

Morphology of Polyurethane- Isocyanurate Elastomers

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Synopsis

The dynamic viscoelastic properties and thermal transition behavior of reaction injection molding (RIM) and cast polyurethane-isocyanurate elastomers have been studied as a function of various segments (soft and hard urethane, and hard isocyanurate) content. RIM and cast elastomers were prepared at different concentrations of soft and hard urethane, and hard isocyanurate segments. RIM elastomers with the higher isocyanate index (lower hard urethane and greater isocyanurate segment content) displayed an unchanged T_g (glass transition temperature of soft segment) and increasing T_{gh} (glass transition temperature of hard segment) related to the hard urethane and isocyanurate segments. This is due to the phase separation between the soft and the hard segments. Cast elastomers synthesized from the higher amount of 1,4-butanediol (greater hard urethane and less hard isocyanurate segment content) showed an increasing T_{gs} , decreasing T_{gh} of hard urethane segments, and an unchanged T_{gh} of isocyanurate segments. This is related to the phase mixing between the soft and the hard urethane segments and the phase separation of hard isocyanurate and hard urethane segments.

INTRODUCTION

Polyurethane elastomers are multiblock copolymers consisting of hard and soft segments.¹ The hard segment is the reaction product of diisocyanate and chain extender (diol or diamine); the soft one is formed from the long chain polyester or polyether polyol. The hard and soft portions of the multiblock urethane chains are generally incompatible, and undergo microphase separation into hard and soft domains.¹ This is the main reason for the excellent mechanical properties of these materials, i.e., hard domains act as reinforcing fillers and pseudo-crosslinks.

Recently, polyurethanes with isocyanurate, urea, oxazolidone, and carbodiimide groups²⁻⁴ have been prepared generally to produce modified polyurethanes with enhanced high temperature properties. The thermal resistance (i.e., degradation temperature) of these linkages may be classified as: isocyanurate > oxazolidone > carbodiimide > urea > urethane > biuret > allophanate.⁶⁻⁸ The presence of isocyanurate groups in elastomers increases the crosslink density. This, together with the fact that the decomposition temperature of the heterocyclic isocyanurate is quite high, results in their excellent high temperature properties.

In this paper, various isocyanurate-containing polyurethane elastomers were prepared and their morphologies characterized. The effect of diffusion time, segment compatibility, type of elastomers [reaction injection molding (RIM) vs. cast], and other variables on the hard urethane and isocyanurate segments was determined.

EXPERIMENTAL

Materials

Two types of urethane-isocyanurate elastomers were studied, cast and RIM elastomers. The RIM elastomers were composed of modified 4,4'-diphenylmethane diisocyanate (Isonate 191, Upjohn), an ethylene oxide capped polyoxypropylene adduct of glycerol containing 21 wt % grafted polyacrylonitrile (Niax 31-28, Union Carbide) and 1,4-butanediol (BD, GAF Corp.).

The cast elastomers were prepared from 4,4'-diphenylmethane diisocyanate (MDI, Mobay), polyoxytetramethylene diol (Polymeg 1000, MW = 1000, Quaker Oats), and BD. The catalyst for the urethane reaction was dibutyltin dilaurate (T-12, M & T Chemicals). An ammonium carboxylate (Dabco TMR, Air Products) and *N,N,N''*-tris(dimethylaminopropyl) hexahydrotriazine (Polycat 41, Abbott Labs.) were used as trimerization catalysts due to their well-known activity in forming isocyanurate groups.⁹⁻¹¹

The polyols and chain extender were dried and degassed at 80°C under vacuum for 16 h. All other chemicals were used as received without further purification.

Preparation of Elastomers

RIM Elastomers

The polyol (Niax 31-28) was mixed with chain extender (BD), modified MDI (Isonate 191), and trimerization catalyst (Dabco TMR). The blend was mixed for 30–50 s using a high speed stirrer, and poured into a preheated mold (6 × 6 in.), placed on a laboratory platen press at 100°C for 5–10 min. After demolding, the samples were then post-cured in a circulating air oven at 120°C for 1 h. The isocyanate index (NCO/OH × 100) was varied in order to obtain elastomers with different isocyanurate contents.

Cast Elastomers

NCO-terminated prepolymers were synthesized by reacting isocyanate (MDI) and polyol (Polymeg 1000) at different ratios of NCO/OH in a resin kettle equipped with a heating mantle, stirrer, thermometer, and nitrogen inlet. The reaction was carried out at 70°C until the product reached the anticipated isocyanate content (as determined by the di-*n*-butylamine titration method¹²).

The chain extender (BD) and trimerization catalyst (Polycat 41) were added to the prepolymer and thoroughly mixed. The mixture was poured into a preheated mold and placed on a laboratory platen press and cured for 1 h at 110°C. Samples were then post-cured in an oven at 100°C for 16 h, and conditioned at 25°C and 50% relative humidity for 7 days prior to testing.

Characterization Methods

Dynamic Viscoelastic Properties

A Rheovibron dynamic viscoelastometer, Model DDV-II (Toyo Measuring Instruments Co.), was utilized to measure the dynamic viscoelastic properties of the elastomers. The thickness of the samples was 10–20 mils. The heating rate was 1–5°C/min. Measurements were made at 110 Hz from –120 to 190°C.

Differential Scanning Calorimetry (DSC)

The thermal transition behavior was studied on a Perkin-Elmer Differential Scanning Calorimeter, Model DSC-2. The sample weight was about 20 mg. It was heated from 50 to 250°C at a heating rate of 20°C/min.

RESULTS AND DISCUSSIONS**RIM Elastomers**

The formulations and segment contents of RIM elastomers synthesized from Isonate 191, Niax 31-28, BD, and trimerization catalyst (Dabco TMR) are summarized in Table I. The Rheovibron and DSC results are shown in Figures 1 and 2 and Table I.

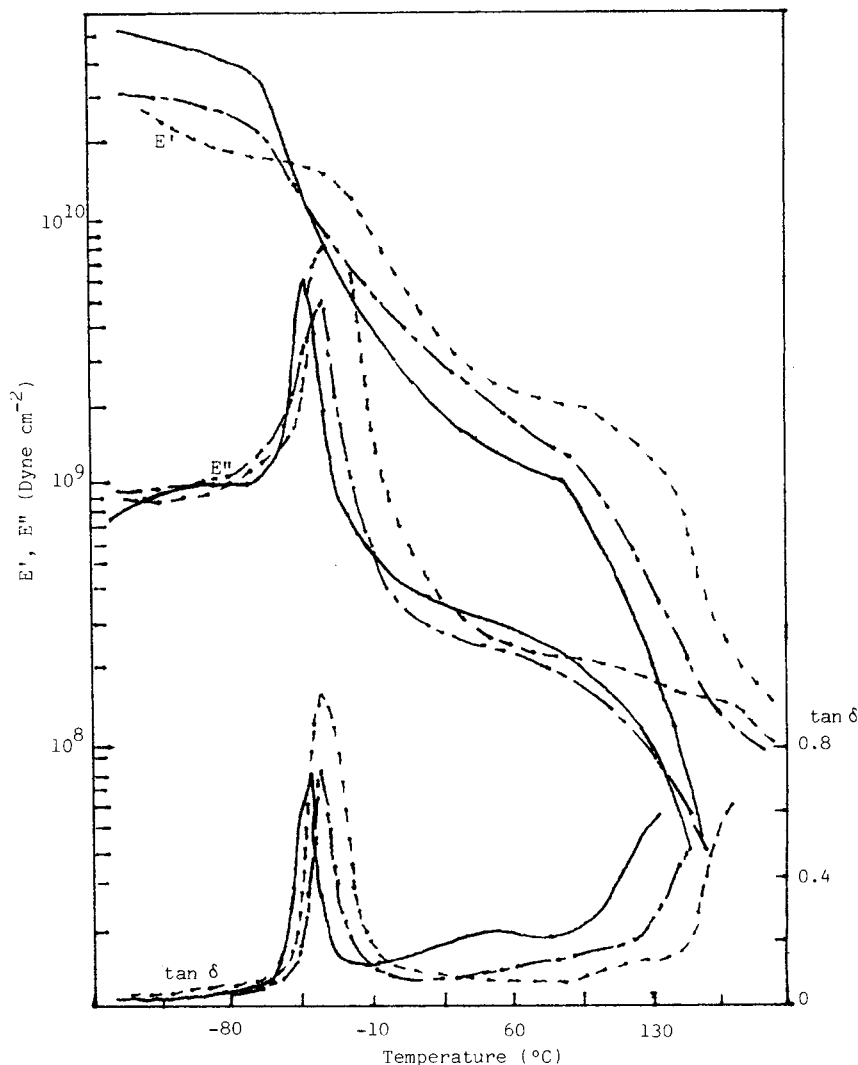


Fig. 1. Temperature dependence of dynamic storage modulus E' , loss modulus E'' , and loss tangent for RIM elastomers having various isocyanate indices: (—) II = 107; (---) II = 125; (- · -) II = 150.

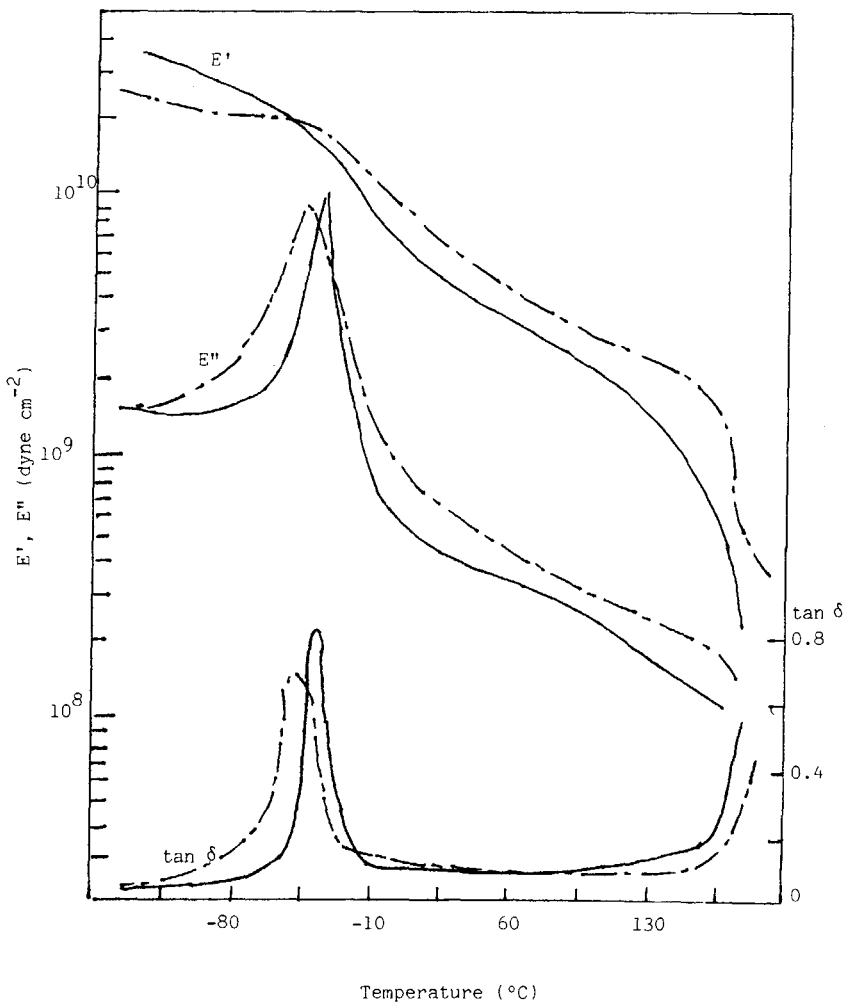


Fig. 2. Temperature dependence of dynamic storage modulus E' , loss modulus E'' , and loss tangent for RIM elastomers having various isocyanate indices: (—) II = 175; (---) II = 200.

TABLE I
Formulations of RIM Elastomers:BD/Niix 31-28 = 15/85 (weight ratio)

Isocyanate index	107	125	150	175	200
Polymer polyol (Niix 31-28) (g)	62.9	59.3	55	51.2	48
MDI Isocyanate (Isonate 191) (g)	41.5	45.7	50.8	55.2	59.1
Chain extender BD (g)	11.1	10.5	9.7	9	8.5
Catalyst Dabco TMR (g)	0.2	0.2	0.2	0.2	0.2
Soft segment (theoret wt %)	57.7	54.7	51.1	48	45.1
Hard segment (theoret wt %)	42.3	45.3	48.9	52	54.9
Hard urethane segment (wt %)	40.3	38.2	35.7	33.5	31.5
Hard isocyanurate segment (wt %)	2	7.1	13.2	18.5	23.4
DSC, T_g (°C)	169	170,215	207	212	216

The isocyanate indices, II, of the elastomers were 107, 125, 150, 175, and 200, respectively. As the isocyanate index of elastomers increases, so does the hard isocyanurate content, while the hard urethane segment content decreases. As can be seen in Figures 1 and 2, a greater value of E' at $T > T_{gs}$ was found in the elastomers having the higher II. This is due to the greater crosslink density resulting from the isocyanurate groups.¹³ As the isocyanate index of the elastomers was raised, the E'' and $\tan \delta$ peaks associated with T_{gs} slightly broadened and shifted toward higher temperatures. The magnitude of $\tan \delta$ peaks related to T_{gs} remained almost unchanged. Because the polyether polyol (Niax 31-28) is trifunctional and contains grafted polyacrylonitrile, there may be a restriction in phase mixing between hard and soft segments. Another $\tan \delta$ peak and E' drop corresponding to T_{gh} appeared at the higher temperatures. When the II of the elastomers continued to increase, the $\tan \delta$ peaks and E' drops associated with T_{gh} moved toward higher temperatures. The samples also became too soft to continue the Rheovibron measurements above 160°C, and DSC results must be relied upon for further information about T_{gh} .

The DSC results confirmed the existence of a glass transition for the hard segments. For the elastomers with II = 107, which have the least amount (2 wt %) of isocyanurate segments, only one T_{gh} appears (169°C). This is due to the hard urethane segments. The acrylonitrile grafts showed no transition (T_g of polyacrylonitrile is 98°C¹⁴) since the content of polyacrylonitrile in the elastomers is only about 10 wt %. There are two T_{gh} 's for the elastomers with II = 125 (7 wt % isocyanurate segments): one at 170°C, the other at 210°C. The lower T_{gh} (170°C) belongs to the hard urethane segments, the higher one (210°C) is related to the hard isocyanurate segments. When the II of elastomers increases to 150, 175, and 200, respectively, only one T_{gh} is observed, close to the higher temperature T_{gh} peak. As the content of isocyanurate segments in RIM elastomers becomes significant (above 7 wt %), the reactivity of RIM elastomers apparently is too high to allow sufficient time for the hard urethane and the hard isocyanurate segments to separate (diffuse). Therefore, these two hard segments are mixed together to form one hard phase. The greater T_{gh} value of elastomers having the higher II is due to the larger content of isocyanurate segments.

Cast Elastomers

The formulations and segment contents of cast elastomers synthesized from MDI, Polymeg 1000, BD, and catalysts (T-12 and Polycat 41) are shown in Table II. The DSC and Rheovibron results of elastomers are shown in Table II and Figures 3 and 4. As the amount of BD used to prepare the elastomers increased, the hard urethane segment content increased while the isocyanurate content decreased. It was found that the higher E' value above T_{gs} for cast elastomers having the least amount of BD is due to the greater crosslink density (isocyanurate segment content). As the content of hard urethane segments increased, E'' and $\tan \delta$ peaks corresponding to T_{gs} decreased in magnitude and broadened. Another $\tan \delta$ peak associated with T_{gh} of the hard urethane segments was also found at higher temperatures (it also broadened). The $\tan \delta$ peaks of T_{gs} shifted toward higher

TABLE II
Formulations of Cast Elastomers

MDI/Polymeg 1000/BD (equiv ratio)	4/1/0	4/1/0.5	4/1/1	4/1/1.5	4/1/2
NCO/OH		2.67	2	1.6	1.3
Catalyst T-12 (wt %)	0.005	0.005	0.005	0.005	0.005
Catalyst Polycat 41 (wt %)	0.08	0.08	0.08	0.06	0.06
Soft segment (theoret wt %)	54.2	52.9	51.7	50.6	49.5
Hard segment (theoret wt %)	45.8	47.1	48.3	49.4	50.5
Hard urethane segment (wt %)	11.4	19.1	26.4	33.4	40.1
Hard isocyanurate segment (wt %)	34.4	28	21.9	16	10.4
DSC, T_g (°C)	204	188	184	173	170
		204	205	204	204

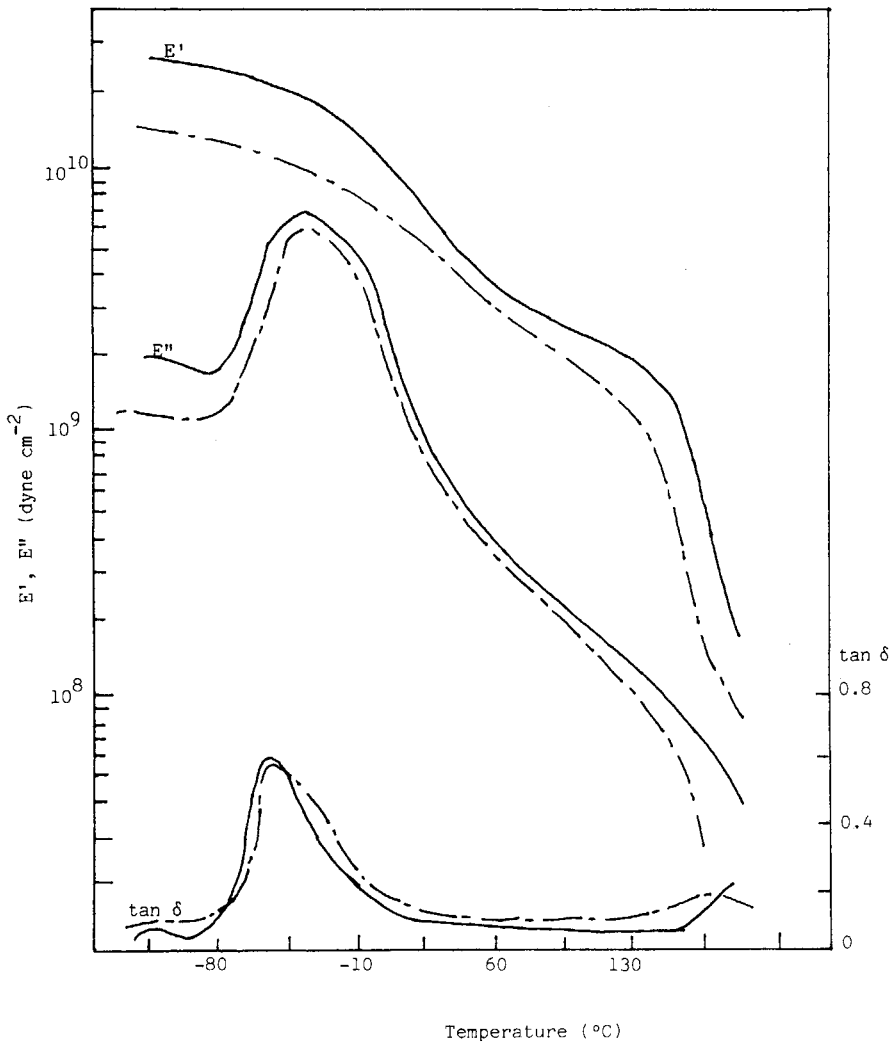


Fig. 3. Temperature dependence of dynamic storage modulus E' , loss modulus E'' , and loss tangent for cast elastomers: (—) 4/1/0; (---) 4/1/0.5.

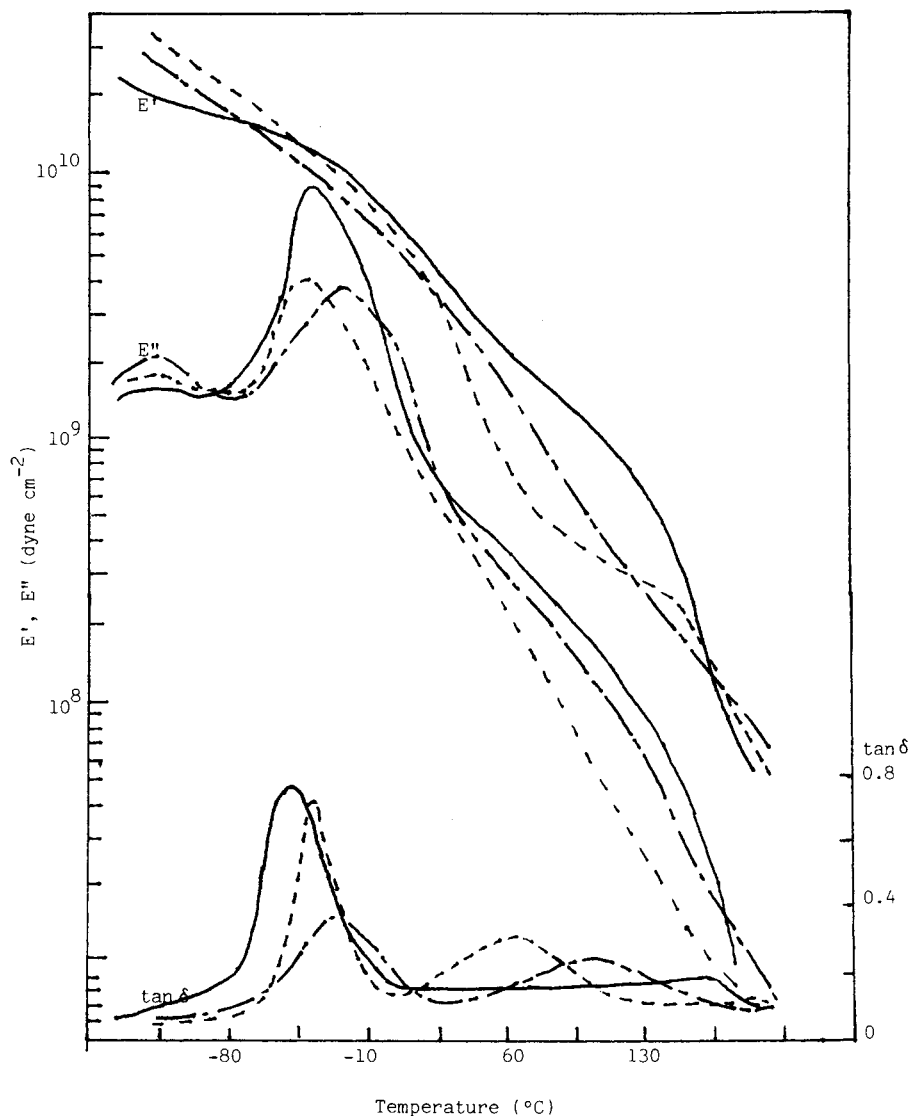


Fig. 4. Temperature dependence of dynamic storage modulus E' , loss modulus E'' , and loss tangent for cast elastomers: (—) 4/1/1; (— —) 4/1/1.5; (- - -) 4/1/2.

temperatures and those of T_{gh} related to the hard urethane segments moved toward lower temperatures.^{15,16} There is thus some phase mixing between soft and hard urethane segments in cast MDI elastomers. It is much easier for the hard urethane segments to dissolve in the linear chain of soft segments (Polymeg 1000).

The DSC results verify this behavior. For the elastomers having the ratio of MDI/Polymeg 1000/BD at 4/1/0 (containing the greatest amount of hard isocyanurate segments), only one T_{gh} (204°C) corresponding to isocyanurate segments is observed. As the content of hard urethane segments increases, another T_{gh} , related to the hard urethane segments, appears. The temper-

ature of this transition decreases as the urethane segment content increases, while the temperature of the isocyanurate transition remains unchanged. The reaction rate for cast elastomers is much slower than that for RIM elastomers, thereby providing more time for diffusion and subsequent phase separation. The hard urethane and isocyanurate segments thus possess two distinct glass transition temperatures, respectively, and therefore must form their own separate phases. It is also possible that the prepolymer technique used to prepare these cast elastomers (as opposed to the one shot technique for RIM elastomers) results in the formation of a separate isocyanurate phase.

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