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Synthesis and characterization of polyisobutylene propellant binders*

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ABSTRACT

Substantial gains in rocket motor cost-effectiveness or performance can be achieved through improved propellant aging characteristics or better and more reproducible mechanical properties. The approach to achieving these goals is the development of a new binder based on ideal networks formed from polyisobutylene (PIB) prepolymers. PIB has a greater resistance to oxidation than polybutadiene which is used in many current composite systems.

The ideal networks are generated through the use of PIB prepolymers with controlled molecular weight distributions and well defined functionality. PIB prepolymers evaluated in this study were synthesized by Dr. J. P. Kennedy at the University of Akron using the "inifer" process which allows close control of molecular weight distribution, functionality and types of end group. Hydroxy-terminated PIB's with molecular weights that varied from 1500 to 6000 and functionalities of 2 or 3 were synthesized. After a thorough characterization, gumstocks were prepared with isocyanate curatives of controlled functionality. The effects of M_c and plasticizer content on mechanical properties were determined in addition to the aging characteristics of the systems. Accelerated aging studies of the gumstocks were conducted.

INTRODUCTION

Currently, hydroxy-terminated polybutadiene (HTPB) is the polymer of choice for most of the composite propellant development work. Its low

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viscosity is appealing for high solids systems and the isocyanate cure chemistry is well established. Nevertheless, there are several problems associated with the use of HTPB polymer. Its functionality is considerably higher than required, is variable from lot-to-lot and is not uniformly distributed, i.e., the functionality is concentrated in the higher molecular weight fractions. In processing, anhydrous conditions are required to prevent undesirable side reactions between isocyanate and water. Additionally, the unsaturated polymer is susceptible to oxidative crosslinking which results in mechanical property degradation with age. Use of antioxidants slows but does not prevent this phenomenon.

To ultimately improve the properties of rocket propellants, a technology base which allows the design of polymer networks with the desired properties and the synthesis of the prepolymers necessary to generate those networks is required. In the present program, well defined, efficient load-bearing binder networks were formulated through the use of telechelic, strictly di-and/or trifunctional PIB prepolymers. The prepolymers were synthesized by Professor J. P. Kennedy at the University of Akron using unique synthetic techniques which provide precise control of the functionality and molecular weight. The PIB backbone provides inherent resistance to oxidative hardening. Prepolymers were synthesized with a variety of reactive ends including: olefin (OTPIB), hydroxyl (HTPIB), sulfonic acid and epoxy.

DISCUSSION OF RESULTS

Prepolymer Synthesis

Novel techniques developed by Kennedy(1) were used to synthesize the PIB prepolymers. An essential feature of the technique is the use of chain initiator/transfer agents (inifers) which yield polyisobutylene of a preselected molecular weight carrying exactly 2 or 3 tertiary chlorine end groups. The chloride terminated PIB serves as the starting material from which the other prepolymers are prepared.

The first PIB derivative prepared from the chloride was OTIB. The HTPIBs have been prepared from the OTPIB. The reaction details have been published(2).

The difunctional sulfonated PIB was prepared by reaction of the OTPIB with acetyl sulfate. The sulfonation was carried out in n-hexane at room temperature. Since the free acid was found to decompose at room temperature, it was converted to the potassium salt by neutralizing with KOH/EtOH. The epoxy-terminated prepolymer was prepared by epoxidation of the OTPIB. A solution of m-chloroperbenzoic acid in chloroform was added to a solution of OTPIB in dry chloroform dropwise at room temperature over a four hour period. Then the solvent was removed and the product redissolved in n-hexane.

Prepolymer Characterization

Characterization of all of the prepolymers included determining molecular weight, functionality, glass transition temperature and viscosity. Infrared and NMR spectra were also obtained. Molecular weights were measured by two techniques: vapor phase osmometry (VPO) and gel permeation chromatography (GPC). The number average molecular weight (M_n) was determined by VPO, while GPC was used to measure the molecular weight distribution and the polydispersity (M_w/M_n). Functionality was measured by two independent techniques. In the first method, proton NMR was used to determine the ratio of the terminal vinyl protons to the aromatic protons in the OTPIB chains(2). All of the OTPIB precursors were checked with this technique. For example, the ratio of olefinic protons to aromatic is 1:1 for difunctional OTPIB and 3:2 for trifunctional OTPIB. In the second method, the equivalent weight of the prepolymers was determined by a quantitative analysis of the end groups, generally by infrared spectroscopy. The equivalent weight is then divided into M_n to obtain the functionality. Glass transition temperatures were measured by means of differential scanning calorimetry (DSC-DuPont 1090), which was also used to determine the high temperature decomposition behavior. Prepolymer viscosity was measured on the Rheometrics mechanical spectrometer over a range of shear rates.

The characteristics of the prepolymers are summarized in Table I. As shown in the table all of the prepolymers were synthesized with functionlities of 2 or 3, as designed. The molecular weights were within 20% of the original targets. The T_g values, are generally less than -60°C, which is satisfactory for propellant applications.

Table I

Summary of Prepolymer Characterization Results

PIB Prepolymer	Mn	Mw/ Mn	Fn	T_g (°C)	Amount Synthesized (Grams)
Diolefin	3100	2.0	2	-70	125
Disulfonated	5500	---	2	---	125
Diepoxide	3850	1.9	2	-76	135
Diamine	5000	1.6	2	-87	150
Diol	2050	1.9	2	---	130
Diol	3700	1.9	2	-70	110
Diol	4800	1.9	2	-70	135
Diol	4800	1.7	2	-66	210
Diol	5000	1.9	2	-69	540
Triol	1500	1.6	3	-65	135
Triol	3500	1.7	3	-80	125
Triol	4000	1.6	3	-61	215

Rheological characterization of the PIB's was carried out using the cone and plate geometry in the rheological mechanical spectrometer over a temperature range of 32°C to 60°C. The materials were essentially Newtonian, that is, the viscosities were independent of the shear rates. The temperature dependencies of the viscosities of the HTPIB and OTPIB are shown in Figure 1 along with comparable data for HTPB. All three polymers showed a similar temperature dependence with an activation energy of about 14 kcal/mole. The HTPB viscosity was less than the PIB's by a factor of 7.

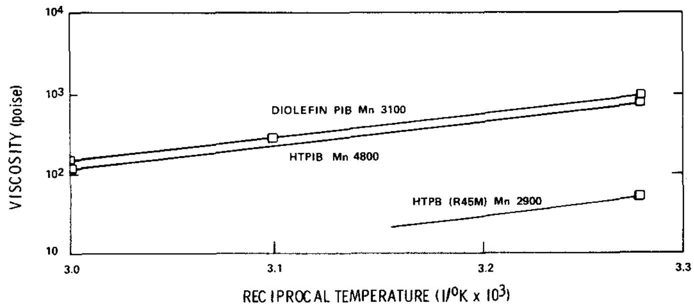

Figure 1. Temperature Dependency For Viscosities Of Polyisobutylenes

Prepolymer Evaluation - Gumstock Studies

The prepolymers were evaluated in gumstocks to assess their potential as propellant binders. The polyisobutylene prepolymers were synthesized to have functionalities of precisely 2 or 3. A series of gumstocks were prepared to determine the dependence of mechanical properties on the structure of the polymer network. Parametric variations of the chain lengths between branching sites (M_c), plasticizer-to-polymer ratio and curative type were carried out. In general, the networks were formulated for complete reaction of the prepolymer to preclude unreacted groups which would give dangling polymer chains. Therefore, stoichiometry was varied over the relatively narrow range of 0.9 to 1.3 to define the optimum crosslink density. The relationship of gumstock properties to propellant mechanical properties was not quantitatively known. Hence, guidelines used to select the optimum gumstock properties were based on HTPB gumstocks. Specifically, the mechanical properties of the HTPB binder in a state of the art reduced smoke propellant were used as target properties for the HTPIB work.

Of the four moieties, only the HTPIBs gave successful cures in the initial gumstock studies. The sulfonate salt had a high fusion temperature. The epoxide did not cure with the usual reagents and the OTPIB underwent only partial cures. While the epoxide and OTPIB have potential in spite of the difficulties encountered here substantial effort was required to develop these networks. For that reason the gumstock studies focused on the HTPIB.

In the following sections the gumstock formulation and characterization are discussed. In the formulation studies the theoretical M_c was varied from approximately 1000 to 10,000. This was achieved by combining the di-and/or trifunctional HTPIB's with the appropriate curative as shown in Table II.

The effect of plasticizer was also determined as indicated in the Table. The networks generally had branching points with a functionality of three although in the case of N-100 the functionality is nearly four. Various isocyanate curatives were used including hexamethylene diisocyanate (HDI), triphenylmethane triisocyanate (TPMTI) and N-100. TPMTI was used to attain a perfect trifunctional branching site for networks based on the diol prepolymers. HDI was used with the triols and combinations of triols and diols. Due to limitations in the amount of prepolymers a relatively small matrix of gumstocks could be prepared, considering the number of potentially interesting combinations.

Table II

COMPOSITION VARIATIONS AND THEORETICAL M_c FOR HTPIB GUMSTOCKS

M_n Prepolymers (g/mole)		Ratio	Curative	Plasticizer	M_c (g/mole)	
Di	Tri	Di:Tri			Theo.	Measured
-	1500	-	HDI	-	1200	2800
2050	-	-	TPMTI	-	2200	-
-	3500	-	HDI	-	2500	-
3700	-	-	TPMTI	-	3900	4700
4800	-	-	TPMTI, N-100	-	5000	5100
4800	-	-	TPMTI, N-100	IDP, PIB	5000	-
3700	3500	1:1	HDI	-	6400	16000
4800	3500	1:1	HDI	-	7500	-
3700	3500	2:1	HDI	-	10,400	16000
3700	3500	2:1	HDI	IDP, PIB	10,400	-

Gumstock Preparation/Characterization

The HTPIB's were cured successfully with a variety of isocyanates. Approximately 40 HTPIB gumstocks were prepared in which parametric variations in M_c, polymer-to-plasticizer, NCO/OH, and catalyst content were made. The relationship of parametric variations to physical properties is discussed below, preceded by a brief description of the preparation and characterization techniques.

The gumstocks were prepared in a dry box under a blanket of dry nitrogen. The ingredients were weighed and mixed, evacuated to remove entrapped nitrogen and siphoned into 6.4 mm (I.D.) Teflon tubes. The tubes were sealed and cured at 60°C for seven days. Characterization focused on two principal areas: the physical property-network structure relationship and the aging behavior. The relationship of network structure to physical properties was delineated through the measurement of the following properties of cured gumstocks: 1) uniaxial tensile properties 2) gel content 3) crosslink density and 4) T_g. A knowledge of the interrelationships of these properties and their dependence on network structural parameters such as M_c and plasticizer-to-polymer ratio provided a basis for designing propellant binder networks with optimum properties.

Uniaxial tensile testing was conducted with an Instron testing machine. End bonded cylindrical specimens, 6.4 mm diameter by 25.4 mm long, were used. Tests were carried out at 25°C and -54°C at a strain rate of .042 cm/s. Gel content was determined by extracting the cured gumstock with a large excess of tetrahydrofuran (THF). After two extractions the THF was evaporated and the residual gel was weighed. Crosslink density was determined by means of the standard swelling technique and the Flory-Huggins equation.

The effect of M_c variation on the stress strain curves of HTPIB based gumstocks is shown in Figure 2. As the theoretical M_c increases from 2400 to 7500 the modulus decreases from 336 kPa to 45.5 kPa. Strain increases from approximately 130% to nearly 900% while stress at failure undergoes a relatively small decrease from 301 kPa to 210 kPa. The toughness of the gumstock, which is correlated with the area under the stress-strain curve increases up to an M_c of ~5000 and is relatively constant from 5000 to 7500.

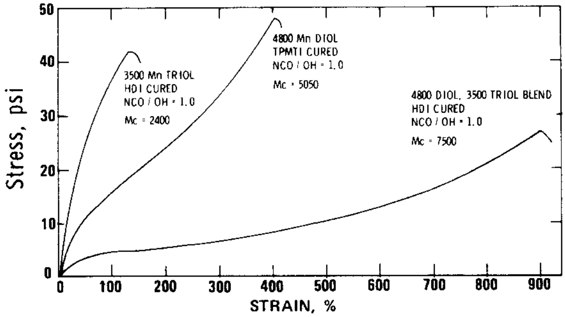

Figure 2. Dependence of Gumstock Tensile Properties On Mc

Incorporating plasticizer into the polymer network decreases modulus and crosslink density. A gumstock formulated at a polymer-to-plasticizer (IDP) ratio of 3:1 has a modulus (at 50% strain) of 175 kPa compared to 595 kPa for the unplasticized network. This reduction reflects the decrease from 17.5×10^{-5} to 6.3×10^{-5} moles/cm^3 in crosslink density. The incorporation of the plasticizer greatly improves the low temperature properties, for example, the modulus decreases from approximately 27,000 kPa to 1253 kPa at -54°C, for a gumstock with an M_c of 3700. A commensurate reduction in T_g is observed, i.e., the unplasticized gumstock had a T_g of -59°C compared to -75°C for the plasticized formulation.

Modulus and crosslink density was found to increase as NCO/OH was increased from 0.9 to 1.1 (or 1.3). Theoretically, the modulus should reach a maximum value at an NCO/OH of 1.0. The continued increase of modulus and crosslink density beyond the theoretical maximum may be due to loss of isocyanate in side reactions or reaction of excess isocyanate with urethanes to give allophanates. The modulus values are proportional to gumstock crosslink densities as theoretically predicted.

Figure 3 is a plot of experimentally determined crosslink density against the modulus. The plot includes a variety of curatives, prepolymers, stoichiometries and plasticizers. Nonetheless, a single linear function fits all of the data within experimental error. By establishing the gumstock modulus that corresponds to optimum propellant properties the crosslink density can be determined from the relationship shown in Figure 3. Consequently, the optimum M_c can be calculated and used to select goals for prepolymer molecular weights.

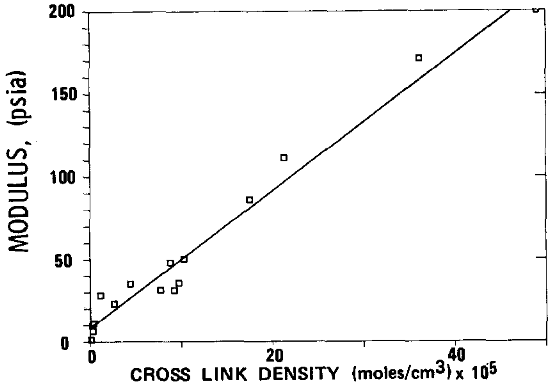

Figure 3. Modulus As A Function Of Cross Link Density For HTPIB Gumstocks

The experimental M_c is consistently higher than the theoretical value for all of the gumstocks tested. This discrepancy can arise from two sources 1) side reactions that consume isocyanate thus leaving some hydroxy unreacted and 2) errors in the experimental determination of M_c. The former consideration is always a factor in isocyanate cures and cannot be precluded here. With regard to experimental error the most likely source is the solvent-polymer interaction parameter of the Flory-Huggins Equation, which was estimated based on solubility considerations.

Aging of PIB Based Gumstocks

The primary advantage anticipated for PIB over PB binders is their resistance to oxidation. To establish a direct comparison between the two polymers a series of gumstocks were subjected to an accelerated aging study. Three HTPIB and two HTPB gumstocks were aged at 74°C for periods up to four months. Mechanical properties, weight changes and changes in their infrared spectra were monitored. No stabilizers were incorporated in the gumstock formulations. The FTIR spectra of the HTPIB based gumstocks showed no change after 8 weeks at 74°C. In contrast, a small increase was observed in the carbonyl region of the HTPB gumstock spectrum after the same exposure. This was probably due to incipient oxidation of the HTPB at the unsaturated bonds in the polymer.

The mechanical properties of the PIB gumstocks were quite stable with extended exposure at 74°C while the PB gumstocks showed signs of oxidative hardening. Figure 4 shows the effect of aging at 74°C for eight weeks on the modulus of the respective polymers. The PIB gumstocks were essentially unchanged after the 8 weeks exposure. The presence of plasticizer and/or the use of a different curative had no apparent effect. In contrast, the PB gumstocks showed an increase in modulus under the same conditions. Weight loss studies confirmed the stability of the PIB binder. After an initial loss of about 2% the weight of the PIB gumstocks is constant for 120 days at 74°C. The initial weight loss is due to residual solvent which is driven out with the initial heating. A similar weight loss was observed upon heating the unreacted prepolymer.

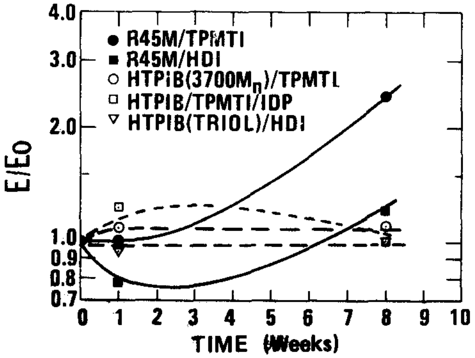

Figure 4. Effect of 165°F Exposure On Modulus of HTPB and HTPIB Gumstocks

CONCLUSIONS

A series of polyisobutylene prepolymers were prepared in which a novel synthetic method was used to control functionality and molecular weight. The synthetic approach was quite flexible allowing the synthesis of telechelic polymers with a variety of terminal functional groups including epoxy, amine, olefin, sulfonate and hydroxyl. Polymer structure mechanical property relationships were defined using di and trifunctional HTPIB's covering a range of molecular weights.

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