

Thermoset Polyurethanes Containing Hydroquinone Di(β -hydroxyethyl) Ether*

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Synopsis

A thermoset polyurethane resin extended with hydroquinone di(β -hydroxyethyl) ether (HQEE) was found to have good thermomechanical properties suitable for external elastomeric automotive applications. A resin composed of diphenylmethane diisocyanate (MDI), ethylene glycol, and a primary polyol was found to have good mechanical properties but was too reactive for processing as a one-component resin. Replacing the liquid ethylene glycol extender with the solid HQEE substantially increased the pot life of the resin as well as improving the modulus properties. When catalyzed with zinc stearate this resin had sufficient pot life at room temperature, at least 4 hr, to be processed as a one-component system but still cure rapidly at elevated temperatures. The HQEE-extended materials required only 50% hard-block content (isocyanate plus extender) to have the same modulus at room temperature as ethylene glycol-extended materials containing 60% hard block. By using a graft or polymer polyol, the required hard-block content could be reduced to 40%. The polyurethane of MDI/SAN graft polyol/HQEE containing 40% hard block had a flex modulus of 230 MPa, tensile strength of 18 MPa, and 240% elongation. The ratio of flex moduli measured at -29 and $+70^\circ\text{C}$ was 2.7, which compared very favorably to conventional RIM systems. The modulus at elevated temperatures was particularly improved, which is important in painting operations.

INTRODUCTION

The use of a one-component polyurethane offers a number of advantages relative to current reaction injection molding (RIM) technology. The mixing and molding steps are separated so that complete mixing can be obtained before the material is molded. This also allows the use of simpler mixing and molding equipment for RIM. The one-component system can also be molded with a cold runner system to reduce scrap formation.

For this process to work, a resin is required that has a long pot life at room temperature for the necessary mixing and storage time prior to molding. The resin must then cure rapidly, preferably 2 min or less, at the molding temperature for a sufficiently rapid cycle time. The polyurethane is being developed to meet the requirements for automotive fascia or soft front end.¹ Generally, these requirements are a low T_g for cold impact resistance and a shallow slope to the modulus-versus-temperature curve to retain sufficient modulus to prevent the part from bending under its own weight at elevated temperature (hot sag resistance).

The polyurethanes under consideration are two-phase systems resulting from the reaction of three components: a polyether polyol, a dihydroxyl chain extender, and a diisocyanate. The rigid segments, formed by the combined isocyanate-extender units, constitute a hard phase dispersed within the soft-seg-

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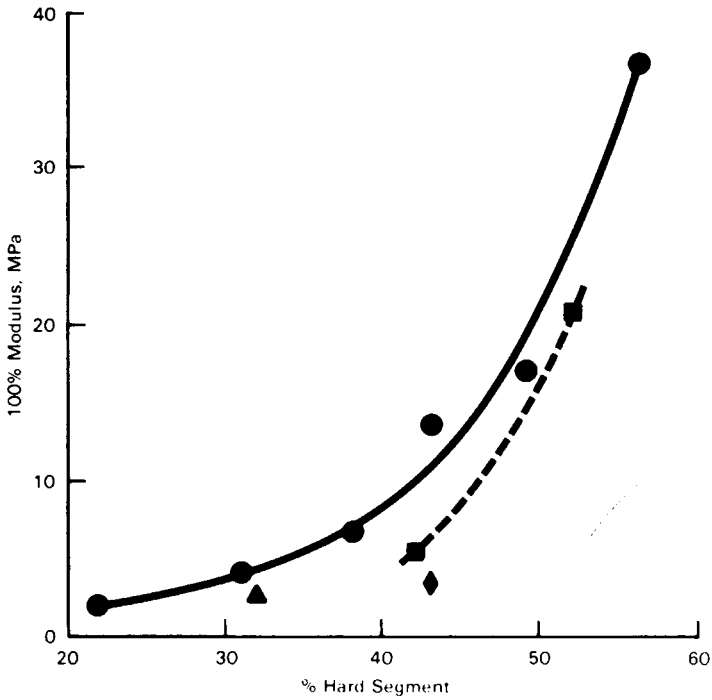


Fig. 1. 100% Modulus vs hard-segment content for various molecular weight polyols: (●) 2100; (▲) 1250; (■) 830; (◆) 530. Data from Seefried.²

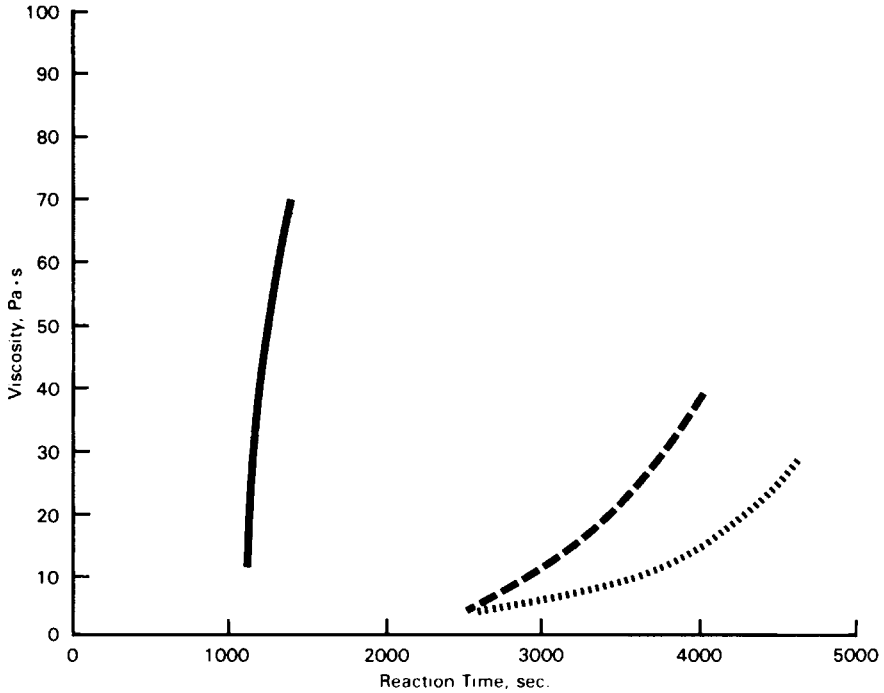


Fig. 2. Effect of urethane resin composition on viscosity rise. Resin Composition: (—) Isonate 180/N1134/EG; (- -) Isonate 180/TP4040/EG; (····) SF50/N1134/EG. All containing 50% hard segment.

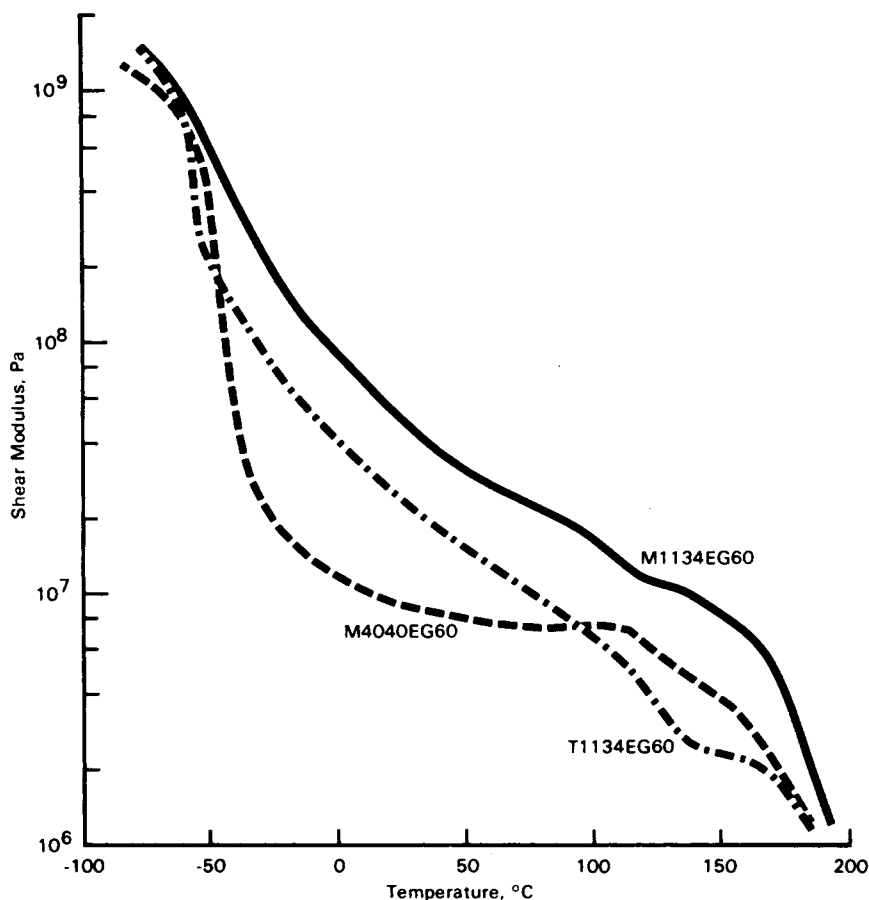


Fig. 3. Modulus vs temperature for polyurethane samples

TABLE I
Materials Used in Polyurethane Formulations

Material	Designation	Equivalent weight	Description	Supplier
SF-50	T	129	modified TDI	Union Carbide
Isonate-180	M	180	modified MDI	Upjohn Polymer Chemicals
TP-4040	4040	1370	polyether triol, secondary hydroxyl	BASF Wyandotte
Pluracol 667	667	2170	polyether triol, primary hydroxyl	BASF Wyandotte
Niax 11-34	1134	1650	polyether triol, primary hydroxyl	Union Carbide
Pluracol 581	581	2080	polyether triol, primary, SAN graft	BASF Wyandotte
PA 19336-A1	AN	2040	polyether triol, primary, AN graft	BASF Wyandotte
Ethylene glycol	EG	31	extender	Eastman
Hydroquinone di(β -hydroxyethyl) ether	HQEE	99	extender	Eastman
Zinc stearate	—	—	catalyst	Diamond Shamrock Allied Chemical

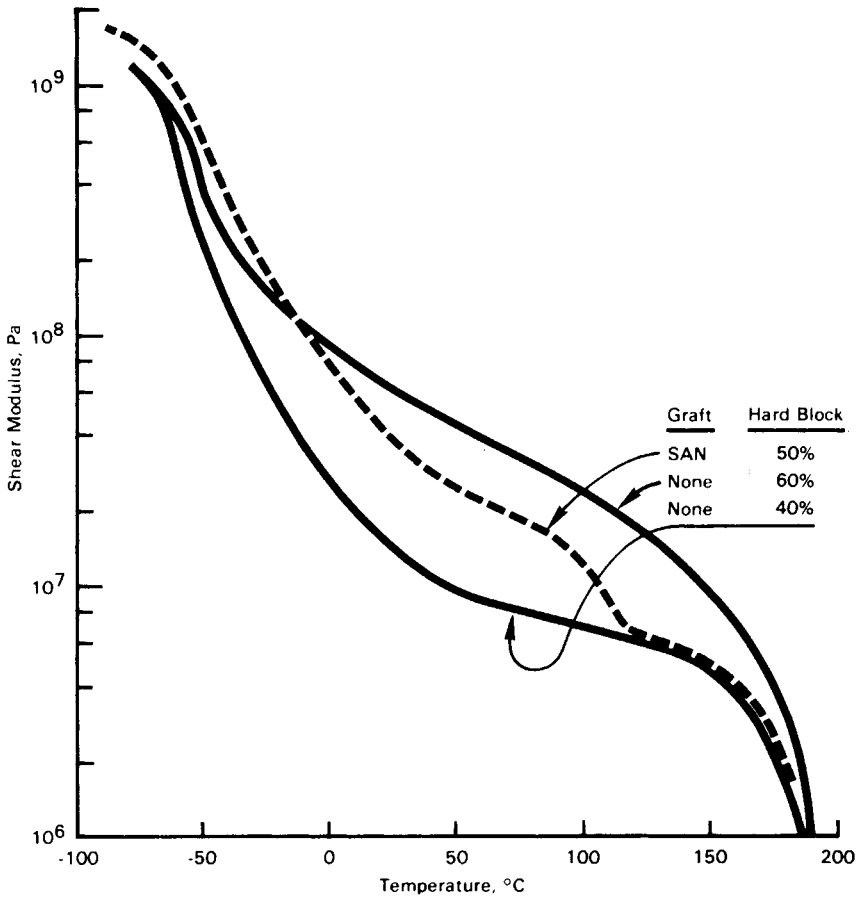


Fig. 4. Effect of graft polyol on modulus-vs-temperature behavior.

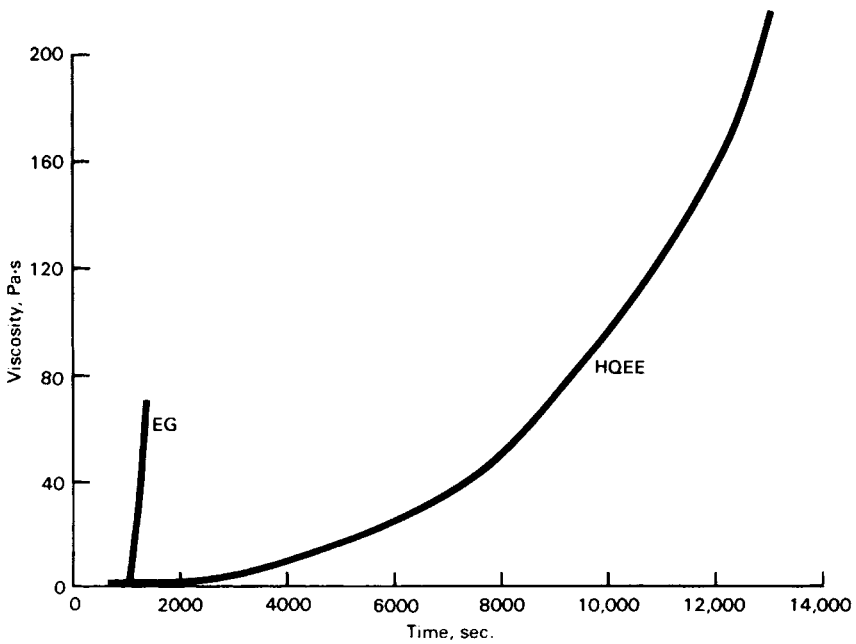


Fig. 5. Effect of extender on viscosity increase for one-component polyurethanes.

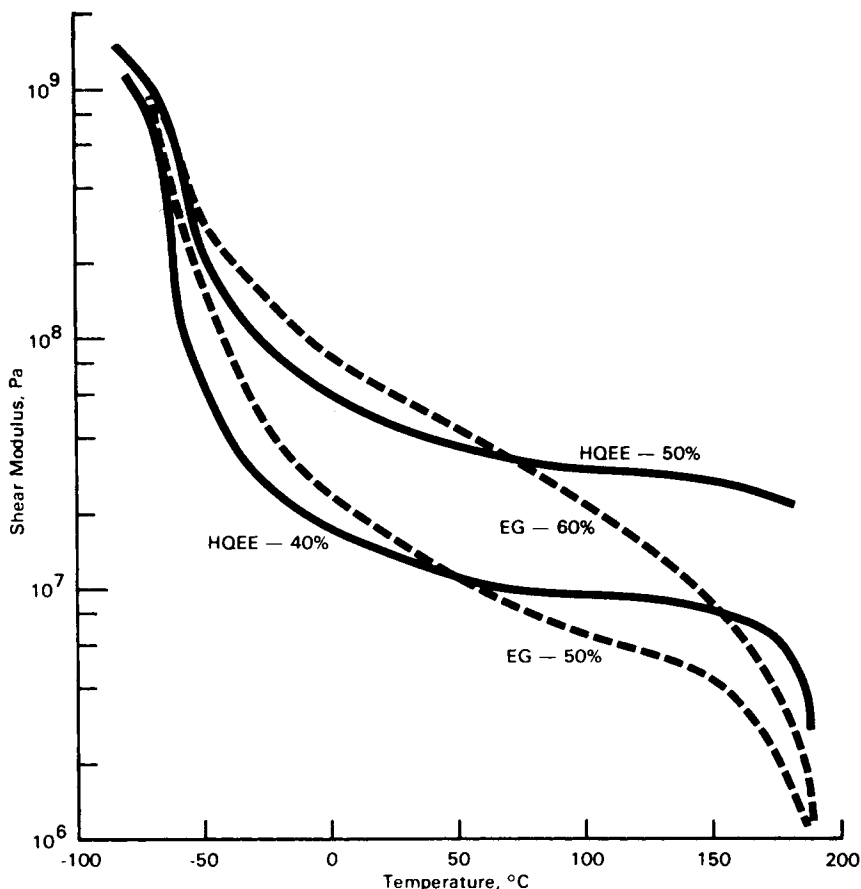


Fig. 6. Effect of extender type and hard-block content on modulus-vs-temperature response.

ment polyol matrix. Since the polyol segments are chemically bound to the rigid segments, the hard phase acts as a reinforcing filler. The stiffness of the polyurethane depends primarily on the concentration of rigid segment material and the degree to which it is incorporated into the hard domains. Only the rigid blocks actually incorporated into the hard phase contribute to the physical properties.

Previous studies on the structure-property relationships of elastomeric polyurethanes have been published by Critchfield and co-workers mostly on thermoplastic urethane (TPU)² with some on reaction-molded polyurethane (RIM).¹ The thermoplastic polyurethanes consisted of polycaprolactone diols, butane diol extender, and diphenylmethane diisocyanate (MDI) or toluene diisocyanate (TDI). Stress at 100% elongation (100% modulus) is shown in Figure 1 as a function of hard-segment content and polyol molecular weight. Increasing both the hard-segment content and the polyol molecular weight increased the 100% modulus. This latter result is opposite to what would be expected based on rubber elasticity theory, which states that the modulus is proportional to crosslink density (or the polyol equivalent weight in this case). For the RIM polyurethane, increasing the polyol molecular weight was found to increase the

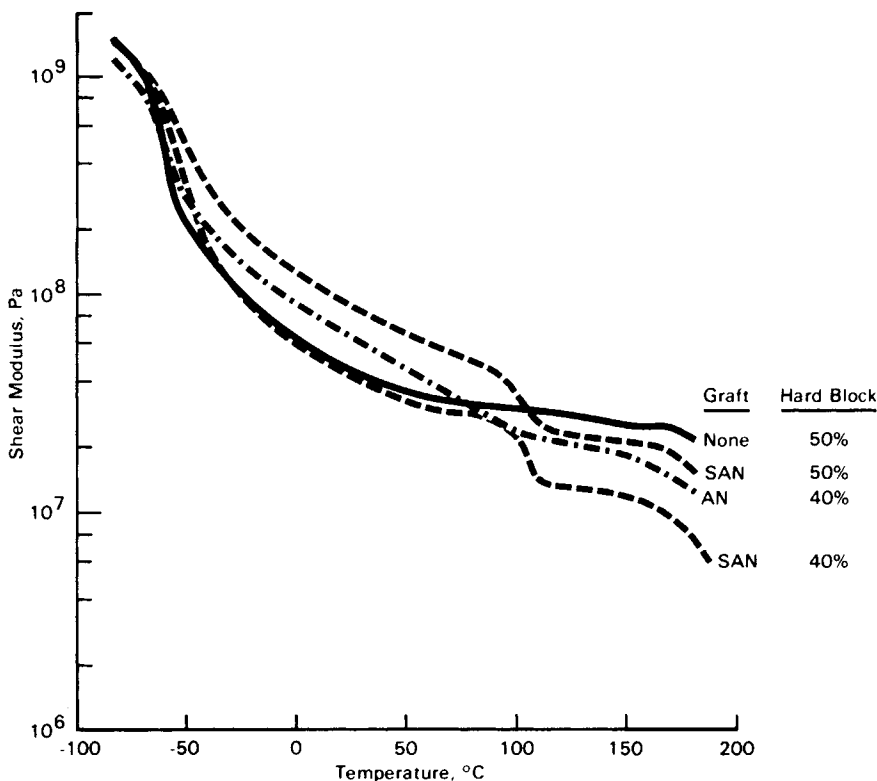


Fig. 7. Effect of graft polyol and hard-block content on modulus-vs-temperature response.

high-temperature modulus while simultaneously reducing T_g . Apparently with the higher molecular polyols a higher percentage of the rigid segments are incorporated into the hard phase. At constant hard-segment content, the MDI thermoplastic polyurethanes had a lower T_g and higher 100% modulus, while the TDI samples had a higher ultimate strength and elongation. The RIM polyurethanes had about the same ratio of low-temperature to high-temperature moduli measured at -29° and $+66^\circ\text{C}$ for both isocyanates.

Our approach to developing the one-component resin has been to survey a number of polyurethane formulations for sufficient pot life by following the viscosity as a function of time. The mechanical properties were then optimized primarily by determining the modulus-versus-temperature curves, which gave both the transition temperatures and the modulus values over the temperature range of interest.

EXPERIMENTAL

The materials used are listed in Table I. The sample nomenclature is by a character string giving in order the isocyanate, polyol, extender, and hard-segment percentage using the symbols in Table I. Thus, M667EG60 is a compound of Isonate 181, P667 polyol, ethylene glycol with 60% hard-segment content. Hard-segment content is calculated as the weight percent of isocyanate plus chain extender in the resin.

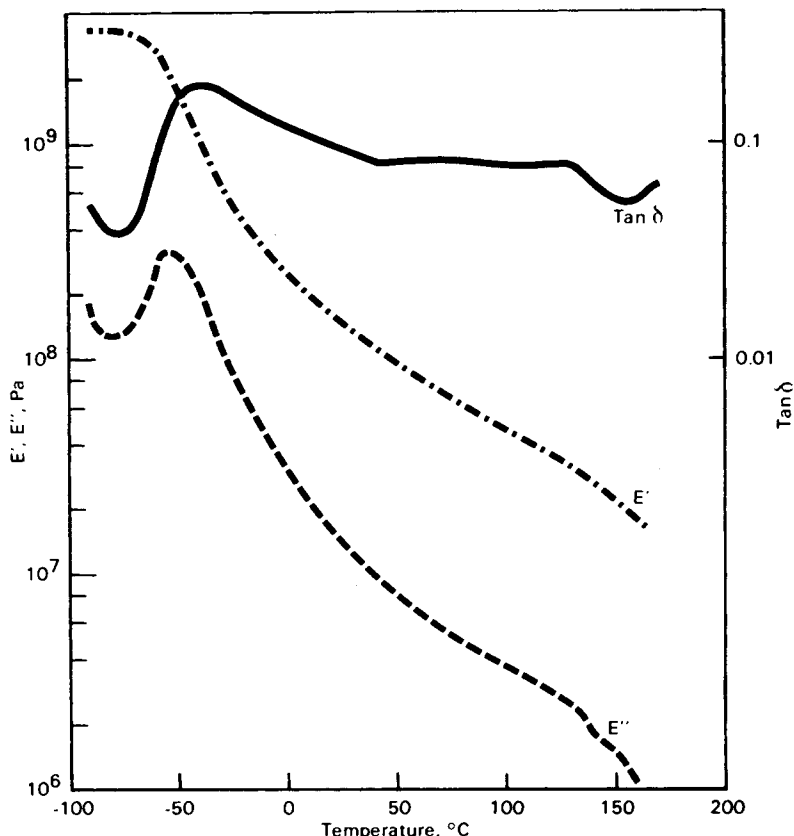


Fig. 8. Dynamic modulus for M667EG50 at 3.5 Hz.

Samples were prepared for initial property screening by dispersing the powdered HQEE and zinc stearate catalyst into the polyol, mixing in the isocyanate, casting into a mold, then curing in a compression press generally at 150°C for 15 min.

Resin was prepared for injection molding in a two-step process. First the HQEE and zinc stearate were dispersed into the polyol, generally at 100–120°C. After cooling to room temperature, the isocyanate was stirred into the polyol mixture.

Injection-molded samples were obtained with a Model 75 New Britain injection molding machine. It has a nominal 38-mm diam. screw with a 72-cm³ shot capacity and 9×10^5 N (100 ton) press. A standard thermoplastic screw with check ring and a water-jacketed barrel were used. ASTM D790 flexural modulus samples (100 × 25 × 3.2 mm) were molded with a 1.6-mm deep fan gate. Nominal molding conditions were: barrel temperature, 10°C; mold temperature, 150°C; mold closed time, 2 min; injection pressure, 10 MPa.

The shear modulus was measured with a Gehman torsion stiffness tester using samples with dimensions 3 × 1.9 × 28 mm gauge and a heating rate of 2°C/min. Dynamic Young's modulus measurements were made with a Model DDV-III-C Rheovibron on samples with dimensions 6 × 1.9 × 35 mm gauge length. Flexural modulus was measured according to ASTM D790 on 75 × 25 × 3.2 mm samples.

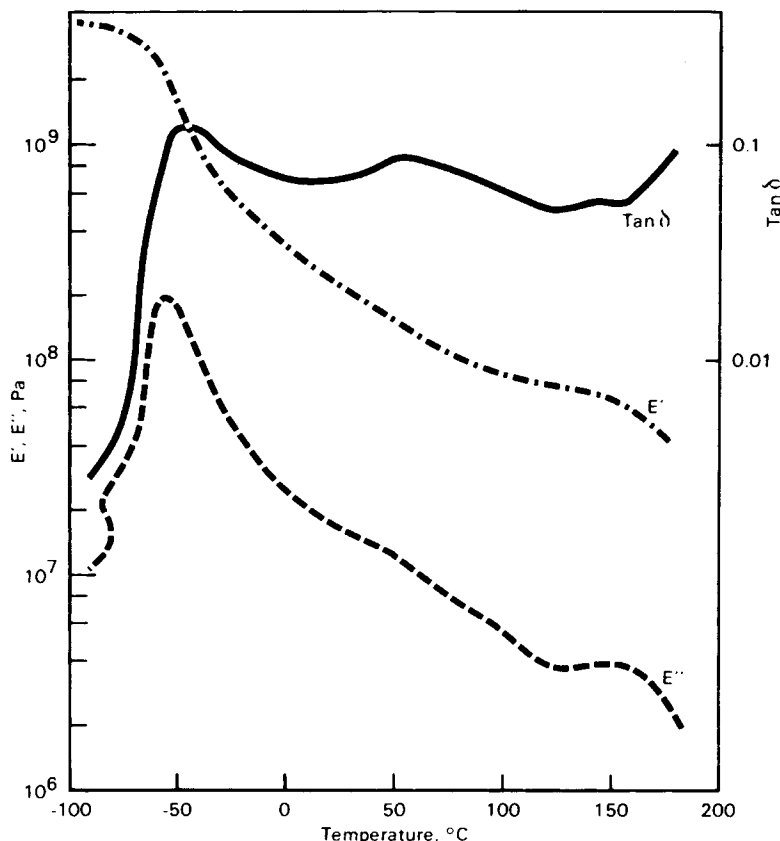


Fig. 9. Dynamic modulus for M667EE50 at 3.5 Hz.

RESULTS AND DISCUSSION

The first phase in developing a one-component polyurethane resin was to determine the type of resin system which would produce a sufficient pot life. Figure 2 shows the viscosity–time curves for several polyurethane formulations all containing 50% hard block: TDI–primary polyol, MDI–primary polyol, and MDI–secondary polyol. The TDI and the secondary polyol gave the longest pot life formulations and thus from this viewpoint are the best candidates for one-component formulations.

The initial mechanical property survey was accomplished by measuring the shear modulus as a function of temperature. The cure was catalyzed with zinc stearate which had little effect on the reaction rate at room temperature and thus did not affect the pot life of the resin. The modulus–temperature curves are shown in Figure 3. These results show that the primary polyol–MDI polyurethane gives the highest modulus values. Thus, from a mechanical property consideration, the system which gave the shortest pot life is required to give the suitable physical properties.

Within the constraint of the fast kinetics of the MDI–primary polyol system, the pot life can be increased only by reducing the reactive group concentrations. Since this is a second-order reaction,³ reducing the polyol and isocyanate concentrations by a factor of 2 would reduce the reaction rate by a factor of 4, substantially increasing the pot life.

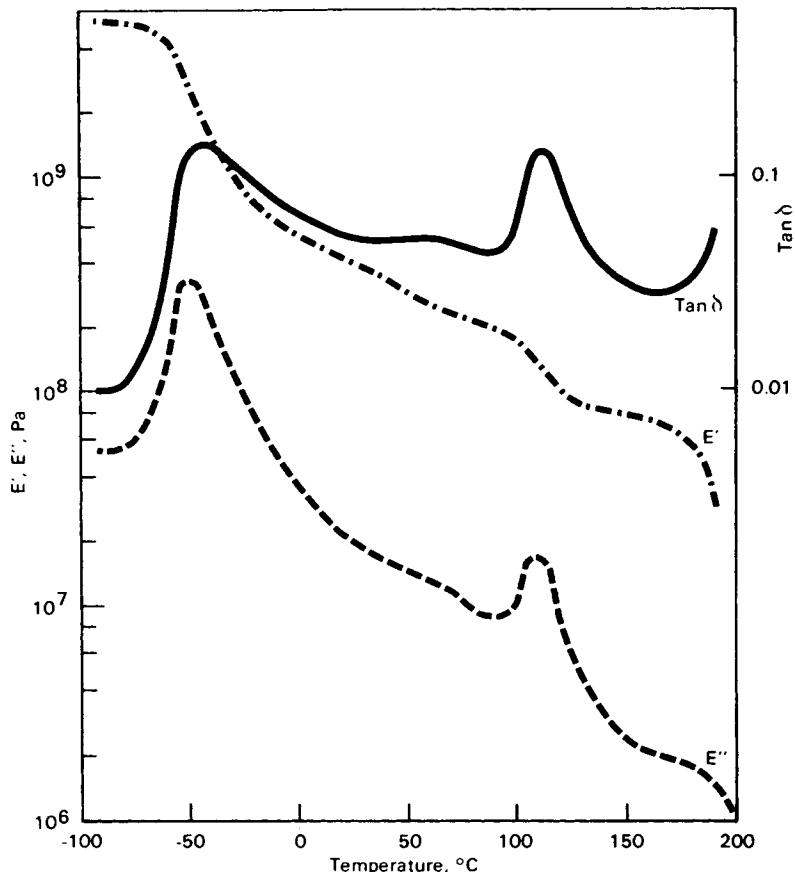


Fig. 10. Dynamic modulus for M581EE40 at 3.5 Hz.

The effectiveness of a graft polyol in increasing the modulus of the polyurethanes was also tested. These polyols contain 20% of a vinyl polymer polymerized "in situ" and grafted to the polyol.⁴ Two types of graft polyol were evaluated: one contained acrylonitrile (AN) and the other styrene acrylonitrile (SAN) as the vinyl polymer. Figure 4 shows that a substantial increase in the modulus was obtained, since the graft polyol samples with 50% hard block content have about the same modulus values as the nongraft sample at 60% hard block content. Thus, a reduction in the isocyanate and hydroxyl concentrations was obtained but not enough to substantially increase the pot life.

In the 50% hard-block formulation, the extender contributes nearly ten times as many hydroxyls as the polyol to the reaction mixture. Thus, removing the extender from the hydroxyl concentration should substantially reduce the reaction rate. This was accomplished by substituting hydroquinone di(β -hydroxyethyl) ether (HQEE), a solid dihydroxyl compound insoluble in the reaction mixture, for the ethylene glycol chain extender. The ethylene glycol formulation gelled within $\frac{1}{2}$ hr, while the HQEE-extended formulation was fluid for nearly 4 hr as is demonstrated in Figure 5. This now gives a polyurethane formulation with sufficient pot life for convenient processing.

The modulus-temperature curves in Figure 6 show that substituting HQEE

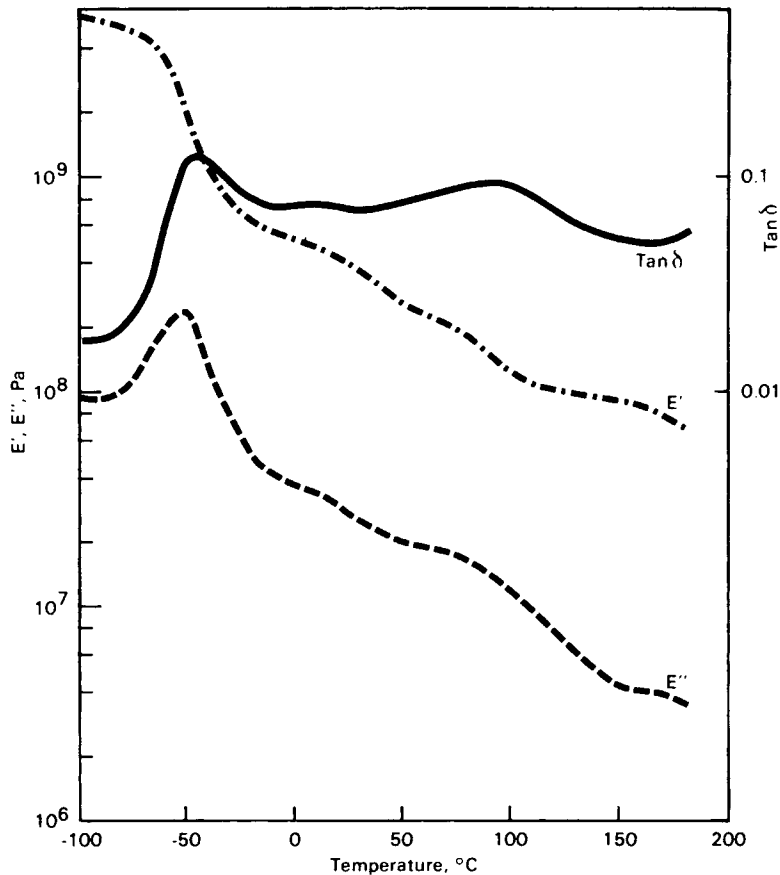


Fig. 11. Dynamic modulus for MANEE40 at 3.5 Hz.

for ethylene glycol in the polyurethane substantially increases the modulus. At 50% hard segment, the modulus of the HQEE-extended polyurethane is nearly equal to that of the 60% hard-segment ethylene glycol-extended sample below 50°C and superior to it at higher temperatures. Besides the higher modulus, the HQEE-extended material also has a much shallower slope in the rubbery plateau region, giving much improved properties at elevated temperatures. This effect should be very important for applications such as fascias which require stiffness at higher temperature combined with low-temperature flexibility.

Substituting a graft polyol in the formulation results in a further increase in the modulus due to the rigidity of the grafted polymer. As seen in Figure 7, the AN and SAN graft polyols gave similar modulus-temperature curves, with the main difference being the step in the SAN graft sample near 100°C caused by the SAN T_g . The graft polyol samples require only 40% hard-segment content to have the same modulus values as the nongraft samples at 50% hard-segment content. Thus, the combination of HQEE extender and graft polyol permits an overall reduction in hard-segment content from the 60% required for the nongraft ethylene glycol samples to 40%. A corresponding reduction in isocyanate level is also obtained.

The dynamic modulus (E'), loss modulus (E''), and damping ($\tan \delta$) are shown

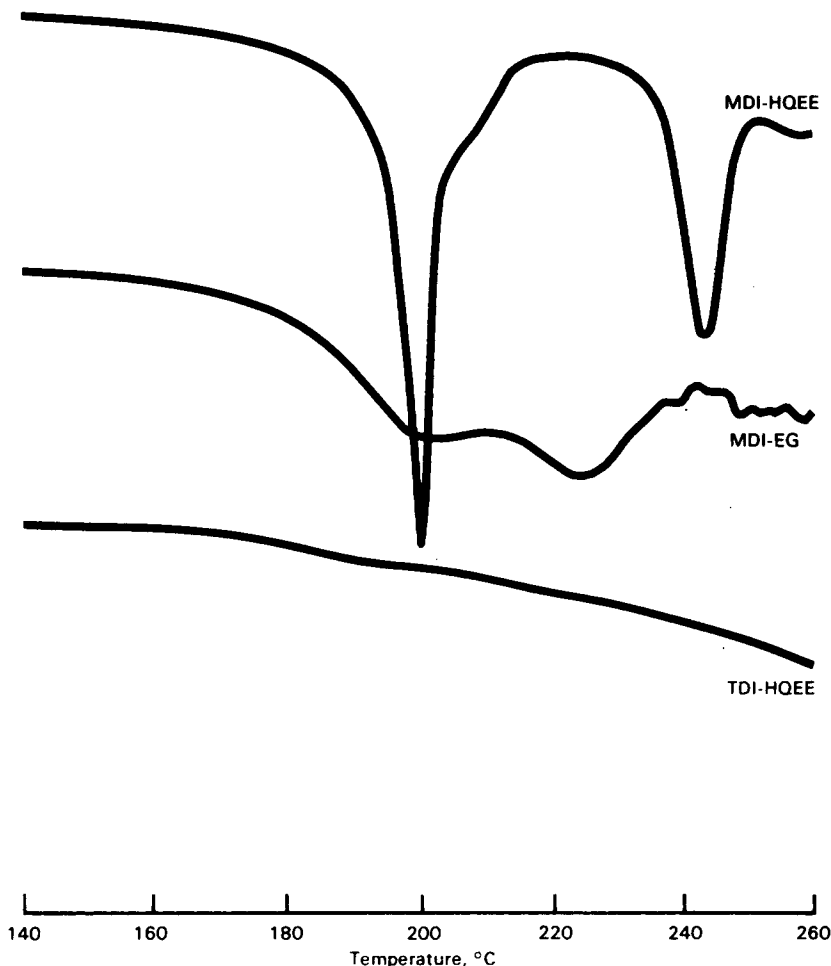


Fig. 12. Effect of isocyanate and extender on DSC curves.

as a function of temperature for several polyurethane formulations in Figures 8–11. The ethylene glycol-extended sample, M667EG50 (Fig. 8), shows a T_g at -55°C , then a smooth decrease in modulus until the hard-phase transition was approached at 160°C . The HQEE-extended sample, M667EE50 (Fig. 9), had a more horizontal modulus curve. Thus, while both samples had similar modulus values at 25°C , the HQEE-containing polymer was nearly three times stiffer than the other at 150°C . A damping maximum at 60°C associated with a slight dip in the modulus curve indicates a transition associated with the HQEE. This may be a partial solubility of the very short hard block segments in the soft phase at this temperature. The SAN graft T_g at 110°C is clearly visible in the curves for M581EE40 (Fig. 10). The broad damping about 90°C for the MANEE40 sample (Fig. 11) is not seen with the other polyols and is probably associated with the AN T_g .

DSC and x-ray both showed evidence of increased crystallinity in the HQEE-containing samples. All the HQEE samples showed strong exotherms at about 200 – 210°C (Fig. 12). A smaller exotherm occurred at 240 – 250°C . The

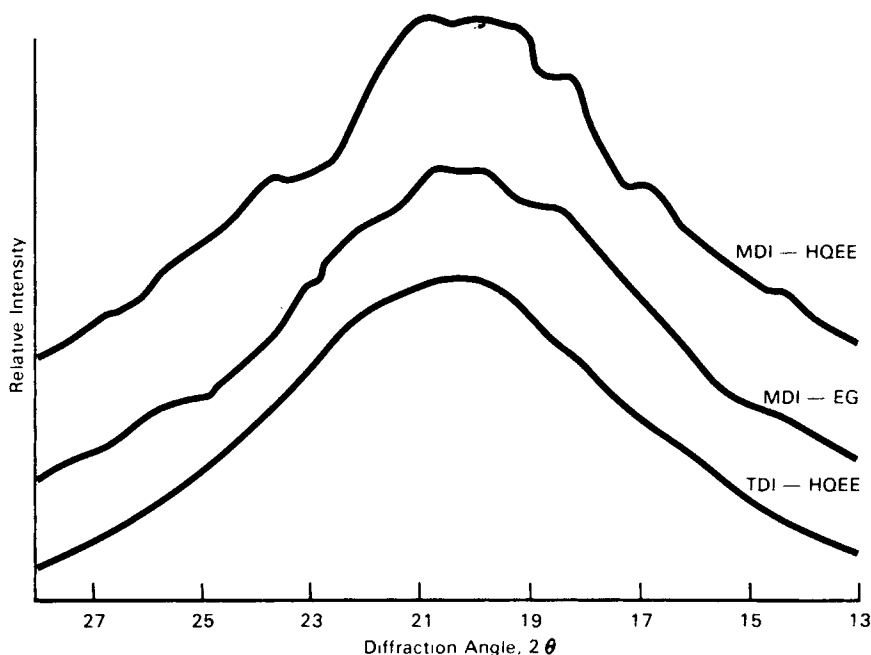


Fig. 13. Effect of isocyanate and extender on x-ray scans.

HQEE itself melts at 105°C, so the high temperature peaks must be the HQEE-MDI adducts. The ethylene glycol samples have broad shallow peaks at 210 and 225°C. The x-ray scans (Fig. 13) show peaks at scattering angles (2θ) of 19°, 21°, and 24°. The ethylene glycol-extended samples show weaker peaks at 2θ of 18°, 20°, and 25.5°. Both measurements show the HQEE-extended material to have more crystalline content in the hard segments accounting for the increased high-temperature modulus compared to ethylene glycol-containing polyurethanes.

It was hoped that the improved properties obtained with the HQEE-MDI samples might also be obtained with TDI. It was found however that this was not the case. Instead, the modulus-versus-temperature curves for these samples in Figure 14 show a single broad transition extending from -80 to 110°C. This is in contrast to the relatively sharp T_g 's and broad rubbery plateau regions observed for the MDI samples. The data indicates compatibility between the hard and soft blocks rather than phase separation into hard and soft domains. Also, x-ray and DSC scans (Figs. 12 and 13) confirm the absence of hard-segment crystallinity. The rigid segments appear to be soluble in the soft phase as evidenced by the single T_g and lack of crystallinity resulting in poorer properties for the TDI material.

The mechanical properties of the HQEE-extended polyurethane are listed in Table II. The ratio of the moduli tested at -29 and 70°C is used as a measure of the flatness of the modulus-temperature response over the temperature range desired in automotive applications. The value of 2.7 obtained for the HQEE formulation is very good. The 2-min mold-closed time appeared to give a complete cure, as no change in properties was obtained with increased cure times. The zinc stearate is definitely catalyzing the cure; samples prepared without the catalyst exhibited very poor elongation even after curing for 1 hr at 150°C.

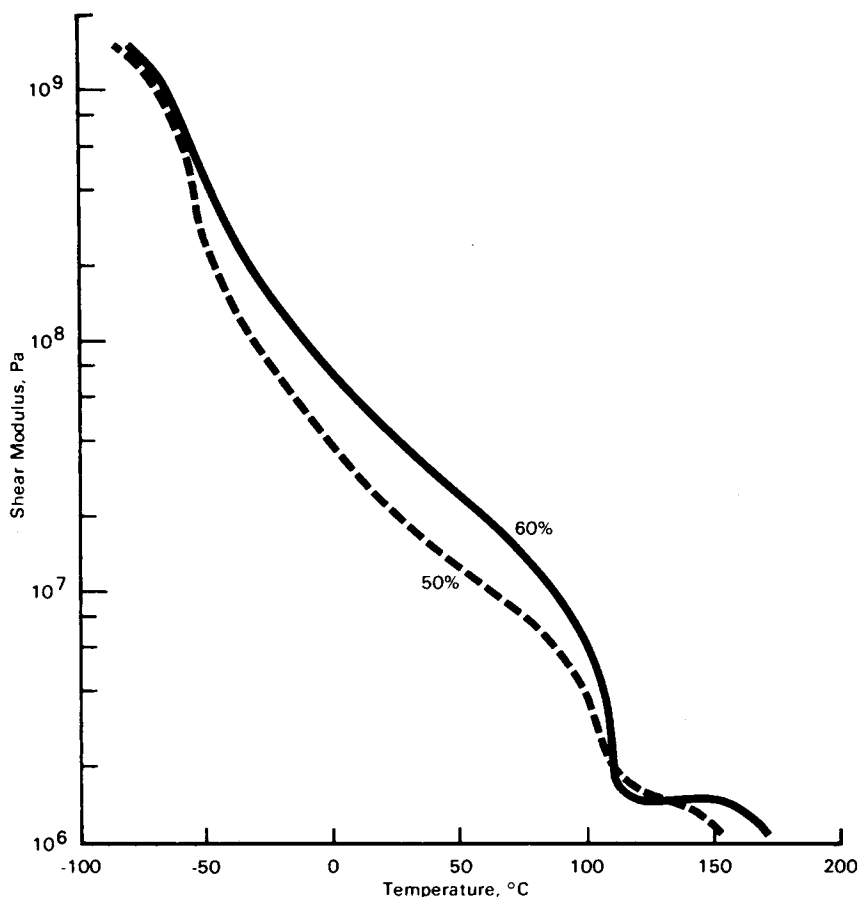


Fig. 14. Modulus-temperature response for TDI-HQEE formulations containing 50% and 60% hard block.

TABLE II
Comparison of Mechanical Properties of M581EE40 to RIM

	M581EE40	RIM ^a
Flex modulus, MPa		
-29°C	425	450
23°C	230	210
70°C	160	83
121°C	52.4	—
163°C	35.2	—
Modulus ratio (-29°C/70°C)	2.7	5.4
Tensile properties (at 23°C)		
100% Modulus, MPa	15	—
Ultimate strength, MPa	18	19
Elongation, %	240	185

^a Data from Ferrari et al.⁵

The modulus-versus-temperature curves for the M667EE50 and M581EE40 formulations are compared to a typical RIM material in Figure 15. The HQEE samples show a substantial reduction in the temperature dependence of the

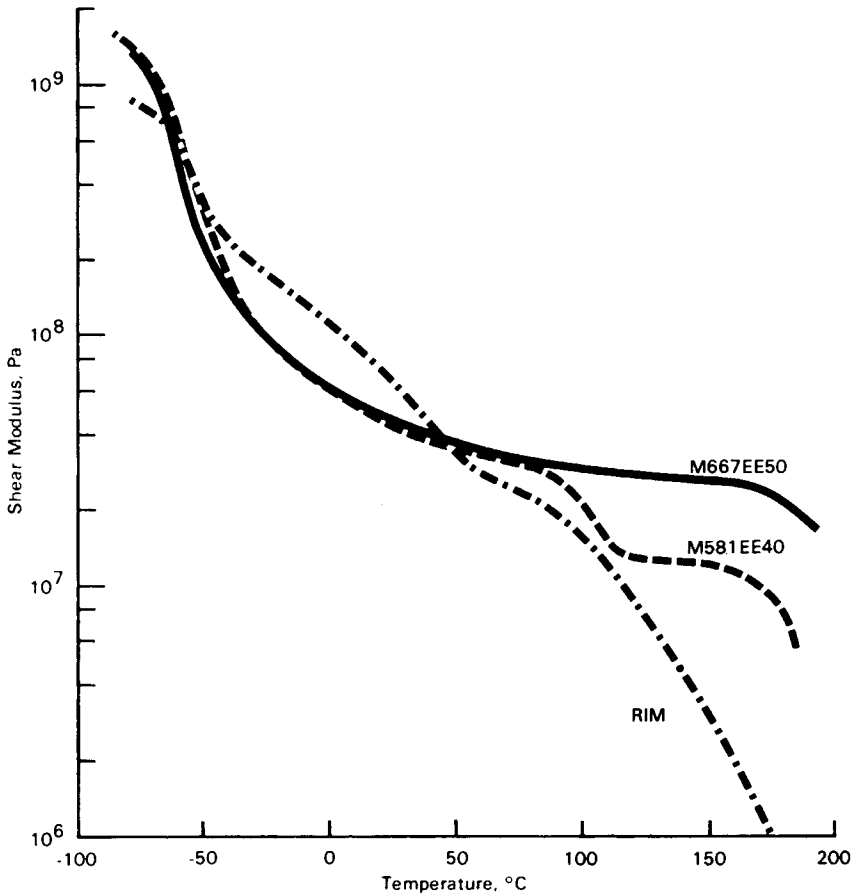


Fig. 15. Modulus-temperature response. Comparison of one-component polyurethanes with RIM material.

modulus over the range of -20 to $+100^{\circ}\text{C}$. The mechanical properties of M581EE40 and RIM are compared in Table II. The HQEE-extended polyurethane had nearly twice the modulus of the RIM at 70°C without using any postcure. The increased modulus at elevated temperatures is important in maintaining the dimensional stability of molded parts during painting operations.

In summary, a polyurethane formulation has been developed which has a sufficient pot life at room temperature for practical processing yet cures rapidly at 150°C . Incorporating HQEE in the polyurethane formulation has improved the modulus obtained with a given hard-block content. The modulus at elevated temperatures was especially improved and should be of use in applications where higher-temperature exposures are encountered.

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