechanical properties. This work was stimulated by the need to attain more insensitive munitions. As the toughness of energetic materials is increased, their sensitivity to stimuli such as impact and cookoff is reduced.

Toughness, indicated by the area under the stress-strain curve of composites, is related to the energy that can be absorbed before fracture occurs. Several major factors influencing toughness have been identified in composite propellants and explosives [1,2]. The most important factor is the backbone structure of the polymeric binder. It must be such that the chains can freely bend and rotate. Another critical aspect is the formation of a regular and fully cross-linked network. The new class of binders developed at the Naval Air Warfare Center Weapons Division (NAWCWPNS), China Lake is superior to conventional polyethers in that the length of the polymer chain between cross-links is increased, while the regularity and degree of cross-linking is enhanced. Other backbones such as polyesters can also be used at comparable functionality and molecular weight.

These polyols are waxes and must be dissolved in non-volatile liquids (plasticizers) that separate the crystalline chains to allow bending and rotation to occur. Plasticizers also provide the liquid necessary to attain a castable composite. Since plasticizers enhance polymer chain mobility, they also retard crystallization at reduced temperatures. Other factors such as the functionality of the curative and its ratio to hydroxyl, the relationship of cross-link density to chain length, level and type of plasticizer, as well as the binder filler interaction, also influence mechanical properties.

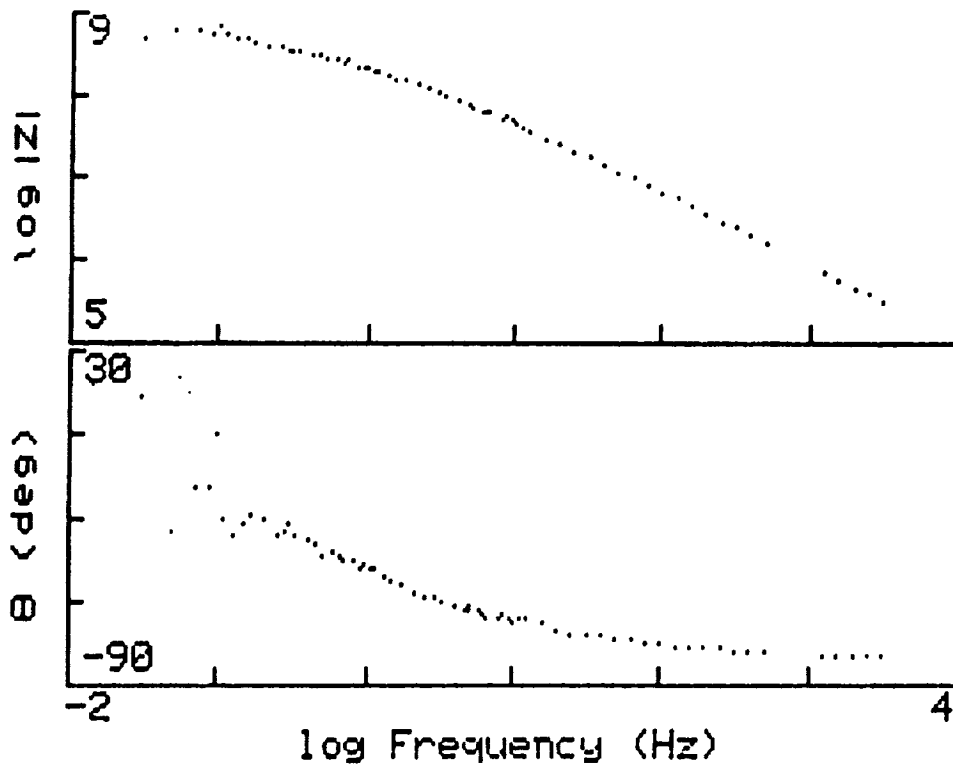[1] Approved for public release; distribution is unlimited.

Figure 7   Bode Plots – 3 Mil Coating

CONCLUSION

The environmental testing of a non-chromated, non-leaded polyurethane single coat primer/topcoat allowed for optimization of the resin and corrosion inhibiting pigmentation system. Additional testing under production environments such as robotic sanding, vapor-blast cleaning and application of TPS materials with aggressive solvents helped prove its compatibility with the SRB environments. The new paint was accepted by technicians preparing and applying it to various substrates, and found it easier to work with than the present two coat system. The polyurethane paint does not require induction time prior to use, and with only one type of paint required greatly simplifies the logistics of shelf life and certification requirements. Applications for many other fields than aerospace exist. Energy and power generation, chemicals, transportation, architectural and many others await its application.

ACKNOWLEDGMENTS

REFERENCES

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The progress in attaining tough composite energetic materials by adjusting the factors cited above is discussed. Variations in mechanical properties caused by altering the polymer structure, plasticizer-to-polymer ratios (Pl/Po), and other factors are presented.

FACTORS CONTROLLING THE MECHANICAL
BEHAVIOR OF COMPOSITES

The major factors that control the mechanical behavior of the new composites are shown in Table 1. These factors, which are not significantly different in the case of inert composites, have been reported for propellants [1,2,3] and explosives [4].

TABLE 1. Factors Controlling Mechanical Behavior.

Polyol	Fillers	Isocyanate Curative
Flexibility and structure of backbone	Binder-Filler Interaction	Functionality
Equivalent Weight	Particle Size	NCO Reactivity
Functionality	Loading	
Hydroxyl Reactivity		
Internal Carbon Cross Links		

Backbone Structure and Flexibility

Of the major controlling factors in Table 1, the most critical is the backbone structure of the polyol. Polyethers are generally preferred for making elastomers because of their ability to bend and rotate. Of the various polyether polyols, polyethylene glycols are the most useful since they are

1) able to retain inert and energetic plasticizers,
2) terminated in primary hydroxyl,
3) attainable in a variety of molecular weights and functionalities,
4) high in the fraction of weight made up by load-bearing carbon and oxygen atoms,
5) chemically compatible with typical fillers.

Other polyethers, some of which are liquids such as polypropylene glycol (PPG), polytetramethylene glycol (PTMG), and butylene glycol (BG), are incompatible with inert and energetic plasticizers. PPG and BG have secondary hydroxyl groups which react more slowly and less completely than primary hydroxyls. It is more difficult to attain toughness with these glycols than with polyalkylene oxide (PAO) and polyethylene glycol (PEG).

Polyol Equivalent Weight

Equivalent weight determines the length of the flexible segments existing between cross-links or urethanes. In the relaxed state, the flexible segments may form coils. Upon extension, the flexible segment uncoils and then ruptures. The length of the coiled segments limits the extension that can be achieved prior to rupture.

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Polyol functionality has a dominant effect on the area under the stress-strain curve (Figure 1). Difunctional PEG compositions display a slowly rising area as chain length, measured by skeletal or backbone atoms, increases. In the case of PEG, there are two carbons and one oxygen, or three skeletal atoms per mer unit. As these are increased, elongation at rupture increases modestly while stress decreases because of the continuing decrease in cross-link density. Compositions containing F3 and F4 polyols are much tougher and exhibit a greater dependence on skeletal atoms. At these functionalities, a given chain length is more effective because the quaternary and tertiary carbon cross-links in F3 and F4 polyols are more efficient than those containing urethanes. Urethane linkages may be relatively fragile, since they are polar and rigid in nature, as compared to the resilient carbon cross-links in the polyol moiety. The polypropylene glycol units near the polyol central carbon atoms should enhance resilience.
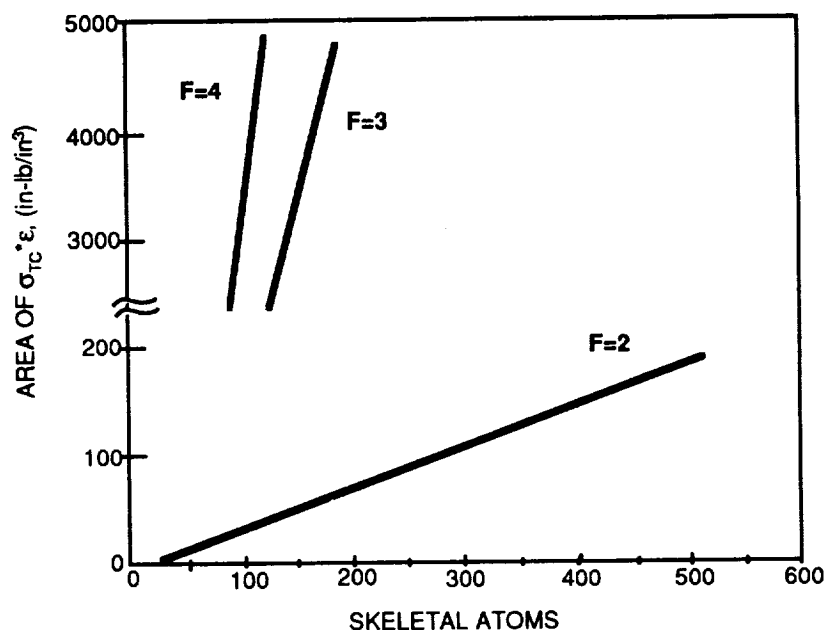

FIGURE 1. Toughness (In-lb/In³) of Gumstocks vs. Skeletal Atoms for Di-, Tri-, and Tetrafunctional Polyols.

Hydroxyl Reactivity

The relative reactivity of hydroxyl groups is instrumental in determining the polymer network structure. All hydroxyl groups should have equal reactivity so that a regular network can be formed. Furthermore, the hydroxyls should be unhindered and primary. Secondary hydroxyl groups react more slowly than primary and, perhaps, less completely, factors which may limit the molecular weight of the network.

Carbon Cross-Links

Carbon cross-links, as mentioned above, are critical in attaining a regular and fully cross-linked polymer network. Some plasticizers such as nitrate esters tend to inhibit cross-linking and, as a result, degrade molecular weight and toughness [5]. Plasticizer retention is also degraded.

Binder-Filler Interaction

The interaction of the solid fillers with the binders has a large effect on modulus, as well as on stress and strain at failure. Polyether binders have an affinity for polar solids. Solids that have a strong affinity for binders are generally not desirable because they reduce elongation, probably by preventing the formation of coiled flexible segments. A weak affinity of the hard urethane linkages for the solid may be desirable to reduce the tendency of the binder to pull away from the solids (dewetting) when the composite undergoes tensile stress. Binders with no affinity for the solids undergo early irreversible dewetting and tend to exhibit poor strain values.

Particle Size and Solids Loading

The particle diameter of the fillers has a dramatic effect on the mechanical properties. As the particle diameter is increased beyond 5-10 μm, the stress values decrease rapidly as the average distance between particles is increased. Elongation is degraded, but to a lesser extent.

As the content of solids increases, the modulus and stress typically increase while strain decreases. Higher levels of solids require that a distribution of particle sizes be used to enhance the packing fraction. The presence of coarser particles tends to degrade mechanical properties. In modern tough propellants the use of energetic plasticizers allows the solids to be reduced so that all fillers can be ≥ 10 μm.

Isocyanate Functionality and Reactivity

The isocyanate curative greatly influences the cross-link density and molecular weight of the polymer network. Energetic compositions containing nitrate esters are known to inhibit the formation of cross-links and thus reduce cross-linking density. As a result, comparatively higher functionality isocyanates (F3 and F4) are required to attain an adequate cross-link density equivalent to that of inert or non-nitrate-ester-containing compositions. Since the carbon cross-links existing in the F3 and F4 polyols are very likely more robust and flexible, it is advantageous to maximize carbon cross-links relative to isocyanate cross-links so that both stress and elongation can be enhanced. Therefore, difunctional isocyanates such as hexamethylene diisocyanate (HDI) are preferred in inert compositions containing a tetrafunctional binder. This allows the isocyanate to act as a chain extender, while all the cross-links are a result of the PAO quaternary carbon.

Equal reactivity of the NCO groups contributes to the formation of regular, high molecular weight polymer networks, enhancing toughness.

PLASTICIZERS, THEIR EFFECTS, AND INTERACTIONS WITH POLYOLS

In addition to polymer structure, another factor that affects toughness in urethane compositions is the plasticizer type and content.

Liquids that are nonvolatile and soluble in polymeric binders have been widely used to plasticize binders in castable energetic materials. Some of the effects of plasticizers on the properties of propellant binders have been discussed by Oberth [1]. Plasticizers generally enhance the following properties:

- processibility,
- low temperature mechanical properties,

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- energy,
- toughness,
- insensitivity.

Plasticizers increase the mobility of the polymer backbone in the polyol (in the case of polyurethane binders) and, therefore, decrease viscosity and generally enhance processibility of propellants and explosives. Carboxylated polybutadienes tend to be viscous because of the association of the carboxyl groups, a problem that is overcome with plasticizers. Plasticizers also increase the mobility of the backbone between cross-links in cured propellants so that the tendency to form crystallites or glassy regions at low temperatures is reduced. For example hydrocarbon esters are added to propellants containing polybutadiene binders to improve elongation at -65°F. An ester such as isodecyl pelargonate tends to dissolve the glassy polybutadiene polymers at low temperatures, thus lowering their melting range and allowing them to retain a rubbery matrix. While polybutadiene binders use modest levels of plasticizers (Pl/Po of $\leq$ 0.2), modern binders such as PEG and PAO are waxes and have to be dissolved in plasticizers to attain a processible propellant slurry. High molecular weight binders tend to be higher in viscosity and may require additional plasticizer (i.e., Pl/Po $\geq$ 3).

Plasticizers are often used to increase energy, particularly in propellants having a PEG binder. Energetic nitrate ester plasticizers increase binder energy, as the inert polymer is being replaced. Conventional PEG polyols (F2) limit the Pl/Po to about 3 due to exudation at reduced temperatures. In addition, the tensile stress at failure is decreased to unacceptable stresses, as plasticizer is increased beyond a Pl/Po of 3.5. Energetic plasticizers are especially advantageous in modern high energy propellants because they increase binder energy and allow the solids levels to be reduced. As solids are reduced, it is possible to reduce their average particle size, while maintaining processibility. In the absence of coarse particles, toughness can be achieved if tri- and tetrafunctional polyols having a chain length of 4500 daltons or more are used to form the polyurethane binder.

Tri- and tetrafunctional binders that are comparatively high in molecular weight ($\geq$ 18,000 daltons) have been found to retain high levels of plasticizer (Pl/Po $\geq$ 10) while maintaining toughness [6]. At a Pl/Po of 5 or 6, they have exhibited elongations of 900% when pulled to failure. Compositions containing energetic plasticizer and fine solids such as cyclotetramethylenetetranitramine (HMX) exhibit high tensile stress at failure and high elongation. Past work has shown that F3 and F4 polyols such as polyethers, PAO, and polycaprolactones (PCP) form tough compositions retaining high levels of plasticizer [7] (Table 2). Polyols having large pendant groups such as the oxetanes exhibit somewhat less toughness, an effect that may be due to the internal plasticization contributed by the pendant group. In addition, the pendant group effectively reduces the load-bearing atoms between cross-links. Toughness appears to decrease as the length of the segments between cross-links is reduced [2,7].

TABLE 2. Polyol Properties.

Binder (Polyols)	Molecular Weight	Functionality	Load-Bearing Atoms**	Source
PAO 24-17*	21,000	3	474	BASF
PCP-1	21,000	3	427	UCC
PAO 24-13	18,000	4	315	BASF
PCP-2	25,000	4	381	UCC
PEG E-4500***	4,500	2	306	DOW

* A polypropylene glycol, polyethylene glycol copolymer.
** Load-bearing carbon and oxygen atoms (skeletal) between cross-links.
*** PEG E-4500 is a conventional binder widely used in modern propellants.

More recently, the tetrafunctional polyol PAO 24-13 (Table 2) has been found to be superior to its trifunctional analog in plasticizer retention and toughness [2,8,9]. The formation and structure of PAO 24-13 is given in Figure 2. PAO 24-13 has been used for most of the work at China Lake because of such factors as cost, availability, and superior toughness as compared to multifunctional PCP and BAMO/NMMO polyols.
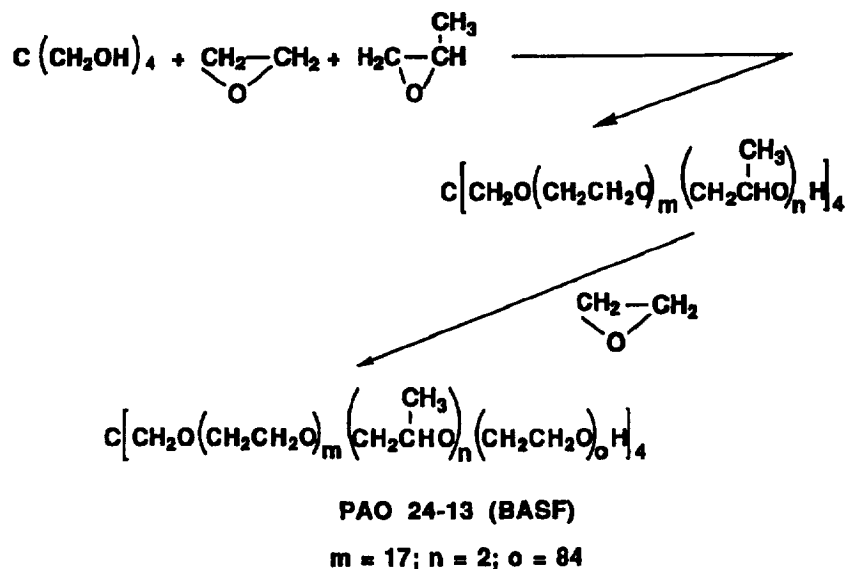
$$C\left(CH_2OH\right)_4 \; + \; CH_2\!\!-\!\!CH_2 \; + \; H_2C\!\!-\!\!\underset{O}{CH}^{CH_3} \longrightarrow$$

$$C\left[CH_2O\left(CH_2CH_2O\right)_m\left(CH_2\overset{CH_3}{CHO}\right)_n H\right]_4$$

$$CH_2\!\!-\!\!CH_2$$

$$C\left[CH_2O\left(CH_2CH_2O\right)_m\left(CH_2\overset{CH_3}{CHO}\right)_n\left(CH_2CH_2O\right)_o H\right]_4$$

PAO 24-13 (BASF)

m = 17; n = 2; o = 84

FIGURE 2. Formation of PAO.

The mechanical properties of energetic compositions containing the PAO 24-13 polyol are markedly superior to those of corresponding formulations containing the conventional PEG 4500, a polyol that is widely used in high energy, Class 1.1, high elongation propellants. The superiority of PAO 24-13 may be due to several factors including: 1) increased functionality (F4), 2) a favorable relationship of cross-link density to chain length, 3) enhancement of cross-link density by the tertiary carbon at the center of the PAO, 4) the relatively long chain lengths between cross-links, and 5) the ability of the plasticized chains to freely bend and rotate due to the ether linkages.

Plasticized compositions containing the difunctional PEG 4500 (4500 daltons) tend to have values of tensile stress at failure and elongations that are one-half or less than those of corresponding PAO compositions. Such properties are the result of incomplete cross-linking and a partially formed polymer network. Chi and Hartman have reported that cross-link density of PEG/NG gumstocks decrease markedly as a Pl/Po of $\geq$ 3 is reached [5]. This lack of regularity in the polymer network tends to degrade mechanical properties.

This problem is in large part overcome by the use of tetrafunctional PAO polyols having quaternary carbon atoms which act as cross-links. Another factor in determining toughness is the length of the polyether segments between cross-links. In the relaxed state, segments between cross-links tend to form coils. As the elastomer is extended, the polyether is uncoiled easily so that stress increases slowly as strain increases. Continued elongation brings the chains closer together so that interaction between urethane cross-links or chains can occur, and, as a result, the stress rises increasingly with additional strain (Figure 3).
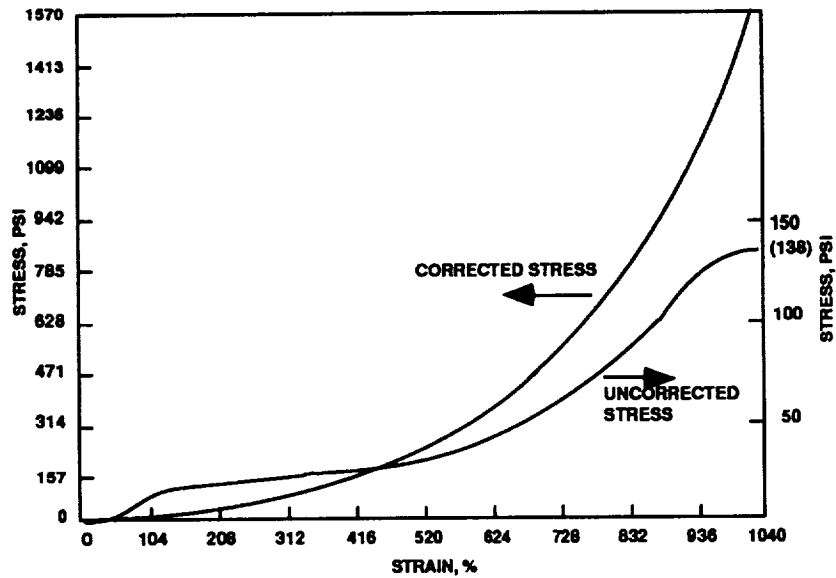
FIGURE 3. Typical Stress-Strain Curve for PAO 24-17 (F3) / BTTN (Pi/Po = 3) HMX Composition.

The mechanical properties of PAO compositions are different from those of many inert and energetic composites. When dog bones are pulled, PAO compositions show a typical rubber expansion in that the stress is increasing as extension increases. Volume expansion on dilatation (Figure 4) is relatively small and appears reversible. Typical compositions containing PEG 4500 show a decreasing stress as extension increases and exhibit much greater volume expansion. The dilatation is not reversible upon relaxation. Thus indicating that chemical bonds in the binder are being broken even early is the extension. PAO composites tend to be more fully cross-linked to form a higher molecular weight network able to take up energy without bond breaking.
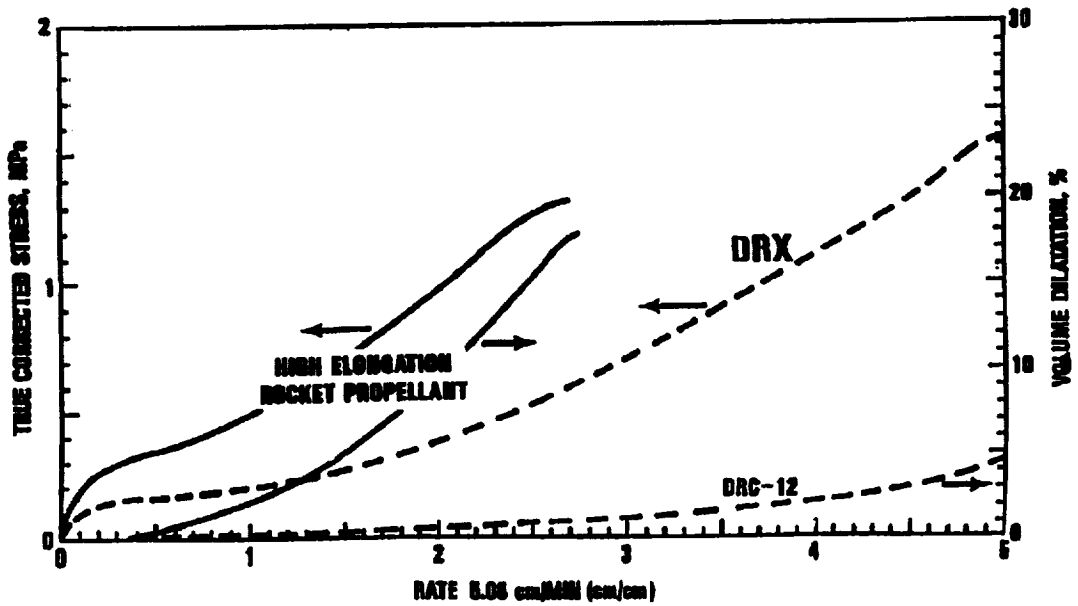

FIGURE 4. Mechanical Damage Behavior.

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The properties of plasticizer retention are superior in propellants containing PAO 24-13 because of the tetrafunctionality and the formation of a more complete cross-linked network as compared to corresponding formulations having PEG 4500 binder. Plasticizer-to-polymer ratios of 5 to 6 can be achieved in compositions having excellent toughness; ratios from 6 to 10 do not exude, but toughness decreases because of a decrease in tensile stress at failure.

Generally propellants having PEG 4500 are limited to a Pl/Po of about 3 because of exudation.

Sensitivity is directly related to solids loading, particle size, and toughness. The addition of energy to the binder by adding energetic plasticizers while reducing solids is, in effect, transferring energy from the crystalline phase to that of the rubbery binder matrix. By reducing the solids level and particle size, the tendency to form hot spots as a result of crystal fracture is minimized, and sensitivity is reduced. Additionally, binder toughness plays a large role in protecting crystalline solids from damage by absorbing energy of physical stimuli. As a result, higher plasticizer levels and tougher binder systems should, in theory, minimize sensitivity.

EXPERIMENTAL STUDY USING NMR

In recent years, solid-state nuclear magnetic resonance (NMR) spectroscopy has become increasingly important in the study of polymer phase structure, molecular dynamics, and blend miscibility [10-14]. Two sets of experiments were conducted to investigate the effects of Pl/Po variations.

A series of cured gumstock compositions were made in which the ratio of polymer (PAO 24-13) to plasticizer (1,2,4-butanetriol trinitrate (BTTN)) was varied from 0.5 to 6.0. N-100, the biuret trimer of hexamethylene diisocyanate, was used as the curing agent.

^{13}C Magic-Angle Spinning (MAS) nuclear magnetic resonance (NMR) spectra were obtained for the compositions. Representative spectra are shown in Figure 5, and chemical shift values for the series are given in Table 3. It is clear from comparing the two spectra that the resonance at ~70 ppm may be assigned to the PAO. The four remaining resonances arise from the BTTN. The changes in chemical shift, as one goes down any column of the table, are comparatively small from the standpoint of solid-state NMR which supports the view of the plasticizer (BTTN) as an extender that does not react with the PAO.
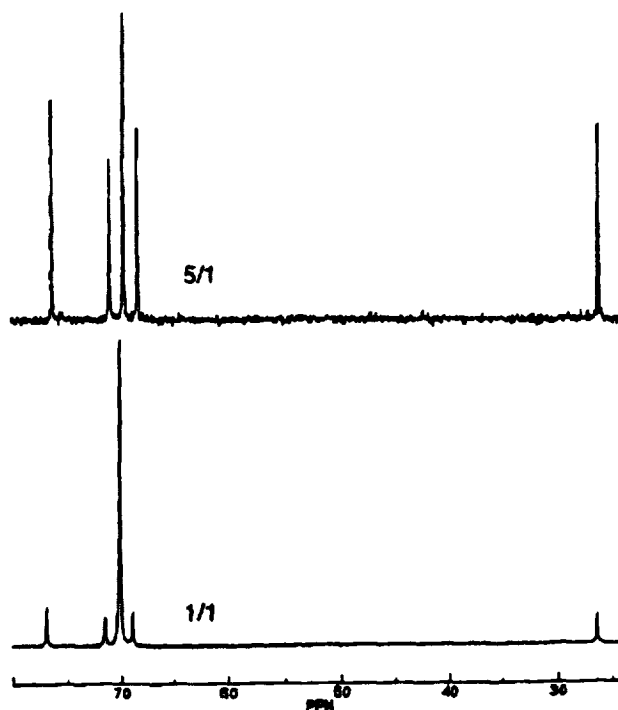
FIGURE 5. ^{13}C MAS NMR for 5/1 and 1/1 BTTN/PAO Composition Cured Gumstocks. For both spectra, the largest resonance line represents the PAO and the four remaining lines arise from the BTTN.

TABLE 3. Solid-State ^{13}C NMR Chemical Shifts.

Sample	[13]C Chemical Shift [a]				
PAO			70.0		
GS-0.5	76.8	71.4	69.9	68.9	26.1
GS-1	76.9	71.4	70.1	68.9	26.3
GS-2	76.7	71.3	70.0	68.7	26.3
GS-3	76.5	71.1	69.9	68.6	26.2
GS-4	76.4	71.0	69.8	68.4	26.2
GS-5	76.3	70.9	69.7	68.4	26.1
GS-6	76.3	70.9	69.7	68.3	26.1

[a] Referenced to TMS, ± 0.1 ppm.

Due to the high levels of plasticizer being evaluated, there was a question on whether some of the relatively volatile BTTN would be driven off during processing. This question was resolved by quantitative evaluation of the MAS NMR spectra. In Figure 5, the BTTN resonances are proportionately larger in the 5/1 sample than the 1/1 sample. Figure 6 shows the plasticizer content as determined by MAS NMR plotted against the calculated plasticizer content for the compositions. This figure indicates that there is no loss in plasticizer during processing or cure.
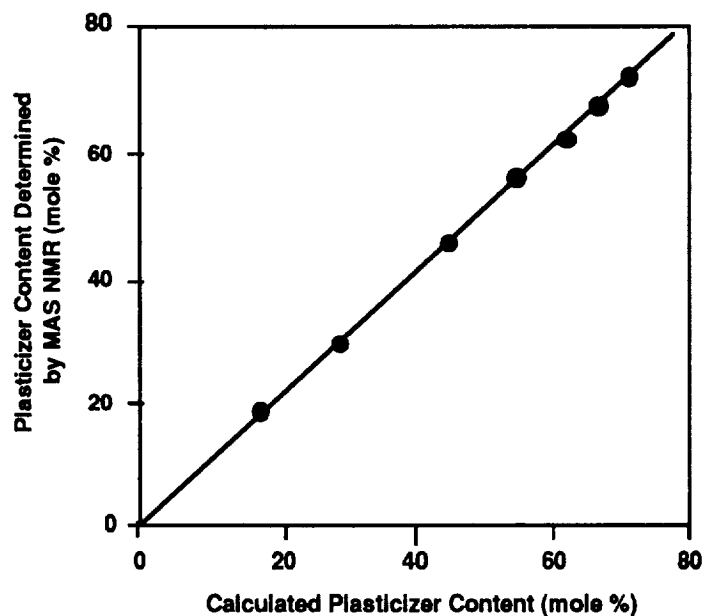
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FIGURE 6. Verification of the Plasticizer Content of the Cured Gumstocks by Solid-State MAS NMR. The linear relationship indicates that no plasticizer is lost during gumstock processing.

The solid-state ^{13}C NMR spin-lattice relaxation times (T_1) were also determined for the cured gumstock compositions. For ^{13}C, the T_1 value is generally site-specific within a molecule, and may be seen to reflect the degree of megahertz frequency motions at that particular site. The spin-lattice relaxation results are given in Table 4. The 69.7 ppm column represents the relaxation of the PAO line, while the remaining columns contain data for the four BTTN resonances.

Two main conclusions may be drawn from the relaxation study. First of all, in comparison with the pure PAO relaxation time of 184 ms, the T_1 value of 147 ms for the PAO resonance of the GS-0.5 composition is significantly reduced, with no subsequent systematic change. The initial drop in T_1 may be seen to result from the plasticizer "breaking up" or extending the PAO. From that point onward, the unchanging T_1 suggests that the PAO portion of the polymer does not undergo any significant change in its internal mobility or motion. This would further imply that subsequent macroscopic flexibility arises solely from the increased BTTN content. The picture is one of relatively rigid subunits (PAO) dispersed in a soft/rubbery matrix. Increasing the amount of matrix only increases the distance between subunits and does not affect the internal motion or mobility of the subunits.

Secondly, the ^{13}C T_1 values for the BTTN resonances all increase monotonically with increasing BTTN content (Figure 7). The fact of increasing T_1 correlated with an increasing macroscopic mobility (a softer and more rubbery overall consistency) suggests that these materials have already reached what in NMR is called the fast exchange regime, an increasing degree of microscopic mobility with correlation times faster than 1×10^{-9} s. The results indicate that the BTTN component of these systems is highly mobile and that this mobility increases proportionally with BTTN content.

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TABLE 4. ^{13}C Spin Lattice Relaxation Times.

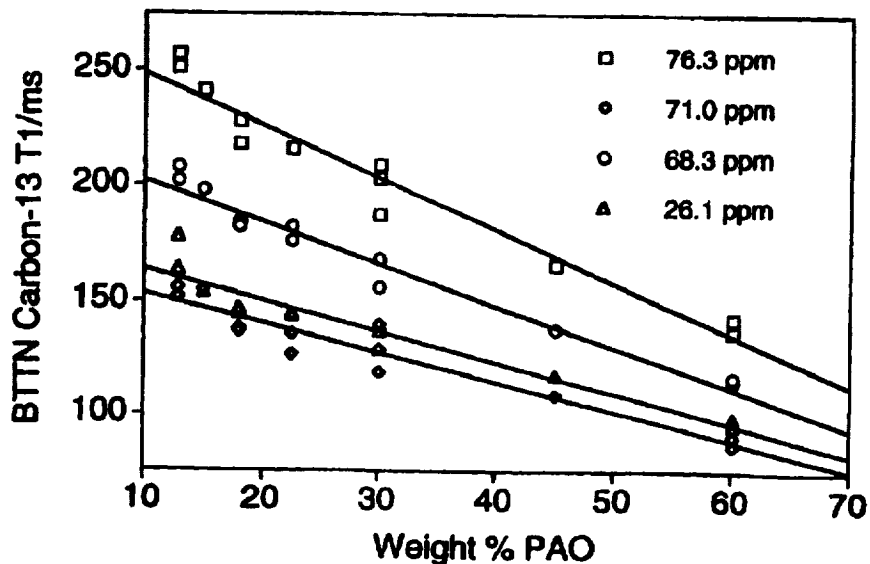| Sample	^{13}C T$_1$/ms				
δ/ppm	76.3	71.0	69.7	68.3	26.1
PAO			184		
GS-0.5	137	91	147	115	99
GS-0.5	143	87	147	117	96
GS-1	166	109	151	138	118
GS-2	203	129	155	156	140
GS-2	187	119	144	156	129
GS-2	209	140	159	168	137
GS-3	216	127	142	176	144
GS-3	216	136	156	182	145
GS-4	218	138	142	184	145
GS-4	228	137	146	182	147
GS-5	241	155	154	198	154
GS-6	251	152	154	202	164
GS-6	257	156	155	108	178
Slope	-2.2	-1.2		-1.8	-1.3
Intercept	271	166		220.8	178.4
Correlation	0.97	0.95		0.98	0.96

FIGURE 7. Plot of the ^{13}C Spin Lattice Relaxation Time (T$_1$) for BTTN as a Function of PAO Content in the Gumstock.

In the second experiment, several compositions consisting of 40% binder (analogous to the gumstock compositions in the first experiment) and 60% HMX (~10 μm) and were also examined. Plasticizer-to-polymer ratios were varied from 0.5 to 6.0 as in the first experiment.

As noted, the T_1 results discussed above reflect molecular mobility on the MHz time scale. However, motions on a slower time scale can be a particularly sensitive indicator of the phase structure of polymers. One method to access such information is through the solid-state NMR experiment referred to a cross-polarization (CP). The magnetization transfer process responsible for CP is sensitive to, among other factors, distance, and the presence of motion in the solid system. The CP transfer process is most efficient for rigid systems in close proximity.

Figure 8 shows the cross-polarization spectra for two of the filled compositions with Pl/Po of 3/1 and 5/1. As is clearly evident, the spectrum of the 3/1 material exhibits the PAO and BTTN resonances expected, as well as a broad resonance arising from the HMX. In the spectrum of the 5/1 material, however, the BTTN resonances have disappeared and the intensity of the PAO resonance has been significantly reduced in comparison to the 3/1 spectrum and to the intensity of the HMX resonance. Remembering that these are CP spectra, it is evident that, in the 3/1 spectrum, the magnetization transfer process responsible for CP is active. Even though the T_1 results indicate that the PAO is extended, this result shows that, to the point of the 3/1 BTTN/PAO ratio, there is still some degree of ordering in the polymer network. This ordering may be envisioned as folding or overlapping of the cross-linked PAO lattice. At 5/1, however, any residual order has been completely lost. The BTTN is now completely mobile on the kHz time scale and cross-polarization to it is no longer possible. The fact that the intensity of the PAO resonance has been significantly reduced also reflects significantly decreased order and increased mobility for the PAO. This threshold or break-point at the 5/1 BTTN/PAO ratio is believed to represent the optimum plasticizer level for this system in terms of producing an elastomeric binder. At 5/1, the system has been fully plasticized, as is shown by the complete loss of the BTTN resonances. Plasticization beyond this point should have little further effect on the ordering of the polymer network.

It is known that other factors influence plasticizer retention levels such as the type and ratio of curative in the composition, functionality of the polymer, chain length between cross-links, surface area of solids (affected by particle size and solids loading), and type of solids. Therefore, it is likely that threshold Pl/Po levels would be altered by varying the compositions. The CP method of determining threshold plasticizer levels of composites would be a valuable formulation tool. Studies should be made to demonstrate the effect of formulation variations on threshold plasticizer levels and correlate these to optimum mechanical properties.

COMPOSITIONS AND PROPERTIES OF HIGHLY PLASTICIZED FORMULATIONS

Recently, tough compositions have been prepared with high plasticizer-to-polymer ratios. A Pl/Po of 5.0 was selected to enhance the energy as well as the mechanical properties of a composition containing PAO binder, BTTN plasticizer, HMX, and Al. A series of compositions were developed ranging in solids from 65% to 75% (Table 5). HMX of variable particle sizes was selected as the energetic filler for its high energy density, processibility, and good mechanical properties. Some compositions contained 10% aluminum (H-5).
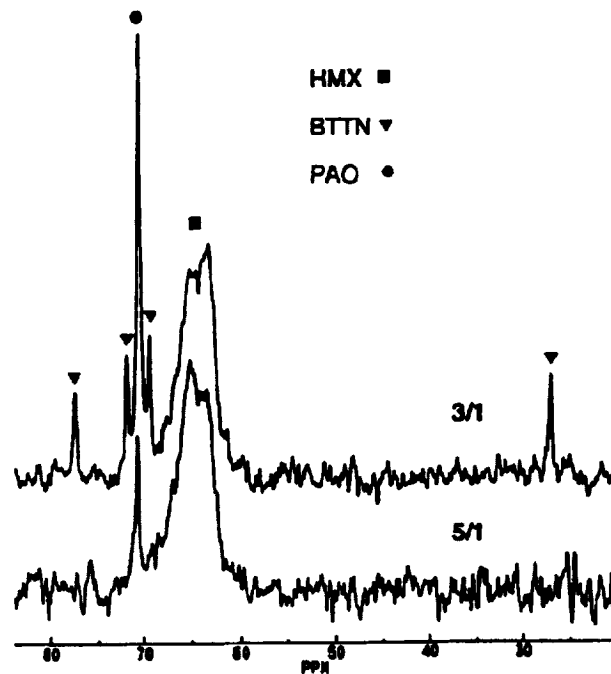
FIGURE 8. ¹³C Cross-Polarization MAS NMR Spectra
of Formulations Containing 60 weight % HMX and 40
weight % BTTN/PAO Binder for BTTN/PAO Ratios of
3/1 and 5/1. The resonances arising from HMX,
BTTN, and PAO are marked. Note the
disappearance of the BTTN resonances
at the higher BTTN/PAO ratio.

TABLE 5. Formulations.

Ingredient	Formulation				
	PBX 1	PBX 2	PBX 3	PBX 4	PBX 5
Binder/curative	5.543	5.543	3.957	3.166	3.957
BTTN	29.167	29.167	20.833	16.667	20.833
MNA	0.291	0.291	0.210	0.167	0.210
HMX (6, 12, 57 μm)	65.000	55.000	65.000	70.000	75.000
Aluminum (H-5)	--	10.000	10.000	10.000	--
Pl/Po	5	5	5	5	5

The mechanical properties of these compositions exhibited high tensile stresses between 150 and 180 psi at failure, and elongations from 400 to >1000% (Table 6). PBX 2 filled with all fine solids (< 10 μm) exhibited the highest degree of toughness with a stress of 180 psi and elongation of 970%. As both particle size and solids level increased, the mechanical properties worsened. While strain values were still respectably high, stress values degraded, reducing toughness. These compositions are extremely flexible with a bend radius of < 1/4 inch (in a 0.3-inch cylindrical rope-like configuration).

TABLE 6. Mechanical Properties.

Property	Formulation				
	PBX 1	PBX 2	PBX 3	PBX 4	PBX 5
Packing fraction	0.639	0.640	0.769	0.768	0.750
EOMV, kP/°F	5.0/120	9.5/116	2-4/123	13.5/124	7.5/121
Modulus, psi	58*	9*	74	118	134
Stress, psi	107	180	46	26	39
Strain, %	1019	970	695	541	740

* Result is uncorrected.

Mechanical properties over a range of operating temperatures were evaluated for three of the compositions (Table 7). Strain values, optimum at ambient temperatures, were still remarkably high at 25°F and even 120°F. As expected, stress values were higher at 25°F and decreased as temperature increased. Even at elevated temperatures, PBX 2 retained its toughness.

TABLE 7. Mechanical Properties of Three Selected Formulations Over a Range of Operating Temperatures.

Property	Formulation		
	PBX 2	PBX 3	PBX 5
Modulus, psi			
25°F	165	319	211
77°F	151	161	243
120°F	161	241	248
Stress, psi			
25°F	235	87	85
77°F	180	46	39
120°F	99	33	25
Strain, %			
25°F	644	455	593
77°F	970	695	740
120°F	614	282	339

In addition, high rate mechanical properties were evaluated (Table 8). Typically, low rate mechanical properties are evaluated at an extension rate of 2 in/min; high rate mechanical properties are evaluated at rates from 10,000 in/min up to and exceeding 60,000 in/min. Generally, mechanical properties at high rates are half or less than those obtained at low rate for the same composition. However, PBX compositions, evaluated at an extension rate of 16,524 in/min, demonstrated strain values greater than half their low rate values, and stress values were virtually unchanged.

TABLE 8. High Rate Mechanical Properties.

Property	Formulation		
	PBX 2	PBX 3	PBX 5
E_0, psi	619	463	538
σ_m, psi	171	31	51
ε_b, %	506	344	420
Work/toughness, in-lb/in^3	419	73	127

Using a high-molecular-weight, high-functionality polymer (PAO 24-13) and a Pl/Po of 5, it is possible to attain unique compositions. With a bend radius of < 1/4 inch, these compositions are flexible, tough (both over a wide range of temperature and extension rates), and exhibit superior performance (~ 15-20% over the developmental baseline).

An inert simulant for the PBX formulation was also developed. In earlier work, an inert simulant matching the mechanical properties of a Class 1.1 high-elongation propellant was prepared and characterized [15]. The objective was to simulate the mechanical properties as well as the density of the PBX formulation. The challenge was to maintain the density of each of the formulation ingredients and the overall density of the composition, as well as the volume % of binder. (In order to simulate mechanical properties it is important to maintain the same volume % of binder in the simulant formulation as in the live one.) Initial inert simulant formulations targeted the PBX 2 composition. Dimethyl phthalate (DMP) (density 1.1 g/cm^3) and a dense (1.9 g/cm^3) mixture of brominated diphenyl ether and aryl phosphate esters (DE 60F and DE 62) were blended to achieve the density of BTTN (1.52 g/cm^3) and used with PAO 24-13 as the binder. Dechlorane Plus, a chlorinated tricyclic hydrocarbon flame retardant (1.82 g/cm^3) was used as the inert filler to replace HMX (1.9 g/cm^3). Aluminum levels were increased slightly to adjust for the lower density of Dechlorane Plus.

A series of compositions were evaluated varying plasticizers (DE 60F vs. DE 62) and curatives (N-100 vs. HDI) (Table 9). The compositions using HDI (IPBX 3 and 4) as a curative exhibited superior mechanical properties (Table 10) compared to those made with N-100 (IPBX 1 and 2). Nitrate esters used in live formulations require high levels of isocyanate (F3 to F4) to achieve an optimal cross-link density. Inert plasticizers do not exhibit this cure-inhibiting effect and, as a result, do not require high functionality isocyanates at increased levels to achieve optimal cures. Since the properties of IPBX 3 and IPBX 4 were virtually equivalent, IPBX 3 was selected for further development because of the enhanced aging characteristics expected with DE 62 (a cleaner version of DE 60F with respect to acid content). Table 11 compares the mechanical properties of PBX 2 to those of IPBX 3 at both low and high extension rates. The strain values at high loading rates are high, but, otherwise, the properties of the inert simulant closely reflect those of the live PBX 2. Some inert simulant compositions have exhibited high rate strain values in excess of 2000% and low rate strains in excess of 1000%. These results have been observed after varying cure catalyst and temperature profiles.

TABLE 9. Inert Simulant Formulations.

Ingredient	Formulation			
	IPBX 1	IPBX 2	IPBX 3	IPBX 4
PAO 24-13	5.482	5.482	5.663	5.663
N-100	0.326	0.326	--	--
HDI	--	--	0.145	0.145
DMP	15.838	15.838	15.838	15.838
DE 62	13.329	--	13.329	--
DE 60F	--	13.329	--	13.329
Aluminum H-5	15.000	15.000	15.000	15.000
Dechlorane 515	50.000	50.000	50.000	50.000
TPB	0.015	0.015	0.015	0.015
DNSA	0.010	0.010	0.010	0.010

TABLE 10. Properties of Inert Formulations.

Property	Formulation			
	IPBX 1	IPBX 2	IPBX 3	IPBX 4
EOMV, kP/°F	5.0/121	3.5/123	4.4/122	4.2/123
E_o, psi	168	127	115	134
σ_m, psi	48	47	126	138
ε_m, %	260	377	876	884
ε_b, %	273	377	884	885

TABLE 11. Comparison of Mechanical Properties.

Property	Formulation			
	PBX 2	IPBX 3	PBX 2 (HR)	IPBX 3 (HR)
E_o, psi	151	115	619	324
σ, psi	180	126	171	132
ε, %	970	884	506	940

DISCUSSION

Liquids that can be cured to form elastomers have an inherent ability to bond to fillers and to substrates since they are composed of relatively small molecules that are able to penetrate into the surface microstructure of solids to a degree not possible for the macromolecules contained in many latices. In situ polymerization of polyols occurring in the microsurface tends to enhance the polymer-filler adhesion. The polar nature of the urethane groups tends to enhance bonding to many substrates. The urethane group is similar to the amide linkage in proteins, one which is well known to bond tenaciously to polar substrates. Unfortunately, proteins tend to have amide units that are not separated by long flexible segments. Hence, they have little elasticity. Further, even synthetic amides are not conveniently formed by the curing of liquids at ambient temperature.

The rate of curing to form polyurethane rubbers can be varied widely (minutes to days) by the choice and amount of cure catalyst, as well as the cure temperature. Triphenylbismuth and acidic activators can be used to achieve pot lives of 1-3 days. Ferric acetonyl acetate can affect curing in a few minutes. Small amounts of dibutyltin dilaurate may take 4 to 8 hours to gel, where larger concentrations can cause curing within 10 minutes. Curing can be accomplished at temperatures from ambient to 70°C.

Filled urethanes made from the tri- and tetrafunctional PAO polyols tend to show relatively little increase in volume when extended. The volume dilatation appears reversible and largely disappears when extended samples are relaxed. Generally filled polyurethanes using the conventional binder PEG 4500 show much greater dilatation upon extension, much of which is not reversible, and is, therefore, evidence of the rupture of the polymer chains. It is likely that the more robust nature of the PAO is due to the formation of a more completely cross-linked network higher in molecular weight. The quaternary carbon cross-links in the PAO may be more resilient than the more rigid and polar urethane. There are about 3% of propylene glycol polyether groups near the center of the PAO, which should enhance the flexibility of this region of the polymer.

These characteristics allow the composites to repeatedly stretch without causing much damage to the polymer. The existence of a relatively large high-molecular network allows the stress to be dissipated over a large volume to minimize rupture of the polymer. Samples that are cut 25% of the distance through a dog bone also show comparatively little loss in elongation and tensile stress at failure. Thus, these samples display unusual toughness.

Urethanes can be made by simple processing techniques which do not require high pressures or elevated temperatures. Curing times can be varied widely and are easily reproduced. Mechanical properties can be tailored for a variety of applications making urethanes uniquely advantageous as liquid curable elastomers an resins.

APPLICATIONS OF LIQUID CURED ELASTOMERS

Liquid mixtures capable of being cured to yield tough elastomers are potentially useful in a variety of applications including coatings, caulking compounds, potting liquids, adhesives, and cast parts with intricate shapes.

Adherent coatings with hydroxyl terminated polyethers and polyesters can be formed without the presence of volatile solvents. Volatile solvents are not desirable since voids or microporosity can be introduced when the solvents evaporate. Nonvolatile isocyanates such as polyols capped with isocyanates, which are relatively non toxic, can be used.

In addition, these liquid curable elastomers have some potential application in the fabrication of bladders, gloves, and condoms. When these products are made from rubber latices, small holes tend to form occasionally where the coagulation of the rubber particles is interrupted by solid impurities. The liquid curable plasticized urethanes are single-phase and contain no volatile substances, therefore no voids or holes would be created. As polymerization occurs there is essentially no shrinkage or exotherm because of the relatively high molecular weight of the polyol (~18,000 daltons).

Since the polyols are dissolved in a plasticizer to form these compositions, a variety of solid ingredients such as medicinals or antiseptics can be added by dissolving them in the liquid binder solution.

NOMENCLATURE

BAMO/NMMO	copolymer of poly-3,3-bis(azidomethyl)oxetane and 3-nitrato-3-methyl methyloxetane
BG	butylene glycol
BTTN	butanetriol trinitrate
CP	cross-polarization
DE 60F	brominated diphenyl ether
DE 62	aryl phosphate ester
DMP	dimethyl phthalate
DNSA	3,5-dinitrosalicylic acid
EOMV	end-of-mix viscosity
F	functionality
HDI	hexamethylene diisocyanate
HMX	cyclotetramethylenetetranitramine
HR	high rate
kP	kilopoise
MAS	Magic-Angle Spinning
MNA	n-methyl-p-nitroaniline
N-100	Desmodur multiisocyante curative (Mobay Chemical Company)
NCO/OH	ratio of isocyanate and hydroxyl
NG	nitroglycerine

NMR	nuclear magnetic resonance
PAO	polyalkylene oxide
PCP	polycaprolactone polymer
PEG	polyethylene glycol
Pl/Po	plasticizer-to-polymer ratio
PPG	polypropylene glycol
ppm	parts per million
PTMG	polytetramethylene glycol
T_1	spin-lattice relaxation times
TMS	tetramethylsilane, an NMR standard
TPB	triphenyl bismuth
UCC	Union Carbide Corp.

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