Role of Functionality in MDI-Based Elastomer Preparation

WALLY L. CHANG,* TOM BARANOWSKI, and TOM KARALIS

Witco Corporation, Polymer R&D Laboratories, Chicago, Illinois 60638

SYNOPSIS

In our study of functionality, a control 4,4'-diphenylmethane diisocyanate (MDI)-based elastomer prepared from a linear polyester and a linear chain extender was compared to (1) those having functionality synthesized into the backbone of the polyester and (2) those having the functionality added as part of the chain extender package. A wide range of physical and mechanical properties of the finished elastomers were compared. The resultant information offers a strong basic understanding of the role of functionality in an MDI-based polyester elastomer and also provides the complex chemical relationships involved in formulating a desired elastomer. This information will better enable the urethane researcher and manufacturer to pick and choose those attributes of elastomeric functionality that are necessary to fulfill their needs. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polyurethane chemistry and technology have grown enormously in scope and importance in the last 40 years and now provide a very broad spectrum of products.[1,2] The role of functionality in urethane elastomeric preparation has taken on new importance as demanding uses for polyurethane elastomers continue to increase in an expanding global market. In this era of competitive product quality and cost consciousness, research and development can be used to systematically select those products that result in premium urethane performance, thus enabling the urethane manufacturer to supply the best product for a desired application at the lowest possible price. This threefold study was undertaken in an effort to evaluate the role of functionality as an integral part of product performance.

In control phase I, a 1000 equivalent weight ($\sim$ 56 hydroxyl number) of linear poly(ethylene adipate)glycol was reacted with 4,4'-diphenylmethane diisocyanate (MDI) to form a prepolymer having a NCO % of roughly 6.80. The resulting prepolymer was then extended with 1,4-butanediol and compression cast into standard ASTM plaques and buttons.

In phase II, 1000 equivalent weight of branched poly(ethylene adipate)glycols with varying levels of trimethylolpropane (TMP), synthesized into the backbone of the polyols, were compression-molded into standard ASTM plaques and buttons using MDI and extended with 1,4-butanediol (1,4BD). Phase III again used a 1000 equivalent weight of linear poly(ethylene adipate)glycol and various combinations of 1,4BD and TMP as chain extenders, reacted with MDI.

The hard-segment content [(MDI + 1,4BD + TMP)/(MDI + 1,4BD + TMP + polyester) × 100%] was held constant at 34 wt % for all reactions in all phases. We determined a range of physical and thermal properties and compared the results of the phase I control to the phase II backbone functionality and to the phase III extender functionality. This information presented will lead to a more proficient choice in polyol and extender, enabling the urethane elastomer producer to furnish premium performance products.

EXPERIMENTAL

Prior to elastomer preparation, all the polyester glycols, the 1,4-BD, and the TMP were vacuum-de-

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hydrated to a moisture content of less than 0.03% by weight. MDI was handled per manufacturer's recommendation and was decanted and filtered at 50°C to eliminate any insolubles. The materials are listed in Table I.

The control phase I elastomer was made by following standard prepolymer production, i.e., a calculated amount of dry poly(ethylene adipate)glycol at ~ 70°C was added to MDI at 50°C with stirring under a nitrogen blanket. The prepolymer was then synthesized for 3 h at a controlled temperature of 80°C. NCO % analysis confirmed the finished prepolymer, which was then extended with 1,4-BD.

All cross-linked elastomers, phases II and III, were prepared by the so-called one-shot process, i.e., all coreactants mixed in a single step. Designation and preparation methods are outlined in Table I.

The I.I. [isocyanate index, (NCO/OH) × 100] was 105 for all elastomers. Elastomers were cast into ASTM plaque and button molds, preheated to 110°C, cured at ~ 120°C for 1 h in the mold, and postcured at 100°C for at least 16 h. Cured elasto-

mers were then conditioned at room temperature for a minimum of 1 week prior to testing.

Using Chang's equation, functionality was calculated at 2.0 for the phase I control elastomer and at levels of 2.3, 2.5, 2.8, and 3.0 for phase II and III elastomers. Differentiation of the elastomers uses the following system as outlined in Table I:

TO Phase I control elastomers, having no added TMP with a functionality of 2.0.

TS Phase II elastomers, having the TMP functionality synthesized into the backbone of the 1000 equivalent weight of branched poly(ethylene adipate)glycols. The numerical value following the TS designation indicates the amount of functionality.

TH Phase III elastomers, having the functionality as a result of TMP addition into the extender (hard-segment) portion of the elastomer. Again, the numerical value following the TH designates the amount of functionality.

Table I Designation of Materials and Products

Designation	f	EW	MW	Description	Supplier
EG	2.0	31.0	62	Ethylene glycol	Texaco
1,4BD	2.0	45.0	90	1,4-Butanediol	Arco
TMP	3.0	44.7	134	Trimethylolpropane	Celanese
AA	2.0	73.0	146	Adipic acid	DuPont
Organotin				Organotin compound	Witco
22-56-2.0	2.0	1000.0	2000	PEAG-2000	Witco
1022-56-2.3	2.3	1000.0	2300	PTEAG-2300	Witco
1022-56-2.5	2.5	1000.0	2500	PTEAG-2500	Witco
1022-56-2.8	2.8	1000.0	2800	PTEAG-2800	Witco
1022-56-3.0	3.0	1000.0	3000	PTEAG-3000	Witco
MDI	2.0	125.0	250	4,4'-Diphenylmethane diisocyanate	BASF

Elastomers	Method	Phase	Hard %	Description	Appearance
TO2.0	Prepolymer	I	34	MDI/(22-56-2.0)–1,4BD	Opaque
TS2.3	One-shot	II	34	MDI/(1022-56-2.3)–1,4BD	Opaque
TS2.5	One-shot	II	34	MDI/(1022-56-2.5)–1,4BD	Opaque
TS2.8	One-shot	II	34	MDI/(1022-56-2.8)–1,4BD	Opaque
TS3.0	One-shot	II	34	MDI/(1022-56-3.0)–1,4BD	Opaque
TH2.3	One-shot	III	34	MDI/(22-56-2.0)–1,4BD/TMP(f = 2.3)	Transparent
TH2.5	One-shot	III	34	MDI/(22-56-2.0)–1,4BD/TMP(f = 2.5)	Transparent
TH2.8	One-shot	III	34	MDI/(22-56-2.0)–1,4BD/TMP(f = 2.8)	Transparent
TH3.0	One-shot	III	34	MDI/(22-56-2.0)–TMP(f = 3.0)	Transparent

f: functionality; EW: equivalent weight; MW: molecular weight; PEAG: poly(ethylene adipate)glycol; PTEAG: poly(trimethylolpropane/ethylene adipate)glycol.

RESULTS AND DISCUSSION

Functionality

We calculated the functionality of the hydroxyl-terminated polyester resins and extenders using the following equations derived by W.L.C.:

1. Equation for Polyester Functionality:

$$f = \frac{2}{1 - (n - 2) \cdot EW/Y} \quad (1)$$

where f is the functionality of polyol; n, the functionality of the modifier; EW, the equivalent weight of polyol $(56,100/OH^{\#})$; and Y, the yield based on 1 mol of modifier.

Simplified equations using different modifiers are illustrated in Table II. A typical polyester formulation and calculated functionality is shown in Table III.

The functionality of mixed chain extenders can be calculated as follows:

2. Equation for Chain Extender Functionality:

$$f = \frac{\sum f_i N_i}{\sum N_i} \quad (2)$$

where f is the functionality of mixed chain extenders; f_i, the functionality of individual chain extenders; and N_i, the molar number of individual chain extenders.

Also, the hydroxyl number of mixed chain extenders can be obtained by the following equation:

$$OH_m^{\#} = \frac{\sum N_i \cdot MW_i \cdot OH_i^{\#}}{\sum N_i \cdot MW_i} \quad (3)$$

or

$$OH_m^{\#} = \frac{\sum W_i \cdot OH_i^{\#}}{\sum W_i} \quad (4)$$

Table II Functionality of Polyesters EG + AA + (Modifier)$_n$

Modifier	n	Example	f
R—OH	1	C_8H_{17}—OH	$2/(1 + EW/Y)$
R—(OH)$_2$	2	HO—(CH$_2$)$_4$—OH	2
R—(OH)$_3$	3	TMP or glycerine	$2/(1 - EW/Y)$
R—(OH)$_4$	4	Pentaerythritol	$2/(1 - 2EW/Y)$

Table III Polyester Formulation and Calculated Functionality

EG	1033 g
TMP ($n = 3.0$)	134 g (1 mol)
AA	2433 g
Organotin catalyst	0.12 g
Total weight	3600 g
H$_2$O	−600 g
Yield	3000 g
OH$^{\#}$	56.1
f	3.0

Calculation of functionality: $EW = 56100/56.1 = 1000$; $Y = 3000$; $f = 2/(1 - 1000/3000) = 3.0$.

where $OH_m^{\#}$ is the hydroxyl number of mixed chain extenders; $OH_i^{\#}$, the hydroxyl number of individual chain extenders; N_i, the molar number of individual chain extenders; MW_i, the molecular weight of individual chain extenders; and W_i, the weight of the individual chain extenders.

Appearance

Table I differentiates between the clarity appearance of the finished compression cast elastomers. Note that the TO control and TS elastomers are opaque, whereas the elastomers having the functionality added as a part of the extender, TH, are transparent. This can be explained as a function of the TMP breaking down the crystallinity of the hard segment in the TH series, thus approaching a more uniform phase mixing between hard-segment domains and soft-segment matrix throughout the elastomers.[3-6]

Hardness

At 30°C, elastomers made by increasing the functionality in the backbone of the polyester (TS series) produce a very slight increase in Shore A hardness over the TO elastomer. Functionality increases in the hard-segment TH elastomers initially show a much softer Shore hardness than that of the TO control and TS elastomers. However, as was the trend in the TS series, a gradual increase in hardness occurs as the functionality increases (Fig. 1). Of interest is the Shore A hardness over temperature variation. Using an environmental chamber and starting at −60°C, conditioned elastomer plaques were checked for Shore A hardness at 10°C increment increases terminating at 150°C.

Figure 1 compares results of the TS series with the control TO. The TO elastomer shows a more pronounced hardness drop off than does the TS se-
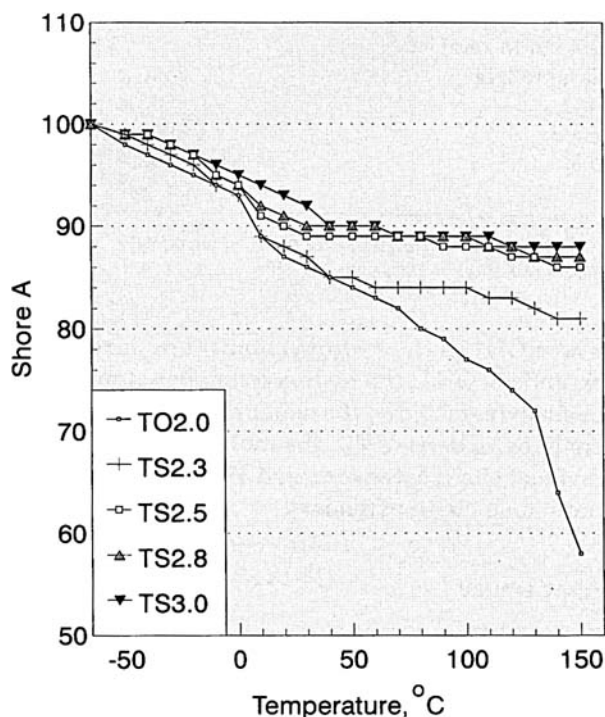
MDI Elastomers
Hard Segment 34%

Figure 1   Shore A of TS series vs. temperature.

ries, which tends to stabilize in increasing order of the amounts of functionality present. At temperatures nearing 130°C, a rapid drop off occurs in the TO elastomers as the melting point is approached. Figure 2 verifies the stabilizing effect on Shore A hardness at higher temperatures by adding functionality, this addition occurring in the extender, TH. Again, increasing functionality increases the leveling point of the Shore A hardness. Note the rapid and continued drop off in Shore A hardness of the elastomer (TO2.0) as compared to the leveling effect of the cross-linked materials. At temperatures below 120°C, the hardness decreases as follows:

TS > TO > TH

However, at temperatures above 120°C, the hardness decreases as follows:

TS > TH > TO

It can be concluded that functionality is advantageous to those elastomers exposed to elevated temperatures that require retention in hardness.

Strength

It can be seen very clearly in Table IV that tensile strengths ranged from a low of 2100 psi for the TH3.0 elastomers to approximately 6000 psi for the TO and TS2.3 and TS2.5 elastomers. Of notable interest is that we found that the TS elastomers do not exhibit any appreciable decrease in tensile strength until the TS2.8 functionality level is approached. Likewise, the TH elastomers, although significantly lower in tensile strengths than their TS counterparts, again show a substantial drop in tensile as the TH2.8 functionality level is approached. Examining the tensile modulus at 100%, two factors are evident:

1. The TS series exhibits a substantially higher modulus than does the TO control series with corresponding increases in stress as the functionality increases. This indicates a more rigid elastomer, which is to be expected as the number of reactive sites per molecule increase.
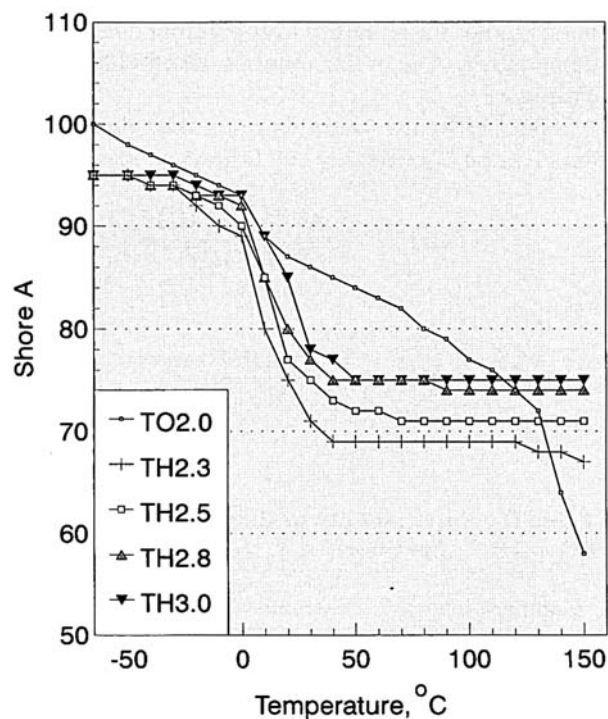
MDI Elastomers
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Figure 2   Shore A of TH series vs. temperature.

Table IV Physical Properties of MDI Elastomers: Hard Segment 34%

Elastomer	Tensile Strength (psi)	100% Modulus (psi)	Elongation (%)	Tear Die C (pli)	Tear Trouser/Split (pli)	Compression 25%	Bashore (%)
TO2.0	6000	856	590	620	525	35	31
TS2.3	6000	971	565	471	152	15	30
TS2.5	6000	1000	445	387	84	13	27
TS2.8	4500	1149	360	288	65	11	25
TS3.0	4200	1172	320	256	60	9	22
TH2.3	3500	429	315	91	39	1	3
TH2.5	3285	488	215	96	44	1	3
TH2.8	2500	645	170	81	42	1	7
TH3.0	2166	907	145	78	41	1	9

2. The TH2.3, TH2.5, and TH2.8 elastomers initially exhibit a substantially lower modulus than does the TO control series; however, they show the same augmented stress as the functionality increases. The TH3.0 elastomer shows approximately the same stress modulus as that of the TO2.0 control.

Table IV also details the ultimate elongation and tear results. As expected, the relationship to functionality is inverse, increased functionality resulting in decreased elongation and tear strength.

The TS series elongation and tear strengths fare much better than those of the TH, showing a gradual decline as functionality increases. The TH2.3 series shows a rapid drop off in tear strength from the TO2.0 control series, but the loss in tear strength remains relatively stable as functionality increases.

Compression Set

Table IV shows the tremendous improvement in compression set results by incorporation of functionality into the elastomers. The TS2.3 series shows an immediate improvement of over 57% from the control TO elastomer and continued gradual improvement at functionality approaching TS3.0. The improvement from the control in the TH series is even more evident. The results show that incorporation of a functionality level of 2.3 in the extender of the elastomer improves compression set by approximately 95%. Additional increases in levels above TH2.3 do little to further enhance this improvement.

Bashore Rebound

An interesting result occurs in the rebound of these elastomers by embodying functionality (Table IV).

The TS series gradually loses Bashore Rebound as the functionality increases from TS2.3 to TS3.0.

The TH elastomers show a tremendous initial drop in rebound from the control followed by a gradual increase as the functionality approaches the TH2.8 to TH3.0 level. In this application, it can be generalized that the addition of functionality is detrimental to rebound.

Flexibility

The role of functionality on flexibility was determined by use of the Ross Flex Machine. Our test procedure uses a texon backing adhered to the elastomer for added tension against the specimen. The 10 mm wide by 6 in. long texon-backed sample was then center-nicked (1 mm), placed in the flexor, and allowed to condition overnight at $-18°C$ ($0°F$). The number of Ross flex cycles for the nick to increase to 500% cut growth and 1000% cut growth (total failure) were recorded (Table V).

The TO2.0 elastomer showed no cut growth at the conclusion of the 50,000 cycle test. Incorporation of functionality has an immediate detrimental effect

Table V Flexibility vs. Functionality at 0°F ($-18°C$) of MDI Elastomers: Hard Segment 34%

Cycles	500%	Failure	50,000 Cycles
TO2.0	Good	Good	Good
TS2.3	5,000	11,800	Failure
TS2.5	4,100	8,000	Failure
TS2.8	2,200	5,000	Failure
TS3.0	1,200	2,500	Failure
TH2.3	500	1,500	Failure
TH2.5	40	135	Failure
TH2.8	40	125	Failure
TH3.0	40	125	Failure

Table VI   Weight % Increase in Solvents After 3 Days at 25°C of MDI Elastomers: Hard Segment 34%

Elastomer	EtOH	IPA	MEK	Toluene	EtOAc	BuOAc	H_2O
TO2.0	9	4.0	68	29	54	29	1.3
TS2.3	10	3.4	57	29	51	30	1.3
TS2.5	10	3.5	58	29	52	30	1.3
TS2.8	9	3.0	47	27	44	27	1.3
TS3.0	9	3.3	55	27	48	29	1.3
TH2.3	12	3.0	68	31	59	38	1.3
TH2.5	13	3.4	73	30	59	41	1.3
TH2.8	12	3.2	59	29	59	38	1.7
TH3.0	11	3.0	61	29	65	36	1.7

on flexibility. The TS series had a maximum flexural strength of 11,800 cycles to failure at TS2.3 with a rapid decrease as functionality increased. Placing the cross-linking in the extender, TH series, fared even worse: from a high of 1500 cycles to total failure at TH2.3 to a mere 125 cycles as the functionality approached 2.8.

Solvent Absorption

In our solvent-absorption test, three preweighed $\frac{1}{2}$ in. wide $\times$ 4 in. long $\times$ ~ 0.075 in.-thick samples of elastomer were immersed by suspending them from a stainless-steel wire in a sealed glass jar containing each of the seven solvents listed in Table VI. After 3 days at 25°C, the samples were removed from the solvents, dried as fast as possible with paper toweling, and immediately weighed. The % increase between the preweight and finished weight of the three samples was averaged and recorded in Table VI.

In general, the functionality levels of 2.8 and 3.0 in the TS elastomers show a slight improvement over the TO control elastomer, whereas the TH

elastomers indicate a slight loss of resistance to absorption in the majority of solvents tested. However, as can be seen by the table, and factoring in the subjectivity of the test method, there are neither significant improvements nor detractions in solvent absorption by incorporating functionality into the elastomers.

Solvent Resistance

A more conclusive result on the effect functionality has on solvent resistance was obtained by following a similar procedure to the solvent-absorption test except that ASTM tensile dumbbells were substituted for the rectangular absorption samples and the immersion period was extended from 3 to 7 days.

The % decrease in tensile strengths are shown in Table VII. Correlating tensile results to solvent resistance shows the following trends:

All elastomers tested show a decrease in tensile strength properties after the 7-day immersion. The TO series retained the greatest amount of tensile strength in all cases. The TS series showed the next

Table VII   Percentage Retention of Tensile Strength in Different Solvents for 7 Days at 25°C: Hard Segment 34%

Elastomer	EtOH	IPA	MEK	Toluene	EtOAc	BuOAc	H_2O
TO2.0	66	81	23	60	28	43	95
TS2.3	54	74	23	52	27	41	94
TS2.5	48	47	16	27	25	31	74
TS2.8	34	51	16	28	22	26	73
TS3.0	29	43	16	27	21	24	53
TH2.3	19	28	6	16	10	12	66
TH2.5	15	13	6	15	9	11	31
TH2.8	13	19	6	14	8	10	28
TH3.0	10	24	6	10	2	6	27

amount of retention with loss of tensile generally correlating to the amount of functionality synthesized into the backbone of the polyester. The TH series had the least amount of tensile retention with more loss in tensile as the functionality increased. The conclusion here is that the addition of functionality does not improve the solvent resistance of the MDI-based elastomers.

Dynamic Mechanical Analysis (DMA)

Glass Transition Temperature

Figures 3 and 4 depict the effect of functionality on the glass-transition temperature (T_g) of the elastomers by use of the dynamic mechanical analyzer (TA 983 DMA Analyzer with Thermal Analyst 2100 Control/Acquisition Data System). The results verify the detrimental effect of cross-linking on T_g. The TS series shows a gradual increase in T_g as the functionality increases. The TH series shows a rapid
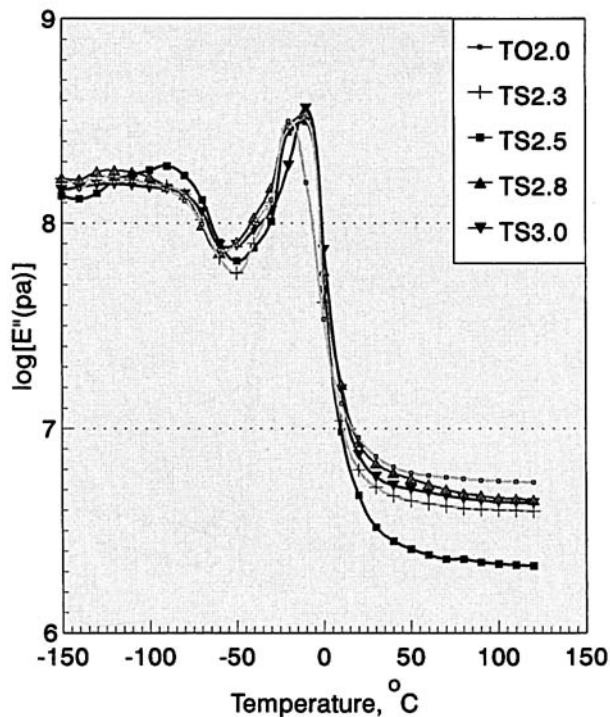
MDI Elastomers
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Figure 3   Loss modulus E'' of TS series vs. temperature.

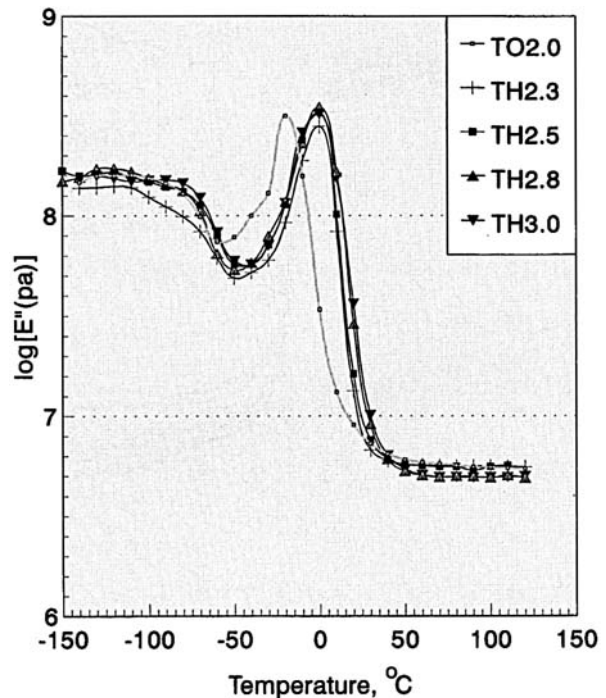## MDI Elastomers
Hard Segment 34%

Figure 4   Loss modulus E'' of TH series vs. temperature.

increase in T_g, which remains relatively stable as the functionality increases. Again, we attribute this to the breakdown in the crystallinity of the hard segment, resulting in more phase mixing between the hard domains and soft matrix.

Storage Modulus

As the hard-segment morphology of the TO and TS elastomers is the same, there are no significant differences in storage modulus between these elastomers (Fig. 5). The TH series exhibit no significant differences in storage modulus at temperatures below T_g. However, at temperatures above T_g, we observed significant differences between the TO and TH elastomers. We attribute this decline in TH storage modulus to the breakdown in the crystallinity of the hard segment from the addition of TMP. The resulting amorphous hard segment allows for more phase mixing between the hard and soft segments and, thus, the downward shift in storage modulus (Fig. 6). The results of these tests and the transparent appearance of the TH elastomers as first
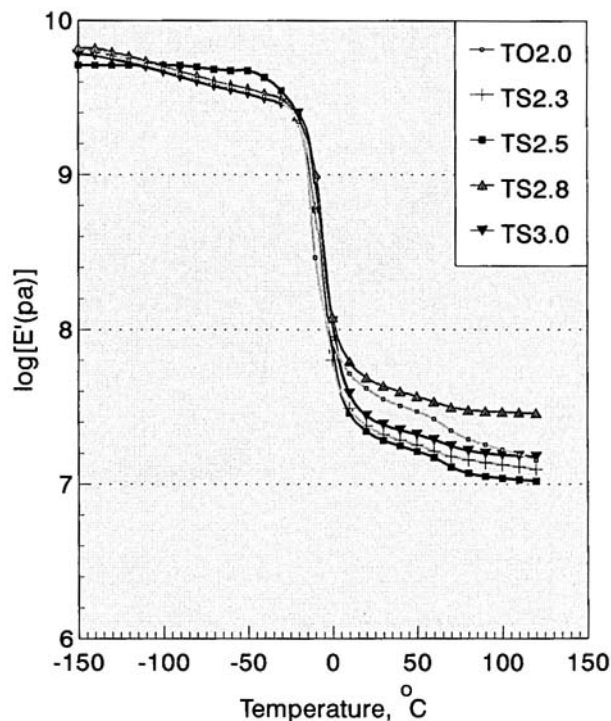
MDI Elastomers
Hard Segment 34%

Figure 5 Storage modulus E' of TS series vs. temperature.

described in Table I give further credence to the crystallinity breakdown/phase mixing explanation.

Thermogravimetric Analysis (TGA)

Addition of functionality to the elastomer does not significantly change its resistance to thermal degradation. In this test, using the thermogravimetric analyzer (TA 951 TGA Analyzer with Thermal Analyst 2100 Control/Acquisition Data System), samples are exposed to heat increases of 5°C/min under air until decomposition occurs. All samples show approximately the same temperature point (300°C) degradation regardless of the presence or amount of functionality.

CONCLUSION

A comprehensive study comparing the effect of functionality as backbone and extender cross-linking to a control MDI-linear polyester elastomer was investigated (Table VIII).

The following results outlining the effects of functionality were obtained:

Enhancements

1. Appearance—Functionality added to the extender of the elastomer results in a transparent product.
2. Hardness—A wide range of hardness variations can be obtained by varying the placement and amount of cross-linking while retaining the same hard-segment percentage of the overall elastomer.
3. Functionality is extremely advantageous to those elastomers, requiring excellent resistance to compression set.
4. Synthesis of functionality into the backbone of the polyester improves 100% tensile modulus.
5. Resistance to hardness loss at elevated temperature is enhanced by incorporation of functionality.
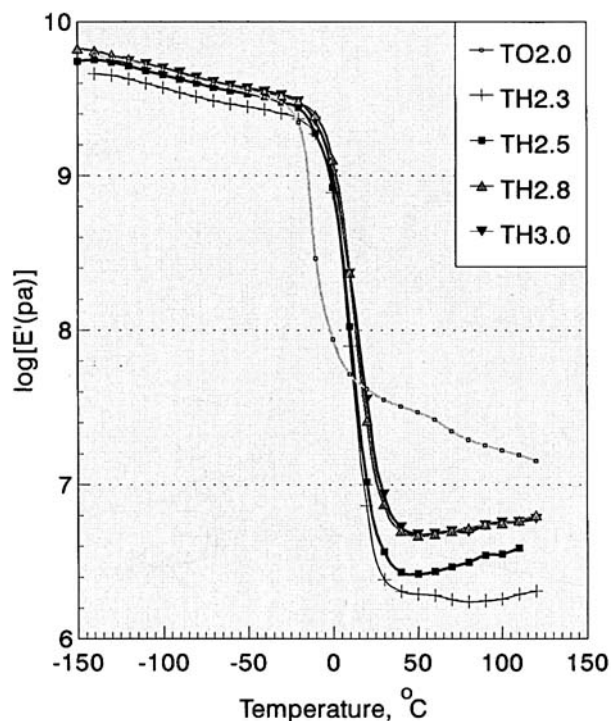
MDI Elastomers
Hard Segment 34%

Figure 6 Storage modulus E' of TH series vs. temperature.

Table VIII   Comparison of Physical Properties

	TO2.0	TS2.3	TS2.5	TS2.8	TS3.0	TH2.3	TH2.5	TH2.8	TH3.0
Appearance	Opaque	Opaque	Opaque	Opaque	Opaque	Transparent	Transparent	Transparent	Transparent
Shore A, 30°C	Control	1	1	1	1	-4	-3	-2	-1
Shore A, 150°C	-4	-2	-1	0	0	-3	-2	-1	-1
Tensile	Control	0	0	-2	-3	-3	-4	-4	-4
100% Modulus	Control	1	2	3	4	-4	-3	-2	0
Elongation %	Control	-1	-2	-3	-4	-4	-5	-6	-6
Die C tear	Control	-1	-2	-3	-5	-7	-7	-7	-7
Split tear	Control	-5	-6	-7	-7	-8	-8	-8	-8
Compression set %	Control	-5	-5	-6	-6	-10	-10	-10	-10
Bashore rebound	Control	-1	-2	-3	-4	-10	-10	-8	-7
Flexibility	Control	-4	-5	-6	-7	-8	-9	-10	-10
Solvent absorption	Control	0	0	0	0	0	0	-1	-1
Solvent resistance	Control	-1	-2	-3	-4	-7	-7	-8	-8
Decomposition temp.	Control	0	0	0	0	0	0	0	0
T_g	Control	1	1	1	1	7	7	7	7
Storage modulus, below T_g	Control	0	0	0	0	0	0	0	0
Storage modulus, above T_g	Control	0	0	0	0	-4	-3	-2	-2

+, increase; −, decrease; 0, no significant change.

6. Rebound of the elastomers, as indicated by the Bashore Rebound results, can be varied by the placement and amount of functionality.

Detriments

1. Strength properties of overall tensile, tear, and elongation decrease as functionality is introduced.
2. No improvement in solvent resistance was observed by the addition of functionality.
3. Functionality causes an increase in the T_g of the elastomers.
4. Addition of functionality does not improve or detract from thermal degradation.

This work is offered as one source of information enabling the urethane researcher and manufacturer to better choose the final formulatory necessary to meet their needs. However, other factors such as processing conditions, type of isocyanate, stoichiometry, polyester backbone, molecular weight, and type of extender should also be factored when determining the final effect on the urethane elastomer.

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