27
2/14/78
25 DUT LC
SAND77-0822
UNLIMITED RELEASE

MASTER

3151

DEVELOPMENT OF A STRUCTURE-PROPERTY CORRELATION FOR CASTABLE URETHANE ELASTOMERS

Robert R. Lagasse

Prepared by Sandia Laboratories, Albuquerque,
New Mexico 87115 and Livermore, California 94500
for the United States Department of Energy under
Contract AT (29-1)-789.

January 1978

Sandia Laboratories

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Issued by Sandia Laboratories, operated for the United States
Department of Energy by Sandia Corporation.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Printed in the United States of America

Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

Price: Printed Copy \$4.50; Microfiche \$3.00

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

SAND77-0822
Unlimited Release

Development of a Structure-Property Correlation
for Castable Urethane Elastomers

R. R. Lagasse
Polymer Research and Development Division 5813
Sandia Laboratories, Albuquerque, New Mexico 87115

Abstract

A significant problem in electronic encapsulation is the poor load bearing performance of existing replacements for Adiprene-MOCA urethane elastomer. In response to this problem, the present study defines the structural features that control the viscoelastic properties of the following liquid castable elastomers: Adiprene-MOCA, EN-7, and 3121-S. A review of previous investigations on a related class of materials suggests that viscoelastic properties may be more directly related to the physical structure or morphology of these elastomers, rather than their chemical structure. Accordingly, the morphology of the subject elastomers is characterized by means of electron microscopy and x-ray scattering measurements. These measurements reveal that within each elastomer incompatible chain segments cluster into separate domains, or microphases on a scale of 10 ± 1 nm. On this basis, it is concluded that the two major thermomechanical transitions present in each elastomer can be assigned to separate transitions within the two microphases. The above-ambient transition, which determines the upper use temperature of the elastomer, is specifically assigned to the glass transition of an amorphous microphase. The significance of this structure-property correlation for the liquid castable elastomers is twofold: (1) it

permits generalization of mechanical property measurements on existing materials in order to predict their performance in unusual applications and (2) it leads to a rational strategy for developing improved elastomers for new, more demanding applications.

Table of Contents

	<u>Page</u>
INTRODUCTION	7
The Need for Fundamental Understanding of Castable Elastomers	7
Plan of Attack	8
CRITICAL REVIEW OF PREVIOUS WORK	10
Comparison of Viscoelastic Behavior of Various Castable Urethane Elastomers	10
Brief Description of the Chemical Structure of the Urethane Elastomers	16
The Significance of Previous Work on Thermoplastic Urethane Elastomers	20
EXPERIMENTAL	22
Characterization Methods	22
Materials	22
RESULTS AND DISCUSSION	23
Characterization of the Physical Structure of the Polybutadiene Based Elastomers (EN-7 and EN-8.)	23
- Wide Angle X-Ray Diffraction	23
- Electron Microscopy	25
- Low Angle X-Ray Scattering	25
Characterization of the Physical Structure of 3121-S and Adiprene-MOCA	31
Summary of the Physical Structure of the Castable Elastomers Studied	34
The Controlling Influence of Microphase Structure on Dynamic Mechanical Properties	36

	<u>Page</u>
IMPACTS OF THIS STUDY	
Generalization of Mechanical Property Characterization	38
Strategy for Developing Improved Castable Elastomers	41
SUMMARY	43
REFERENCES	46

List of Tables

<u>Table</u>	<u>Page</u>
I Urethane Elastomers Characterized with Regard to Physical Structure	22

List of Figures

<u>Figure</u>	<u>Page</u>
1 Estimate of tensile stress relaxation at room temperature of Adiprene-MOCA and existing replacement elastomers. The Adiprene-MOCA was cured for 3 hrs. at 71°C, the EN-7 for 16 hrs. at 80°C, and the 3121-S for 48 hrs. at 25°C. (This figure is reproduced from ref. 4.)	11
2 Dynamic mechanical characterization at 0.1 Hz of existing replacement urethane elastomers. (Reproduced from ref. 6)	13
3 Dynamic mechanical characterization at 0.1 Hz of 70°C cured Adiprene-MOCA. (Reproduced from ref. 6)	14
4 Dynamic mechanical characterization at 0.1 Hz of 25°C cured Adiprene-MOCA. (Reproduced from ref. 8)	15
5 Chemical structure of the constituents of EN-7 urethane elastomer.	17
6 Schematic representation of the molecular backbone in various urethane elastomers.	18
7 Schematic representation of microphase separation known to exist in uncrosslinked thermoplastic urethane elastomers.	21
8 (a) Wide angle x-ray diffraction pattern obtained from EN-8, (b) Wide angle x-ray diffraction pattern obtained from a semicrystalline polymer [poly(vinylidene fluoride)] showing characteristic diffraction rings.	24

<u>Figure</u>		<u>Page</u>
9	Transmission electron micrographs of thin films of EN-8 elastomer: (a) unstained, (b) OsO ₄ stained	26
10	Small angle x-ray scattering patterns obtained from the two polybutadiene based elastomers under the same exposure conditions: (a) EN-8, (b) EN-7.	28
11	Microdensitometer scan on the small angle x-ray scattering pattern obtained from 80°C cured EN-7 (Fig. 10b)	30
12	Microdensitometer scan on the small angle x-ray scattering pattern obtained from 25°C cured 3121-S.	32
13	Microdensitometer scan on the small angle x-ray scattering pattern obtained from 25°C cured Adiprene-MOCA.	33
14	Wide angle x-ray diffraction pattern obtained from (a) 25°C cured 3121-S and (b) 25°C cured Adiprene-MOCA.	35

Acknowledgments

The author wishes to thank A. J. Quant (5813), C. A. Arnold and K. B. Wischmann (both 5811) for many helpful discussions concerning the chemical structure and applications of castable urethane elastomers.

INTRODUCTION

The Need for Fundamental Understanding of Castable Elastomers

Castable urethane elastomers consist of two reactive liquids that are blended together and then hardened by a curing reaction in order to encapsulate electronic assemblies, cables, and cable connectors (see, for example, ref. 1). These elastomers have found widespread use in weapon applications because of their favorable combination of high strength (tensile strength ≈ 4500 psi = 31 MPa), toughness (ultimate tensile elongation $\approx 400\%$), and stiffness (dynamic shear modulus ≈ 3000 psi = 21 MPa). For many years, the specific material of choice for such applications was Adiprene* L-100 prepolymer cured with a chlorinated aromatic diamine, 4,4'-methylene-bis-(o-chloroaniline), commonly referred to as MOCA. However, in 1973, the Occupational Safety and Health Administration (OSHA) issued a ruling that alleged MOCA to be a carcinogen. Although this ruling has been overturned in the courts, suspicions raised by the OSHA action have led to severe, safety-related restrictions on the use of MOCA as a curing agent for urethane elastomers. Thus, there has been considerable interest in finding a suitable replacement for the Adiprene-MOCA system.

A potential replacement elastomer, named EN-7,** had been developed jointly by Sandia and an outside manufacturer before the time of the OSHA ruling.² This new urethane system was unique in having a non-polar backbone of polybutadiene. This feature actually gave EN-7 far superior characteristics to Adiprene-MOCA with regard to chemical stability in a humid environment,³ sub-ambient mechanical properties,² and electrical

* Adiprene is a registered trademark of E. I. DuPont, Wilmington, Delaware.

**Conathane EN-7 is a registered trademark of Conap Inc., Olean, NY.

properties.² The main drawback of EN-7 compared to Adiprene-MOCA is relatively poor performance in load bearing or high temperature applications.⁴ It is clear therefore that while the EN-7 elastomer has some very attractive features, it cannot be considered an across-the-board substitute for Adiprene-MOCA. However, there is the possibility that the EN-7 system could be modified in such a way as to overcome its drawbacks as a structural material while maintaining its many desirable features.

It was felt that any serious effort to develop an improved urethane elastomer would first require a fundamental understanding of the structural features controlling the properties of interest in existing materials. Besides facilitating development of new castable elastomers, a fundamental understanding of existing materials could be very useful in solving problems arising in present applications. Until now, characterization of each material has consisted of compiling an extensive tabulation of its mechanical, thermal, and electrical properties. However, since a given material is used in many different and often unique applications, sometimes dozens of property tests may be inadequate to explain the behavior of the polymer in all these applications. A fundamental understanding of the material could allow us to generalize our property characterization and thereby predict its performance in unusual applications. Specific examples of such property generalizations will be presented later in this report.

Plan of Attack

Accepting the need for developing a correlation between structure and properties of castable urethane elastomers, one must consider what structural features should be examined. These can be broadly classified

into two groups: chemical structure and physical structure. The chemical, or molecular structure of a polymeric material describes the individual polymer chains by such parameters as the identity of the repeating monomer unit (e.g., poly-ethylene vs. poly-styrene), the size of the macromolecules (e.g., average molecular weight and molecular weight distribution), and the molecular architecture (e.g., linear vs. chemically crosslinked polymer chains). In contrast, the physical structure of a polymeric material describes how the macromolecular chain segments are packed together in the solid state. This physical arrangement of chain segments could include such considerations as the degree of crystallinity, the size and shape of both the crystals and crystalline superstructure, and finally the geometry of microphase separation between dissimilar chain segments. Thus, the distinction between chemical and physical structure of a polymeric material can be regarded as the difference between perceiving the constituent macromolecules as isolated, non-interacting chain segments or as strongly interacting chain segments.²⁸

The main idea put forward in this paper is that the chemical structure of a polymeric material does not uniquely control its solid state mechanical properties. Rather, it is more productive to adopt the following viewpoint. Mechanical properties are more directly related to the physical structure of the polymer, which is in turn controlled by both the chemical structure of the macromolecules and the process whereby these molecules are fabricated into a bulk polymer. (The only significant exception to the above generalization is the mechanism of rubberlike elasticity by which the chemical structure of isolated macromolecules can be directly related to mechanical properties in certain cases.)

In this report, the utility of correlating mechanical properties of polymers with their physical structure is illustrated for the case of the castable urethane elastomers. In particular, microphase separation between incompatible chain segments is shown to be crucially important in affecting the low strain viscoelastic properties of these materials. The EN-7 system is studied most intensively, but the conclusions drawn are shown to be valid for other castable elastomers, as well. Finally, on the basis of this structure-property correlation, a strategy for developing new, improved castable elastomers is proposed.

CRITICAL REVIEW OF PREVIOUS WORK

Comparison of Viscoelastic Behavior of Various Castable Urethane Elastomers

As a point of departure, the mechanical properties governing the performance of these materials in load bearing applications will be reviewed to demonstrate quantitatively the severe drawbacks of available replacements for the Adiprene-MOCA system. Figure 1 represents the estimate by Salazar and Curro⁴ of the behavior of various castable elastomers in a stress relaxation test at room temperature. This plot shows the reduction, or relaxation, in modulus of each elastomer while it is held at a fixed tensile strain of 5-10% under isothermal conditions. The room temperature modulus of the Adiprene-MOCA is estimated to decline by about 22% over a period of 2 years (10^6 minutes) in the stress relaxation test, while the modulus of the EN-7 declines by the same relative amount in less than 10 minutes. Another potential replacement elastomer, Uralite^{*} 3121-S⁵, performs better than EN-7 but still much

^{*}Uralite 3121-S is a trademark of the Hexcel Corporation, Chatsworth, California.

Figure 1 - Estimate of tensile stress relaxation at room temperature of Adiprene-MOCA and existing replacement elastomers. The Adiprene-MOCA was cured for 3 hrs. at 71°C, the EN-7 for 16 hrs. at 80°C, and the 3121-S for 48 hrs. at 25°C. (This figure is reproduced from ref. 4.)

worse than Adiprene-MOCA. It is important to note that the same visco-elastic mechanism causing stress relaxation in these elastomers would also cause creep in a constant load experiment. Thus, these stress relaxation results imply a corresponding order ranking of materials with regard to their resistance to creep at room temperature.

These differences in stress relaxation behavior between Adiprene-MOCA and existing substitute elastomers can be rationalized by considering their thermomechanical characteristics. Thermomechanical testing simply

refers to determining the change in mechanical properties of a material as its temperature is raised. In such testing, an abrupt change in properties over a relatively narrow temperature range is referred to as a thermomechanical transition. Broadly speaking, a thermomechanical transition can be caused by softening of an amorphous, non-crystalline material, in which case it is referred to as a glass transition; or the thermomechanical transition can be caused by melting of a crystalline material, in which case it is referred to as a melting transition.

In Figure 2 are plotted the results of Caruthers⁶ showing the temperature dependence of the dynamic shear modulus of the potential replacement elastomers. As a point of reference, the temperature range for weapon applications is normally -55 to +70°C. Fixing attention on the curve for EN-7, one first sees an inflection point at about -90°C indicative of a major thermomechanical transition. It is important to note that EN-7 has a second major transition centered at ~ +50°C. Shifting attention to the thermomechanical data for the other two castable elastomers (Figs. 2 and 3), one notes that the 3121-S has an upper level, above ambient transition around +100°C, while the Adiprene-MOCA has the highest upper level transition temperature, presumably > 140°C.* Thus, the performance of these elastomers in the room temperature stress relaxation test appears to improve as their upper level thermomechanical transition is shifted up in temperature. A sound, physical basis for this empirical conclusion will be developed later in this report by considering the time scale dependence of viscoelastic properties (Ref. 7, p. 344). At any rate, the

*The presence of an upper level transition in the Adiprene-MOCA system becomes directly evident when the elastomer is cured at 25°C rather than 71°C. Figure 4 shows that the room temperature cure shifts the onset of this transition down to ~ 100°C.

Figure 2 - Dynamic mechanical characterization at 0.1 Hz of existing replacement urethane elastomers. (Reproduced from ref. 6).

Figure 3 - Dynamic mechanical characterization at 0.1 Hz of 70 $^{\circ}\text{C}$ cured Adiprene-MOCA. (Reproduced from ref. 6)

Figure 4 - Dynamic mechanical characterization at 0.1 Hz of 25°C cured Adiprene-MOCA. (Reproduced from ref. 8)

preceding empirical correlation suggests that the effectiveness of these elastomers in load bearing applications is dependent on the location of an above ambient thermomechanical transition. Besides serving as an indicator of stress relaxation behavior at room temperature, the upper level thermomechanical transition is also important in controlling the upper use temperature of each elastomer. Accordingly, the first goal of this study was to determine the structural features controlling this upper level transition in the castable urethane elastomers.

Brief Description of the Chemical Structure of the Urethane Elastomers

The EN-7 system was singled out for detailed investigation for two reasons. First, as mentioned above, this material already had some excellent properties (e.g., dielectric strength, volume resistivity, and hydrolytic stability) which are very desirable for encapsulation of electronic components and cables. Thus, if we could learn how to raise the upper transition temperature of EN-7, we would have an all-around excellent material for our applications. A second reason for attempting to develop structure-property correlations for EN-7 was that its chemical structure was already quite well known, since the material had been developed in part at this laboratory.²

The chemical structure of the constituents of EN-7 is summarized in Figure 5.^{9,10} The so-called soft segments of the elastomer are based on polybutadiene having a number average molecular weight ~ 2700 and the indicated isomeric microstructure. These polybutadiene soft segments are linked together through their hydroxyl end groups (not shown) by the so-called hard segments consisting of 2,4 toluene diisocyanate reacted with a mixture of an aliphatic plus an aromatic diol. The macromolecular

POLYBUTADIENE

2,4-TOLUENE DIISOCYANATE

2-ETHYL-1,3-HEXANEDIOL

BIS(2-HYDROXYPROPYL)ANILINE

Figure 5 - Chemical structure of the constituents of EN-7 urethane elastomer.

backbone of linked soft and hard segments in EN-7 is illustrated schematically at the top of Figure 6. It should be noted that chemical

EN-7

3121-S

ADIPRENE-
MQCA

LINEAR
(THERMOPLASTIC)
URETHANE

Figure 6 - Schematic representation of the molecular backbone in various urethane elastomers.

crosslinks in the soft segment give rise to a network structure of polymer chains. These crosslinks arise because there are more than two reactive hydroxyl groups per polybutadiene molecule [average functionality = 2.3^{10}]. Figure 6 also shows that the other two castable elastomers discussed above also have a similar structure of alternating soft and hard segments, although the chemical identity of their constituents is different from that of EN-7.

The reason for depicting the chemical structure of these castable elastomers in this way is that it illustrates the analogy with the previously studied thermoplastic urethane elastomers. As shown in Figure 6, these also consist of alternating hard and soft chain segments, but they differ in two important respects. First, the thermoplastic elastomers are linear molecules having no chemical crosslinks. Figure 6 shows the difference between the uncrosslinked, linear structure of the thermoplastic elastomers and the crosslinked, network structure of the castable elastomers that are of immediate interest for encapsulation of electronic components. Perhaps a more important distinction between the chemically crosslinked and the linear segmented elastomers is the totally different processing method used in the two cases. The linear elastomers are fabricated as pre-formed macromolecules by such methods as melt processing or solvent casting, which obviously involve no polymerization reaction. On the other hand, the crosslinked elastomers are fabricated in a single curing operation combining the polymerization of liquid reactants with the organization of chain segments into the solid state morphology of the bulk polymer. Accordingly, this second distinction between the linear thermoplastic elastomers and the crosslinked elastomers used for encapsulation

might be summarized as the difference between non-reactive and reactive processing methods.

The Significance of Previous Work on Thermoplastic Urethane Elastomers

Studies documented in the open literature have shown that in the solid state the linear, uncrosslinked elastomers can be characterized by clustering of hard segments into separate microphases or domains on a scale of 10 nm, leaving the soft segments to form the continuous, or matrix phase.¹¹⁻¹⁵ This domain structure that is known to exist in the thermoplastic urethane elastomers is illustrated schematically in Figure 7. It should be noted that separation of the hard segments into individual domains does not necessarily imply ordering between the segments within each domain. This point will be illustrated in the Results section.

On the basis of these previous morphologic studies on the thermoplastic elastomers, it has become quite clear that the high strength and modulus of these materials arise from physical crosslinking or reinforcement by the hard segment domains dispersed in the soft segment matrix.¹⁶ Recent investigations¹⁷ have indicated that the cause of the microphase separation in these linear materials is the incompatibility, or resistance to intermixing, of the chemically dissimilar soft and hard segments. In general, this incompatibility between chain segments is now believed to have a much more direct effect on the structure and properties of these urethane elastomers than the purely chemical feature of hydrogen bonding between the chain segments.¹⁸ This conclusion represents a significant departure from earlier ideas.¹⁹

It should be emphasized that the previous studies referred to above were carried out exclusively on uncrosslinked, thermoplastic segmented

Figure 7 - Schematic representation of microphase separation known to exist in uncrosslinked thermoplastic urethane elastomers.

elastomers processed by non-reactive methods. Nevertheless, the presence of the same kind of alternating hard-soft segment backbone in our chemically crosslinked systems was judged to be a sound basis for suspecting that a similar microphase separation could be present in these castable urethane elastomers. Accordingly, a variety of experimental techniques were employed to characterize the physical structure, or morphology, first for the crosslinked EN-7 elastomer and later for the other two liquid castable urethane elastomers of interest.

EXPERIMENTAL

Characterization Methods

X-ray scattering patterns were obtained at both small and wide angles by means of a pinhole-collimated camera mounted on a Norelco unit which generated nickel filtered CuK_α radiation. Sample thicknesses were 1.1 mm for small angle exposures and 0.51 mm for wide angle exposures. The exposure times were varied for the different elastomers studied in order to optimize the resolution of the scattering patterns, but in one case noted below exposure conditions were kept constant to permit direct comparison between materials. The variation in optical density on the scattering patterns was quantified by scanning with an Optronics S-2000 digital microdensitometer. In addition, transmission electron micrographs were taken with a Philips EM-200 operated at an accelerating voltage of 100 kV. In all cases these characterization tests were performed on elastomer samples at room temperature.

Materials

For the x-ray characterization, bulk samples of the castable elastomers were prepared by mixing each two part system in the recommended proportions^{2,5,20} and then curing them in a steel mold.* The curing conditions are tabulated in Table I.

Table I

Urethane Elastomers Characterized with Regard to Physical Structure

<u>Material Designation</u>	<u>Cure Temperature, °C</u>	<u>Cure Time, hr.</u>
EN-7	80°C	16
EN-8	25°C	720
Adiprene-MOCA	25°C	48
3121-S	25°C	48

*The Adiprene-MOCA specimens were prepared in special OSHA-approved equipment at the Bendix Corporation, Kansas City Division.

The EN-8 elastomer listed above has exactly the same composition as EN-7 except for an increased catalyst concentration which permits the cure reaction to be carried out at room temperature. These two polybutadiene based elastomers, room temperature cured EN-8 and 80°C cured EN-7, have essentially the same mechanical properties.²¹

For the electron microscopy studies, very thin (~40 nm) films of EN-8 were prepared by a modified solvent casting technique that is fully described in a forthcoming publication.²² In short, the technique involved solvent casting a film of the two reactive components on a mercury surface, evaporating the solvent, and finally curing the resulting film at room temperature for time periods up to 47 days (940 hr.). Some of these EN-8 films were stained in the vapor above a 1 wt% aqueous solution of osmium tetroxide.

RESULTS AND DISCUSSION

Characterization of the Physical Structure of the Polybutadiene Based Elastomers (EN-7 and EN-8)

Wide Angle X-Ray Diffraction

Figure 8a shows the wide angle x-ray diffraction pattern obtained from the room temperature cured EN-8 elastomer. The diffraction pattern consists of only a single diffuse halo, rather than the sharp diffraction rings that would be obtained from a polymer having crystalline structure. [The wide angle diffraction pattern from a semicrystalline polymer, poly(vinylidene fluoride) has been included in Figure 8b for purposes of comparison.] This result verifies that no appreciable crystallinity exists within the EN-8 elastomer at room temperature. Moreover, a detailed consideration of the chemical structure of EN-8 (same as that of EN-7) leads to a consistent conclusion. That is, the polybutadiene

Figure 8 - (a) Wide angle x-ray diffraction pattern obtained from EN-8,
(b) Wide angle x-ray diffraction pattern obtained from a semicrystalline polymer [poly(vinylidene fluoride)] showing characteristic diffraction rings.

soft segment, being a random copolymer of about 20% cis, 60% trans, and 20% vinyl isomers (Fig. 5 and Ref. 10), is expected to be non-crystalline.²³ Furthermore, the presence of two different diols and the lack of symmetry in both the aliphatic diol and the diisocyanate would seem to preclude crystallinity in the hard segment.

Electron Microscopy

Examination of the EN-8 elastomer film by transmission electron microscopy indicated that a different kind of physical structure was present in this non-crystalline material. An electron micrograph of the unstained elastomer vaguely suggests a pebbly texture of high and low electron density regions, which could imply clustering of the soft segments and hard segments into separate microphases (Fig. 9a). If this texture indeed represents microphase separation of incompatible chain segments, then staining the film with osmium tetroxide should enhance the contrast in the micrograph. The reason is that this high electron density stain preferentially attaches to the double bonds in the polybutadiene soft segments.²⁴ The electron micrograph of the OsO_4 stained EN-8 shows greatly enhanced contrast and therefore strongly suggests the presence of domain structure (Fig. 9b). It should be emphasized that essentially the same micrographs were obtained when a different solvent and when a different surface was used for casting thin films.²² Thus, it is believed that the domain structure appearing in Fig. 9b is genuine and not an artifact of the method used to prepare the films.

Low Angle X-Ray Scattering

In order to prove conclusively that microphase separation exists not only in a thin film but also in a bulk sample of the EN-8 elastomer, a low

Figure 9 - Transmission electron micrographs of thin films of EN-8 elastomer: (a) unstained, (b) OsO_4 stained

angle x-ray scattering experiment was performed. This is similar to the more common wide angle x-ray diffraction experiment that is used to study crystalline structure, except that the intensity of scattered radiation is measured at much smaller angles relative to the main x-ray beam (typically $2\theta = 0.2 - 2.5$ degrees). In qualitative terms, this low angle x-ray scattering experiment gives information regarding larger scale structural periodicity (5-50 nm) within a material than does the wide angle experiment.

The small angle x-ray scattering pattern obtained from EN-8 is shown in Figure 10a. It consists of a dark area around the main beam stop and a broad, but distinct halo at larger scattering angles. This halo is indicative of a quasi-periodic fluctuation in electron density within the elastomer,²⁵ as expected when the dissimilar hard and soft chain segments cluster into separate microphases. Thus, both the transmission electron microscopy and the low angle x-ray scattering methods are in agreement with regard to the presence of domain structure in the EN-8 elastomer. It should be noted that this material provides a concrete illustration of the fact that microphase separation between incompatible chain segments need not necessarily be accompanied by ordering, or crystallinity of the segments within the individual domains.

Electron microscopy was not carried out on the EN-7 elastomer because of difficulties associated with the preparation of thin films due to volatility and toxicity of mercury at the cure temperature of 80°C. The preceding results for EN-8, however, generate confidence in the validity of the small angle x-ray scattering method for detecting microphase separation. The small angle x-ray scattering pattern obtained from EN-7 (Fig. 10b) is seen to be basically similar to that corresponding to EN-8.

Figure 10 - Small angle x-ray scattering patterns obtained from the two polybutadiene based elastomers under the same exposure conditions: (a) EN-8, (b) EN-7.

Clearly a similar microphase structure is to be expected within the two materials on the basis of their very similar chemical structure. A similar line of reasoning leads to the expectation that no crystallinity would be detected in EN-7. This expectation was confirmed by the wide angle x-ray diffraction pattern obtained from EN-7 that showed the same kind of diffuse halo as did the pattern corresponding to EN-8 (Fig. 8a).

A more quantitative representation of the low angle x-ray scattering results on EN-7 is shown in Figure 11, as a microdensitometer scan of the scattering pattern. The peak in the intensity of scattered radiation at an angle of about 1 degree corresponds to the halo seen in Figure 10b. An approximate characterization of the average periodicity between adjacent hard segment domains within the elastomer can be computed by substituting the scattering angle at peak intensity into the well known Bragg equation for x-ray diffraction. This equation yields a computed spacing of 9.3 ± 0.1 nm. This value for EN-7 is quite similar to values measured previously for some uncrosslinked, thermoplastic urethane elastomers.^{13,15,26} The d spacing, however, should only be considered a rough estimate ($\sim \pm 20\%$) of the average periodicity in a material lacking a rigidly periodic lattice structure.²⁷ (Absence of true lattice structure in EN-7 and EN-8 is made evident by the lack of higher order diffraction maxima in their low angle scattering patterns.) Thus, exact correspondence between the d spacing from the small angle x-ray scattering experiment and the average periodicity in the electron micrograph (Fig. 8b) should not be expected. In fact, even the electron micrograph probably does not give an exact representation of the domain structure, because the thickness of the film sample (~ 40 nm) is so much larger than the size scale of the domain structure. Thus, quantitative characterization of the geometry of domain structure in these castable

Figure 11 - Microdensitometer scan on the small angle x-ray scattering pattern obtained from 80°C cured EN-7 (Fig. 10b).

urethane elastomers should be considered approximate at the present time. Nevertheless, the conclusive identification of microphase separation alone will subsequently be shown to lead to significant understanding of the thermomechanical properties of these elastomers.

Characterization of the Physical Structure of 3121-S and Adiprene-MOCA

Neither the soft nor the hard segments of the 3121-S elastomer contain double bonds which could be stained by OsO_4 .⁵ The same is true of the Adiprene-MOCA elastomer.²⁰ Thus, transmission electron microscopy was judged to be unreliable for detecting microphase separation between the hard and soft segments in these two elastomers. The low angle x-ray scattering method was still applicable, however, since it only requires that the microphases differ slightly in electron density.

The low angle x-ray scattering result obtained from the room temperature cured 3121-S elastomer (Fig. 12) shows a peak in scattered intensity indicative of a quasi-periodic distribution of microphases within the elastomer.²⁵ The Bragg spacing corresponding to this intensity peak is ~ 11 nm, which is 15% larger than the corresponding value for EN-7. In contrast to the results obtained with both EN-7 and 3121-S, the low angle x-ray scattering intensity curve for room temperature cured Adiprene-MOCA shows a shoulder rather than a distinct intensity peak (Fig. 13). This change in the shape of the scattering curve indicates a less perfect periodicity in the distribution of microphases within the Adiprene-MOCA elastomer. That is, the finite intensity of x-ray scattering at low angles still clearly demonstrates the presence of microphase separation within the Adiprene-MOCA, but the shape of the scattering curve simply indicates a lesser regularity in the distribution of the microphases than in EN-7 or 3121-S.^{39,40} Indeed, it should be noted that such a shoulder rather than a distinct peak in the small angle x-ray scattering curve has been often observed in previous studies of the microphase separated thermoplastic urethane elastomers.^{15,19}

Figure 12 - Microdensitometer scan on the small angle x-ray scattering pattern obtained from 25°C cured 3121-S.

Figure 13 - Microdensitometer scan on the small angle x-ray scattering pattern obtained from 25°C cured Adiprene-MOCA.

In order to determine if the hard and soft chain segments within the individual microphases are organized into crystallites, the wide angle x-ray diffraction experiment was carried out on the 3121-S and Adiprene-MOCA elastomers. The resulting diffraction patterns (Fig. 14) do not show any sharp diffraction rings and therefore demonstrate the absence of crystallinity in these materials. A similar diffraction pattern was obtained from Adiprene-MOCA cured at 70°C.

Summary of the Physical Structure of the Castable Elastomers Studied

The conclusions derived from the preceding x-ray scattering and transmission electron microscopy results can be summarized as follows. At room temperature, the EN-7, EN-8, 3121-S, and Adiprene-MOCA elastomers can all be characterized similarly. In each material, the hard and soft chain segments separate into microphases on a scale of ~ 10 nm. Within each microphase, the chain segments are not ordered into crystallites to any significant extent (namely, the extent of crystallinity detectable by wide angle x-ray diffraction).

It is interesting to note that despite the presence of this microphase separation between the dissimilar chain segments, the subject urethane elastomers need not necessarily have a turbid appearance. In fact, except for the 3121-S, all the castable elastomers studied appear quite transparent. This near transparency to visible light can be explained by the often quoted generalization^{29,30} that phase separation on a scale much smaller than the wavelength of visible light (~ 500 nm) does not cause appreciable scattering of that light. This generalization has been proven convincingly and quantitatively³¹ by making use of the

Figure 14 - Wide angle x-ray diffraction pattern obtained from (a) 25°C cured 3121-S, and (b) 25°C cured Adiprene-MOCA.

Debye-Beuche³² statistical treatment of light scattering by heterogeneous, isotropic materials.

Accordingly, the exceptional turbidity of the 3121-S elastomer cannot be directly attributed to scattering of visible light by the individual microphases of hard and soft segments. It is possible that the scattering of light by this material is caused by phase separation on a scale of 500 nm, which might be present in addition to the 10 nm scale phase separation detected by low angle x-ray scattering. Another possible origin of visible light scattering by the 3121-S is correlated arrangement of individual hard segment domains into an anisotropic superstructure,¹⁵ again on a scale of 500 nm. Such a superstructure consisting of correlated arrangement of anisotropic domains over distances comparable to the wavelength of visible light is known to cause intense light scattering.³³

The Controlling Influence of Microphase Structure on Dynamic Mechanical Properties

On the basis of the preceding results, we conclude that our chemically crosslinked, castable urethane elastomers can be characterized by the same kind of domain structure as can the previously studied uncrosslinked, thermoplastic elastomers. This conclusion represents a sound basis for generalizing previously developed structure-property correlations for the thermoplastic elastomers^{15,16,17} to our chemically crosslinked materials. Thus, the two major thermomechanical transitions observed in low strain dynamic mechanical testing of the castable elastomers can be assigned to separate transitions in the soft and hard segment microphases. For example, focusing attention on the dynamic mechanical results for EN-7 (Fig. 2), we see that the two major transitions centered at -90 and +50°C can be assigned to the soft segment (polybutadiene) phase and to the

hard segment phase, respectively. Moreover, the absence of crystallinity in EN-7 at room temperature means that the 50°C transition cannot be a crystal melting transition. Hence, this above ambient transition in EN-7 must be a glass transition of an amorphous hard segment microphase.

Obviously, the absence of crystallinity by the room temperature x-ray diffraction experiment does not imply anything about the mechanism of the subambient transition in EN-7. This subambient transition corresponding to the soft segment microphase has also been identified as a glass transition, however, by means of independent calorimetric measurements.²²

On this basis, we conclude that the two thermomechanical transitions in EN-7 are caused by softening of two separate glassy microphases. In the range of temperatures between these two glass transitions, a plateau region of enhanced rubbery modulus arises primarily from physical crosslinking of the rubbery soft segments by the glassy hard segment domains. The absolute value of this plateau modulus depends on both the volume fraction of hard segment domains¹⁷ and the statistical rubberlike elasticity of the soft segments. At temperatures above the softening point of the hard segment microphase (50°C), the modulus of EN-7 asymptotically approaches a low value, which would be dependent solely on the chemical crosslinking in the elastomer. It should be noted that the contribution of this chemical crosslinking to the elastomer modulus (~ 100 psi = 700 MPa) appears to be only about one percent of the modulus in the plateau region.

The two dynamic thermomechanical transitions of the 3121-S and Adiprene-MOCA (Figs. 2,3, and 4) can be analogously interpreted as a subambient soft segment transition and an above ambient hard segment transition. As before, the absence of crystallinity in these elastomers

at room temperature leads to the conclusion that the above ambient transition is a glass transition of the amorphous hard segment microphase.* Independent calorimetric measurements have confirmed that the subambient transitions in Adiprene-MOCA and 3121-S also represent glass transitions.³¹

IMPACTS OF THIS STUDY

Generalization of Mechanical Property Characterization

As discussed earlier, a fundamental understanding of the structural features controlling the mechanical properties of existing castable urethane elastomers can be extremely helpful in solving application problems by enabling mechanical characterization data to be generalized. Two examples of generalizing low strain viscoelastic measurements are presented below.

First, the response of the liquid castable elastomers to dynamic mechanical testing is considered. In this experiment, a low strain oscillatory deformation is applied to the specimen at a fixed frequency, and material properties such as the elastic modulus are measured while the temperature is raised. A massive change in the material's properties over a relatively narrow temperature range signifies the onset of molecular mobility. It is well known that the characteristic temperature corresponding to such a thermomechanical transition always decreases when the frequency of the dynamic experiment is decreased, the magnitude of the effect depending on the mode of molecular motion involved (Ref. 36, p. 299). For example, the glass transition temperature (T_g) of polystyrene, a typical amorphous polymer, drops by about 20°C when the imposed frequency of the dynamic experiment is decreased by two orders of magnitude.³⁷

*Thermally activated breaking of chemical crosslinks in the room temperature cured 3121-S elastomer³⁴ undoubtedly complicates any attempt at a precise interpretation of its upper level thermomechanical transition.

Experimental data showing the frequency dependence of T_g have been published for many different polymeric materials over a frequency range as high as 10^{-2} to 10^{10} Hz.^{37,42,43} Moreover, in the case of a polymer for which experimental data are not available, there are methods for predicting this frequency dependence of the glass transition temperature (Ref. 44, p. 1367).

Thus, the identification of the two thermomechanical transitions in each castable urethane elastomer as glass transitions of the soft and hard segment microphases permits a significant generalization. That is, transition temperatures measured in a dynamic mechanical experiment at one frequency can be used to predict the transition temperatures at a different frequency. For example, the transitions shown by the dynamic mechanical data in Figures 2, 3, and 4 can be generalized to frequencies many orders of magnitude higher than 0.1 Hz. This capability could be very useful for predicting the viscoelastic behavior of these elastomers in applications involving high frequency vibration or shock loading.

Next, we consider the response of the liquid castable elastomers in another viscoelastic test, the stress relaxation experiment. In principle, the behavior of a linear viscoelastic material in a stress relaxation test can be quantitatively predicted (Ref. 7, p. 73) from dynamic thermomechanical measurements of the type discussed above. In practice, this exact procedure generally fails in the case of microphase separated elastomers. The reason is that the thermorheological complexity of these elastomers does not allow construction of a valid viscoelastic master curve by the time-temperature superposition procedure.³⁵ Despite this difficulty, it is still possible to qualitatively predict the stress

relaxation behavior of these elastomers by considering the physical basis for the relaxation process, as shown below.

The stress relaxation experiment involves holding the test specimen at a fixed strain and temperature while monitoring the reduction in stress as time elapses. Now, the idea of frequency dependence of a thermomechanical transition, being simply a manifestation of viscoelastic behavior, can be applied not only to the dynamic mechanical experiment, but also to this stress relaxation experiment. It is only necessary to remember the reciprocal relationship between time scale and frequency.⁴² Thus, the glass transition temperature necessarily decreases as the time scale of a viscoelastic experiment increases. Accordingly, the continuously elapsing time in the isothermal stress relaxation experiment can be viewed as causing a continuous decrease in the effective glass transition temperature of the test material. When the effective glass transition temperature has been reduced to the level of the test temperature, the stress begins to relax, because this equality of T_g and test temperature signifies the onset of molecular mobility.

The various castable urethane elastomers considered presently have hard segment transition temperatures located at various levels above room temperature (Figs. 2,3, and 4). Since each of these transition temperatures corresponds to an amorphous phase glass transition, we expect them all to be similarly affected by the time scale in a viscoelastic experiment. On the basis of the above considerations, therefore, it is easy to understand why the EN-7 elastomer begins to stress relax much sooner than Adiprene-MOCA in a room temperature test (Fig. 1). The reason is that the EN-7's hard segment glass transition is only slightly above the test temperature, whereas the Adiprene-MOCA has its hard segment T_g above 140°C. Thus,

consideration of this time scale dependence of the hard segment glass transition temperature offers at least a qualitative basis for the earlier empirical conclusion that the performance of these castable elastomers in a stress relaxation test can be related to the location of their upper level thermomechanical transition. The analogy between stress relaxation and creep of a viscoelastic material that was discussed earlier permits extension of this conclusion from stress relaxation behavior to the creep behavior of these elastomers.

Strategy for Developing Improved Castable Elastomers

We now consider how the results of this investigation may help in the development of improved replacements for Adiprene-MOCA. Clearly any serious attempt to improve the low strain viscoelastic properties of the existing replacement elastomers, EN-7 and 3121-S, must focus on raising the upper level thermomechanical transition temperature. The simplest way to accomplish this is to change the chemical identity of the hard segment so as to raise its glass transition temperature. A more clever approach, however, would be to carefully choose a symmetrical chemical structure for the hard segment, so that it would be crystallizable. The most obvious advantage of a crystalline hard segment is that melting temperatures of crystalline polymers (in °K) are typically 50% higher than glass transition temperatures of amorphous polymers (Ref. 38, p. 191).

The choice of a crystalline hard segment for a microphase separated elastomer has another advantage, which is less obvious but perhaps more significant. It is related to the dependence of transition temperatures on the time scale of viscoelastic experiments. It will be recalled that the controlling influence of the hard segment glass transition on the

stress relaxation behavior of the existing castable elastomers originates in the dependence of this transition temperature on the time scale of the viscoelastic experiment. The crucial point is that the glass transition temperature of an amorphous polymer is much more dependent on the viscoelastic time scale than is the melting temperature of a crystalline polymer (Ref. 41, pp. 142 and 198).^{*} The significance of this point is illustrated by the hypothetical case of two microphase separated elastomers differing only in the identity of the hard segment, one having an amorphous hard segment and the other a crystalline hard segment. In this case, even if the glass transition and melting temperatures of the two hard segments were exactly the same, the crystalline elastomer would perform much better in the stress relaxation test at any given temperature because the effective crystal melting point would decrease much more slowly with elapsed time. Thus, a crystalline hard segment has the dual advantage over an amorphous hard segment in that not only does the former normally have a higher thermomechanical transition temperature, but also this transition is much less dependent on the time scale of a viscoelastic experiment.

A final point with regard to improved castable urethane elastomers has to do with the prospect for developing elastomeric encapsulants which can be removed in order to permit rework capability on electronic packages. None of the existing castable elastomers can be removed by dissolution in solvent because they are chemically crosslinked into a network structure, as shown schematically in Figure 6. It is significant to note, however, that the results of this investigation show that the low strain viscoelastic properties of these materials are controlled primarily by their

^{*}The reason is that the glass transition differs fundamentally from the melting transition in that the former basically represents an activated, or kinetically controlled process, while the latter represents an equilibrium controlled process (Ref. 38, p. 203).

microphase separation, rather than their chemical crosslinking. This conclusion therefore represents a sound basis for attempting to develop a castable elastomer based on linear, uncrosslinked macromolecules, which would be removable by dissolution in solvent. The synthesis of such a removable urethane elastomer is already being investigated by K. B. Wischmann (5813) in a joint effort with the author.

SUMMARY

This study has investigated the structural features that control the low strain viscoelastic properties of elastomeric urethane encapsulants. The elastomers considered include both the liquid castable Adiprene-MOCA and the existing replacements for this material, EN-7 and 3121-S. The chemical structure of each elastomer is interpreted as a chemically cross-linked molecular backbone made up of two kinds of chain segments, the hard and soft segments. It is concluded that the viscoelastic properties of each elastomer are controlled for the most part by the physical arrangement of chain segments into a solid state morphology. In contrast, the chemical structure of the elastomers exerts a primarily indirect influence on these properties by affecting the physical structure.

The morphology of these castable elastomers is characterized by the scattering of x-rays at both small and wide angles as well as by transmission electron microscopy. The x-ray scattering measurements demonstrate that in each elastomer the incompatible hard and soft segments cluster separately into two microphases on a scale of ~ 10 nm, the hard segment microphase being specifically identified as non-crystalline. Microphase separation in the EN-7 elastomer is confirmed by an entirely independent technique: transmission electron microscopy on stained films. The

ineffectiveness of this microphase separation in scattering visible light is noted.

The domain structure identified in these particular urethane elastomers is found to be quite similar to that observed previously in the so-called thermoplastic urethane elastomers. This conclusion represents a significant generalization of previous results on the thermoplastic elastomers, because the presently considered castable elastomers are distinguished not only by their reactive processing, but also by their chemically crosslinked molecular architecture. Moreover, the identification of domain structure in the castable elastomers represents a sound basis for generalizing previously developed structure-property correlations to these crosslinked encapsulating elastomers. Specifically, the two major thermomechanical transitions in each elastomer are assigned to transitions within the separate hard and soft segment microphases.

This fundamental understanding of the structural features controlling the mechanical properties of liquid castable urethane elastomers has two major impacts on the broad problem of electronic encapsulation. First, this structure-property correlation will facilitate solution of application problems with existing encapsulants by enabling mechanical property measurements to be generalized. Specific examples are (a) the generalization of measured dynamic mechanical data to different frequencies and (b) the successful prediction that the performance of these castable elastomers in a stress relaxation test is related to the temperature of their hard segment glass transition. A second impact of this study is a strategy for developing improved castable elastomers as acceptable replacements for Adiprene-MOCA. Specifically, it is proposed that an elastomer having a crystalline hard segment would have the dual advantage of a high

upper use temperature as well as improved resistance to stress relaxation and creep.

REFERENCES

1. R. D. Elmore, Bendix Kansas City Division Report BDX-613-1135, September 1974.
2. C. Arnold, Sandia Laboratories Report, SLA-73-1013, November 1973.
3. D. J. Caruthers, Bendix Kansas City Division Report, BDX-613-1489, March 1976.
4. E. A. Salazar and J. G. Curro, Sandia Material and Process News Note, April 1975.
5. A. J. Quant, Sandia Laboratories Internal Memorandum, RS 5813/015, September 1974.
6. D. J. Caruthers, Bendix Kansas City Division, Technical Quarterly, Materials Engineering, September 1974, pp. 7-22.
7. J. D. Ferry, Viscoelastic Properties of Polymers (John Wiley, New York, 1970), 2nd Edition.
8. R. M. Smith, F. N. Larsen, and G. K. Baker, Bendix Kansas City Division Memorandum, February 1974.
9. C. Arnold, Materials Review 1975, 7th National SAMPE Technical Conference (Society for the Advancement of Material and Process Engineering, 1975), p. 418.
10. P. W. Ryan, Brit. Polym. J., 3, 145 (1971).
11. S. B. Clough, N. S. Schneider, and A. O. King, J. Macromol. Sci., Phys., B2, 641 (1968).
12. R. Bonart, L. Morbitzer, and G. Hentze, J. Macromol. Sci., Phys., B3, 337 (1969).
13. C. E. Wilkes and C. S. Yusek, J. Macromol. Sci., Phys., B7, 157 (1973).
14. R. Bonart, L. Morbitzer, and E. H. Muller, J. Macromol. Sci., Phys., B9, 447 (1974).
15. Y. P. Chang and G. L. Wilkes, J. Poly. Sci., Poly. Phys. Ed., 13, 455 (1975).
16. T. L. Smith, J. Poly. Sci., Poly. Phys. Ed., 12, 1825, (1974).
17. S. L. Samuels and G. L. Wilkes, J. Poly. Sci., Symposia, 43, 149 (1973).

18. R. W. Seymour and S. L. Cooper, *Macromolecules*, 6, 48 (1973).
19. S. B. Clough and N. S. Schneider, *J. Macromol. Sci., Phys.*, B2, 553 (1968).
20. A. J. Quant, *S. P. E. Journ.*, 15, 298 (1959).
21. C. Arnold, Sandia Laboratories Report, SAND 75-0318, June 1975.
22. R. R. Lagasse, *J. Appl. Poly. Sci.*, in press.
23. D. M. French, *Rubber Chem. Technol.*, 42, 71 (1969).
24. J. F. Beecher, L. Marker, R. D. Bradford, and S. L. Aggarwal, *J. Poly. Sci., Symposia*, 26, 117 (1969).
25. G. L. Wilkes, *J. Macromol. Sci., Rev. Macromol. Chem.*, C10, 149 (1974).
26. R. Bonart, L. Morbitzer, and H. Rinke, *Kolloid Z. Z. Polym.*, 240, 807 (1970).
27. A. Guinier and G. Fournet, Small Angle Scattering of X-Rays (John Wiley, New York, 1955), pp. 140-148.
28. E. H. Andrews, *Intern. J. Polymeric Mater.*, 2, 337 (1973).
29. A. Noshay and J. E. McGrath, Block Copolymers: Overview and Critical Survey (Academic Press, New York, 1977), p. 67.
30. J. A. Manson and L. H. Sperling, Polymer Blends and Composites (Plenum Press, New York, 1976), p. 116.
31. R. R. Lagasse, unpublished results.
32. P. Debye and A. M. Bueche, *J. Appl. Phys.* 20, 518 (1949).
33. R. S. Stein and G. L. Wilkes in Structure and Properties of Oriented Polymers, edited by I. M. Ward (John Wiley, New York, 1975), p. 99.
34. A. J. Quant, Sandia Laboratories Memorandum to Distribution, May 6, 1975.
35. R. E. Cohen and N. W. Tschoegl, *Trans. Soc. Rheol.*, 20, 153 (1976).
36. R. F. Boyer in Polymeric Materials: Relationships Between Structure and Mechanical Behavior, edited by E. Baer and S. V. Radcliffe (American Society for Metals, Metals Park, Ohio, 1975), Chapter 6.
37. N. G. McCrum, B. E. Read, and G. Williams, Anelastic and Dielectric Effects in Polymeric Solids (John Wiley, London, 1967), p. 414.

38. R. F. Boyer, J. Poly. Sci., Symposia, 50, 189 (1975).
39. W. O. Statton in Newer Methods of Polymer Characterization, edited by B. Ke (Interscience, New York, 1964), p. 267.
40. M. Kakudo and N. Kasai, X-Ray Diffraction by Polymers (Elsevier Publishing Co., Amsterdam, 1972), p. 406.
41. A. V. Tobolsky, Properties and Structure of Polymers (John Wiley, New York, 1960).
42. D. W. McCall in Molecular Dynamics and Structure of Solids, edited by R. S. Carter and J. J. Rush, Nat. Bur. Stand. Special Publication 301, 1969.
43. G. D. Patterson, J. Poly. Sci., Poly. Phys. Ed., 15, 455 (1977).
44. R. F. Boyer, Rubber Chem. Tech., 36, 1303 (1963).

Distribution:

V. Burkett, Attn: K. Creed
General Electric
P. O. Box 11508
St. Petersburg, Florida 33733

R. L. Sadler
C. H. Smith
J. D. Steele
Bendix Corporation
Kansas City Division
P. O. Box 1159
Kansas City, Missouri 64141

J. DiChiaro
Monsanto Research Corporation
Mound Laboratory
P. O. Box 32
Miamisburg, Ohio 45342

H. G. Hammon
N. Hetherington
Lawrence Livermore Laboratories
University of California
P. O. Box 808
Livermore, California 94550

G. Dorsey
Union Carbide Corporation
Y-12 Plant
Oak Ridge, Tennessee 37830

2153 D. H. Weingarten
2154 G. H. Donaldson
2316 H. M. Barnett
2316 G. L. Cossac
2351 R. C. Dougherty
2516 J. M. Holovka
5000 A. Narath

Attn: J. K. Galt 5100
E. H. Beckner 5200
O. E. Jones 5300
A. W. Snyder 5400
J. H. Scott 5700

5800 R. S. Claassen
Attn: R. L. Schwoebel 5820
M. J. Davis 5830
H. J. Saxton 5840

5810 R. G. Kepler
5811 L. A. Harrah
5811 C. Arnold
5811 R. A. Assink

5811 M. H. Gonzales
5811 J. A. Wagner
5811 K. B. Wischmann
5813 J. G. Curro
5813 K. T. Gillen
5813 A. J. Quant
5813 P. B. Rand
5813 E. A. Salazar
5814 R. C. Hughes
5814 D. W. Schaefer
5844 F. P. Gerstle
8424 H. R. Sheppard
Attn: R. Gott
9515 J. T. Hillman
9572 E. R. Frye
8266 E. A. Aas (2)
3141 C. A. Pepmuller (5)
3151 W. L. Garner (3)
For DOE/TIC (Unlimited
Release)
3171-1 R. P. Campbell (25)
5813 R. R. Lagasse (50)

This page left blank intentionally.