

Quasi-Prepolymers for High-Performance Applications

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ABSTRACT

Polyurethane molded elastomers prepared by reacting 4,4'-diphenylmethane diisocyanate (MDI)-terminated prepolymers with certain polyfunctional, active hydrogen chain extenders produce elastomeric materials with unique physical and mechanical properties that are distinctly better than those of cold-curing or one-shot polyurethane systems. However, the low percentage of free isocyanate groups (% free NCO) results in high ratios of prepolymer to chain extender and high viscosities. Processing is therefore less flexible, requiring higher temperatures and specialized equipment.

In this paper a new group of MDI quasi-prepolymers (with 23% free NCO) are described. They are liquid at room temperatures and can be processed with conventional one-shot processing equipment at similar ratios, but exhibit properties superior to conventional one-shot systems. By manipulating the backbone linkages, wide ranges in properties and hardness are achieved with ease of processing. This flexibility now allows quasi-prepolymers to be used for a range of applications in the industrial, transportation, sports and leisure industries.

Another objective of this paper is to characterize structure-property relationships of quasi-prepolymers, contrasting them with conventional prepolymers and one-shot polyurethane systems. By testing these elastomers under static and dynamic conditions, the effect of polymer structure on static and dynamic properties is revealed.

INTRODUCTION

In-line skating, the equivalent of high-tech roller skating, is riding a popularity wave that started in the 1980s and has been growing since 1990. To meet this increasing world-wide demand the skating industry has

been focusing on new developments for lighter, faster and durable skates. Wheels for in-line skates have been a critical component of these new developments, and the result has been faster wheels with higher resiliency or rebound. Resiliency is the energy returned from the wheels when the skater pushes off. Wheels with high resiliency or rebound readily absorb the unevenness of skating surfaces and act as shock absorbers, providing a comfortable ride with a certain degree of responsiveness. This performance window is constantly being pushed with new requirements for creating higher abrasion resistance without sacrificing grip.

Throughout the years the basics of in-line skate wheels have remained the same— injection molded hubs surrounded by cast polyurethanes. Performance requirements for the wheels vary with the type of in-line skating: roller hockey, recreational, fitness or aggressive skating. Roller hockey wheels need to be responsive (high resiliency), provide maximum cornering with sufficient friction (grip), have low abrasion resistance (durability) and be fast. In contrast, wheels for aggressive skaters need to provide durability and maneuverability, which translates into low abrasion, high strength and relatively higher coefficients of kinetic friction, while resiliency is not as critical a requirement. Since requirements are varied, wheel material formulation and selection should be geared towards end use and performance. The main physical attributes required from wheels, therefore, are comfort (resiliency or rebound), durability (abrasion resistance and tear strength) and traction (coefficient of friction).

Higher resiliency in elastomers can also be obtained by using systems based on naphthalene diisocyanate (NDI) prepolymers. NDI prepolymers based on both PTMEG and ethylene-co-butylene adipates show excellent resiliency, approaching 60–70%. NDI elastomers based on polyadi-pate diols as the soft segment, in particular, are known for

their high performance and long service life in particularly demanding dynamic applications [9].

In-line skating puts wheels under constant dynamic stress. The dynamic mechanical properties of the elastomeric materials influence wheel performance and are therefore very important. Due to the viscoelastic nature of polyurethanes, part of the dynamic energy is dissipated in the form of heat. Since polyurethane elastomers, like most other polymers, do not have high thermal conductivity, the heat results in an internal rise in temperature of the elastomer, or hysteresis [1,2]. This is generally caused by internal friction among the chains. Overheating can result in failure. It is therefore important for the materials used for wheels to have low heat generation or improved dissipation.

Traditionally, high-performance elastomer requirements for skate wheels have been met with conventional prepolymers. These are intermediates of the isocyanate polyaddition reaction with polyols, prereacted down to less than 13–15% free NCO. The conventional prepolymer method allows for the complete reaction of polyols for the targeted formation of a segmented structure with the formation of the soft blocks and hard blocks in specific steps. This segmented morphology between the hard and soft segments is the main factor that controls the properties of the polyurethane elastomer. Additionally, the prepolymer technique prevents problems commonly seen in one-shot systems, such as [3]:

- insufficient bond formation in hard and soft segments due to widely varying reactivities
- increased side reactions
- overheating of the center
- non-homogeneity in castings from uneven heats of reactions

However, processing of traditional prepolymer castings is complex, occurring at high temperatures (>65°C) to reduce processing viscosities. Specialized equipment is required to handle the higher prepolymer temperatures and the high isocyanate ratios, with the ratio of isocyanate to polyol/extender being in some cases as high as 10:1 rather than the 1:1 or 1:2 observed with typical one-shot systems. These high isocyanate ratios add additional complexity at the mixing stage.

The quasi-prepolymer approach used here targets the problems faced by both one-shot and conventional prepolymer systems. By prereacting isocyanates with long-chain polyols down to between 16–29% free NCO, formation of segmented structure is still accomplished in a step process (soft block formation followed by hard block/soft block segmentation) at processing ratios closer to those of one-shot systems. Thus, conventional one-shot equipment can be used to process the quasi-prepolymers at lower temperatures and at an isocyanate-to-polyol ratio closer to that of one-shot systems. The result is greater control over segregation, reactivities and homogeneity of castings.

The soft phase of the elastomer is critical to final property requirements and is a function of the long-chain polyols. The three main classes of long-chain polyols that influence the soft phase are:

- C3-polyether polyols (for e.g., polypropylene glycol-PPG)
- C4-polytetramethylene glycol or polytetrahydrofuran (PTMEG or PTHF)
- polyester polyols (adipates)

Typically, C3-PPG-initiated polyols contain a high level of terminal unsaturation that results in high amounts of mono alcohols that act as chain terminators [1]. As a result, polyurethane molecular weight buildup and physical properties are limited. In comparison, PTMEG polyols have low unsaturation and strain—crystallize under stress—a feature that improves static physical properties. Ester polyols, though susceptible to hydrolysis, show much stronger resistance to oxidation and have good high-temperature properties because of hydrogen bonding from the polar ester groups [3].

Using these three main classes of long-chain polyols, a new series of diphenylmethane diisocyanate (MDI) quasi-prepolymers has now been developed that offers high-performance elastomers for use in dynamic applications. This paper presents the chemistry, thermal properties, dynamic performance and physical properties of this new series of MDI quasi-prepolymers. Comparisons to conventional prepolymers are made and the effect of changing soft block explored. The paper demonstrates that elastomers made with these MDI quasi-prepolymers offer significant cost/performance advantages for use in in-line skate wheels and numerous other cast elastomer applications.

EXPERIMENTAL CHEMISTRY AND PROCESSING

High-performance elastomers were prepared in a two-step process. An isocyanate-terminated soft-block quasi-prepolymer was prepared by combining MDI and polyol at temperatures between 70–80°C for 1–3 hours, to produce a shelf-life-stable liquid. Based on the soft block needed, excess MDI ("Mondur M" from Bayer Corporation) was reacted with either a C3-PPG polyol ("Mulanol" PPG polyether polyol from Bayer Corporation), a C4-PTMEG polyol (from DuPont Chemicals or BASF), or a polyester polyol ("Desmophen" polyester polyol from Bayer Corporation). This produced an isocyanate-terminated quasi-prepolymer.

In quasi-prepolymers, liquefaction is achieved by both carbodiimide and allophanate addition and this contributes to processing. Modification of MDI by carbodiimide formation or by reacting a portion of the free NCO groups with the polyol to form quasi-prepolymers lowers the melting point. Generally, carbodiimide addition takes place in ester-based elastomers to increase hydrolysis resistance and act as an acid scavenger [9]. Alternately, allophanate groups in the hard segment increase compatibility with the soft segment [4]. How-

Table 1. Chemistry and materials.*

Sample #	Backbone/Chemistry	Hard Block Content	Soft Block Content
A	MDI/CI/C3-PPG	33	67
B	MDI/CI/C3-PPG-blend	34	66
C	MDI/CI/C4-PTMEG	31	68
D	MDI/CI/C4-PTMEG-blend	34	66
E	MDI/CI/Ester	35	65

*These items are provided as general information only. They are approximate values and are not part of the product specification.

Isocyanate: MDI—"Mondur M" from Bayer Corporation; CI—Carbodiimide modification; Soft Block: C3-PPG—"Mulanol" polyether polyol from Bayer Corporation; C4-PTMEG—"Terathane" polytetramethylene glycol from DuPont Chemicals; Ester—"Desmophen" polyester polyol from Bayer Corporation. Chain Extension and Catalyst: Desmophen 2502—2000 MW polyester polyol from Bayer Corporation; 1,4-Butanediol—90 MW diol; Tin catalyst—Dibutyltin-dilaurate.

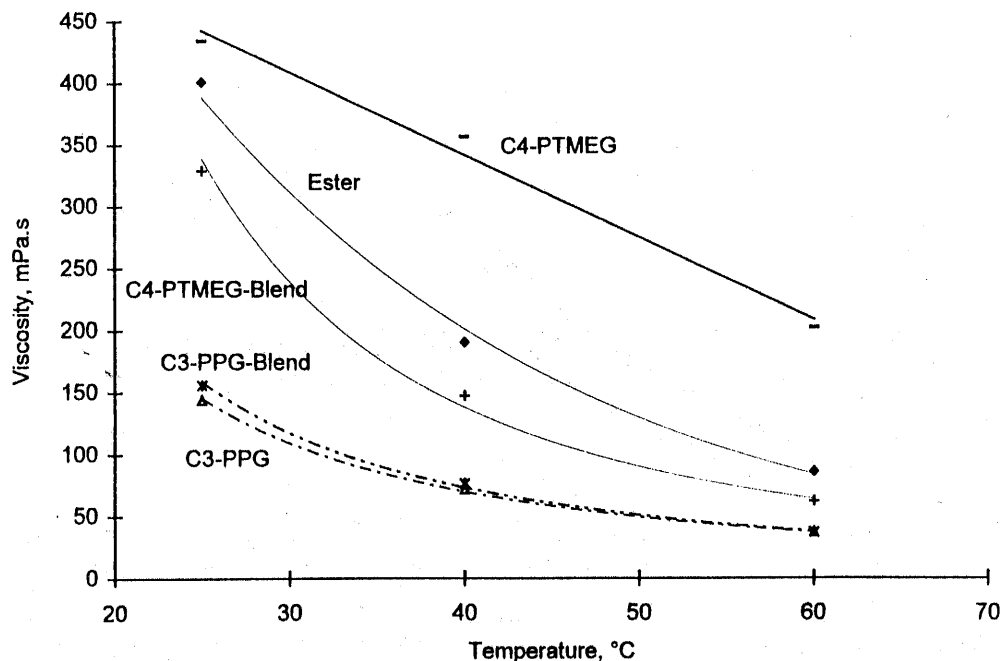


Figure 1. Viscosity profiles.

ever, this study addresses only the quasi-prepolymers modified by carbodiimide addition.

In contrast to conventional MDI prepolymers (<15% NCO), all quasi-prepolymers were stable liquids at 25°C. The relatively low viscosities over the range of 25–60°C improve mixing and make processing easier (Figure 1). The final quasi-prepolymer % free NCO was controlled at a constant 23%.

Table 1 details the different chemistries and materials used in the study.

It has been well-documented that the phase morphology can be controlled by the polyol component (soft block), the diisocyanate and the extender (hard block). Properties are therefore affected by the phase miscibility between the hard and soft segments [5,6].

In order to determine the soft block effect and maintain segmented consistency, all ether-based quasi-prepolymers were extended with a 1000 Molecular Weight (MW) PTMEG polyol/1,4-butanediol (BD) blend, to a final elastomeric hardness of 78–84 Shore A. The ester-based systems were consequently extended with a blend of a Desmophen 2502/BD to an elastomer hardness of 90–94 Shore A. To compare different elastomers it is important to control the hard segment amount re-

gardless of the molecular weight of the polyols. This consequently controls the hardness.

Samples were hand-cast at 25°C and demolded in 25 minutes. To avoid entrapment of air bubbles, mixing was carefully done after both the isocyanate and polyol sides had been degassed at 40–50°C. Systems were catalyzed with a tin catalyst with gel times between 80–120 sec. (By scaling-up to conventional one-shot equipment and catalyzing to gel times between 15–25 seconds, the elastomeric samples can be demolded in 3–5 minutes.)

Processing conditions and reactivities are shown in Table 2.

GLASS TRANSITIONS AND MELTING

Elastomeric samples were run on a Perkin Elmer DSC 7 to determine the glass temperatures and melting behavior. Samples loaded at 25°C were cooled to –100°C, heated to 200°C, cooled back to –100°C and reheated to 200°C, all at the rate of 20°C/min.

Higher glass transition temperatures (T_g) were observed with the C4-PTMEGB-blend based systems than with the C3-PPG based systems. Subsequently, low-temperature

Table 2. Processing and reactivities.*

Sample #	Quasi-Prepolymer	Viscosity @ 25°C, mPa·s	Gel Time, Seconds	Hardness, Shore A
A	MDI/CI/C3-PPG	144	94	80
B	MDI/CI/C3-PPG-blend	156	86	81
C	MDI/CI/C4-PTMEG	434	115	84
D	MDI/CI/C4-PTMEG-blend	329	98	84
E	MDI/CI/ester	401	137	94

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Material Temperature—Isocyanate (Quasi-Prepolymer) = 40°C, Polyol/Extender Blend = 50°C; Mold Temperature—25°C for 10 minutes, 60°C for 15 minutes; Demold Time—25 minutes.

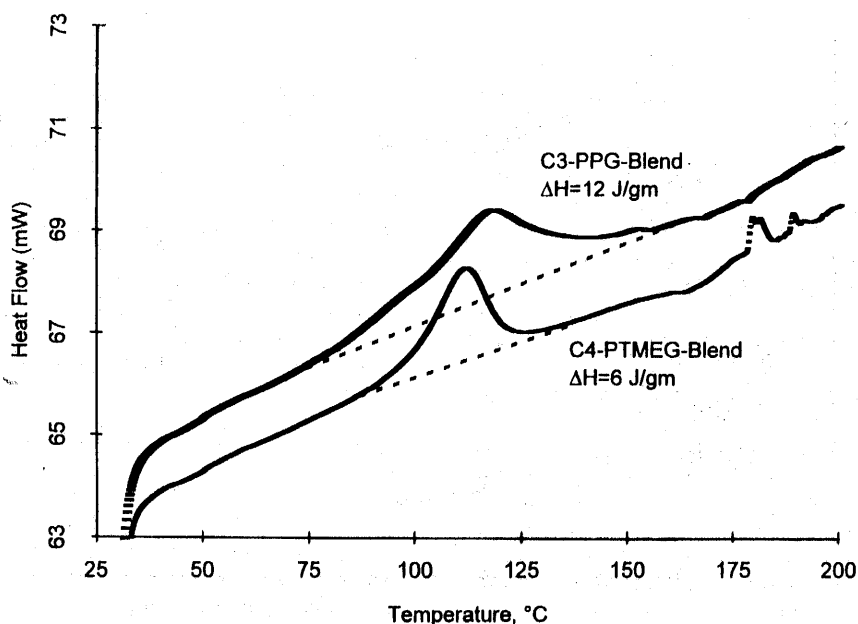


Figure 2. DSC spectra of elastomers based on C3-PPG-blend and C4-PTMEG-blend quasi-prepolymers.

mobility is higher in the blended systems from the presence of the higher molecular weight species. In contrast, the presence of smaller molecular weight species in ester polyols contributes to the formation of hard segments and therefore, in reality, the hard block content is slightly higher than ideal [3]. This shifts the T_g to higher values (Table 3) due to higher length of the hard segment and irregular domains [7].

DSC results do not show any hard block transitions till 200°C (Figure 2). From the DSC spectra the onset of melting was determined. Samples were then postcured for 16 hrs at 10°C below the onset temperatures (Table 3).

Crystallization of the hard segments occurs in all cases (Figure 2). On annealing, the sharp melting peaks are replaced by broad melting regions (Figure 3). The melting range of the hard domains determines the dimensional stability of linear segmented polyurethane elastomers. With mixed chain extension (samples B, D and E), the range is lowered and broadened (Figure 3), forming irregular hard segments which then restrict the soft segment chains [6]. Annealing may help in fixing this irregularity. However, it is unclear whether this irregularity affects properties.

DYNAMIC MECHANICAL PROPERTIES

Dynamic mechanical spectroscopy (DMS) provides information on the ability of a sample to store and dissipate en-

ergy under dynamic conditions over a range of temperatures and frequencies.

To determine dynamic performance, samples were run on a DMS-torsion pendulum machine. The test specimens for Dynamic Mechanical Analysis (DMA) are small strips of elastomer held vertically by clamping at the top and attaching to a small horizontal flywheel at the bottom. A small load (5 gm axial force) is applied on the sample and on comparing the amplitudes of two consecutive oscillations the loss factor or loss compliance ($\tan \delta$) can be calculated. Under cyclic stress, the rate of hysteresis heat generation of the elastomers is directly proportional to the loss compliance of the elastomer [2]. Highly elastic materials show low $\tan \delta$ values. Also determined from the test are the storage modulus G' (elastic behavior) and the loss modulus G'' (energy dissipation). Low values of G'' are indicative of low energy dissipation, low hysteresis, and consequently low heat buildup, an important requirement for in-line skate wheels.

Heat buildup and dynamic performance can be observed under varying conditions by running a temperature sweep at a fixed low frequency (0.1 Hz) or a frequency sweep at a fixed temperature (25°C) to simulate large deformations and vibrations. Results of DMA are shown in Table 4.

Low-temperature behavior of the elastomers is illustrated by the shear modulus G' curve, the modulus increasing with decreasing temperature (Figure 4). All ether-based systems show flat and rubbery plateau regions in the normal-use temperature range between 0–60°C (Figure 5). The rubbery plateau for the higher molecular weight

Table 3. Glass transitions and melting behavior.*

#	Systems	Glass Transitions Temperature °C	Melting Temperature °C	Onset of Melting °C	Postcuring Temperature °C
A	MDI-CI-PPG	-44.8	122.6	105	95
B	MDI-CI-PPG-blend	-49.6	117.2	71	60
D	MDI-CI-PTMEG-blend	-42.9	111	81	70

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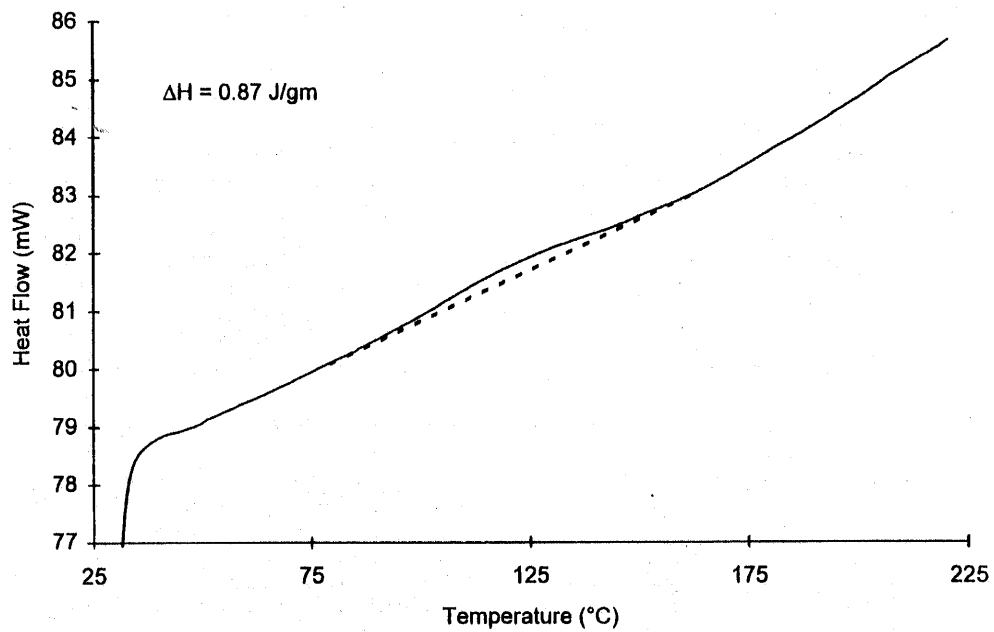


Figure 3. DSC spectra of elastomer based on C3-PPG-blend quasi-prepolymer: reheat cycle.

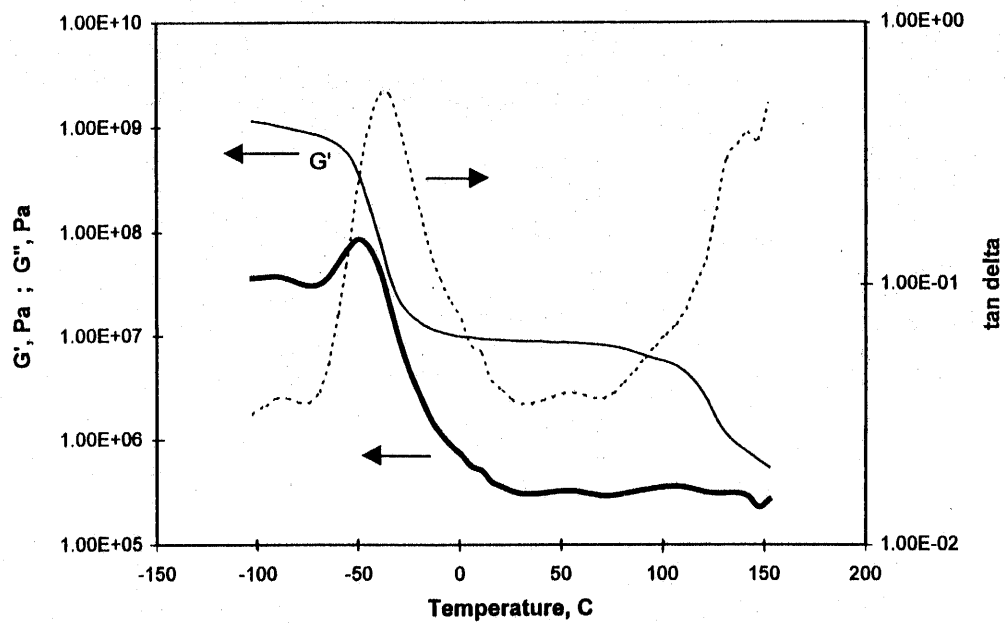


Figure 4. DMA of elastomer based on quasi-prepolymer with a C4-PTMEG blend soft block.

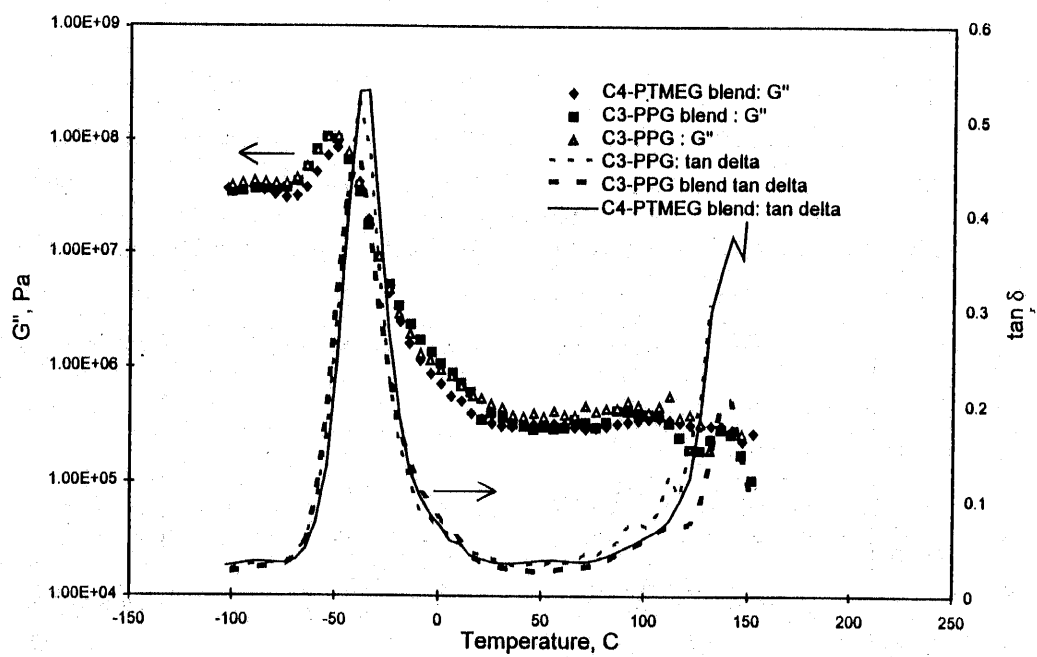


Figure 5. DMA-temperature sweep: effect of soft block.

Table 4. Dynamic mechanical properties—temperature sweep: effect of soft block backbone.*

Sample #	G' Rubbery Plateau Range, °C	G'' Peak (=T _g), °C	Tan δ Peak (=T _g), °C	Tan δ at 25°C
A	-10 to 85	-49.6	-39.0	0.040
B	-8 to 95	-54.6	-38.8	0.034
C	-5 to 60	-44	-29.2	0.010
D	-30 to 100	-49.9	-34.4	0.035
E	-5 to 60	-36.8	-24.6	0.060

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ether blends (samples B and D), is broader, between -8 to 95°C and -30 to 100°C respectively (Table 4), signifying superior phase separation. Good phase separation lies at the root of improved properties. Elastomeric integrity is maintained till 100°C after which a continuous loss of storage modulus occurs with increasing temperature (Figure 4).

Glass transition results obtained from the peaks of the tan δ and loss modulus G'' curves are consistent with literature trends: T_{g(DSC)} values from DSC results are lower than T_{g(tan δ)} from the tan δ peak values and higher than T_{g(G'')} from the G'' peak values (Table 4).

C4-PTMEG (samples C and D) based systems show lower tan δ values at 25°C. Lower tan δ (damping) values in the application temperature range signify a lower ratio of energy-absorbed-as-heat-retained to energy-released-as-heat-dissipated. This lower damping manifests itself as reduced heat buildup, more so in ether-based systems than in ester-based systems. T_g values are also higher in the ester-based systems, a consequence of intermolecular hydrogen bonding [6], and a high degree of phase mixing.

Frequency sweeps (Figure 6) between 0.1–100 Hz on the DMA at 25°C were equivalent to simulating the samples to dynamic loadings at higher vibrations. G', G'' and tan δ curves were relatively linear, with the storage modulus being constant throughout the frequency range. Systems based on higher molecular weight C4-PTMEG-blends

(sample D) showed lower G'' values throughout the frequency range compared to C3-PPG-based systems (samples A and B) (Table 5). Therefore, the C4-PTMEG-blend based samples have lower hysteresis and, subsequently, lower heat buildup. However, at higher frequencies, heat buildup is faster, and both G'' and tan δ values are much larger for all elastomers.

PHYSICAL PROPERTIES

Of significant importance, as seen from this study, is the retention of physical properties (specifically resilience, tear and abrasion resistance) by the final cured elastomer based on the quasi-prepolymers. Therefore, ease of processing combined with the added advantage of higher tear strength and abrasion resistance makes the elastomers based on the quasi-prepolymers attractive for use in many dynamic applications.

Effect of Soft Segment

Resiliency and good tensile properties are characteristic of elastomers based on C4-PTMEG quasi-prepolymers. However, the high properties shown by the C3-PPG- and the C3-PPG-blend-based elastomers are quite unexpected.

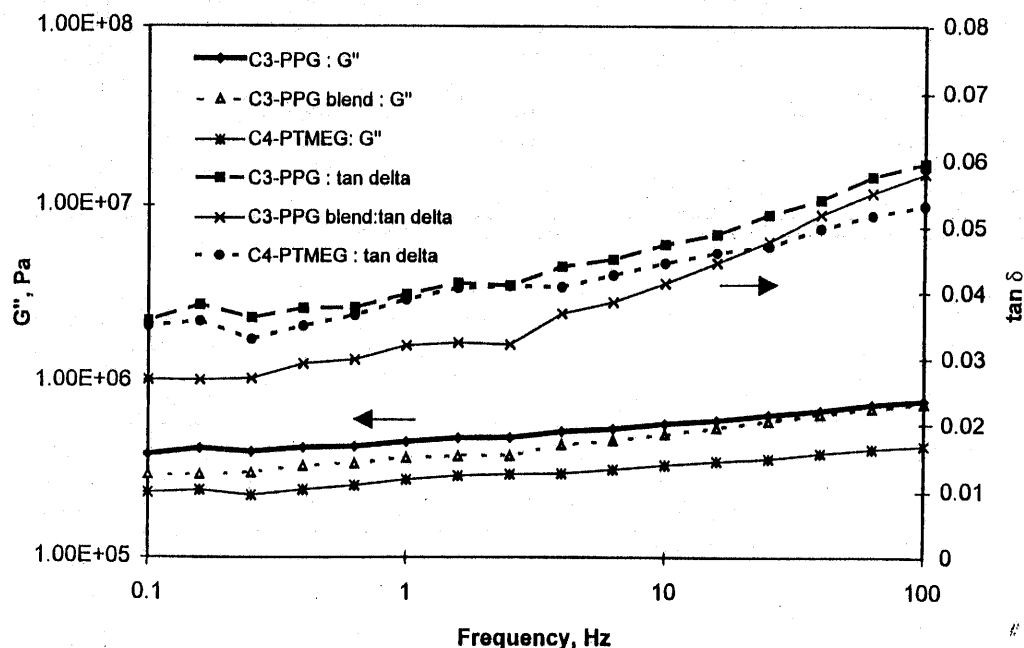


Figure 6. DMA-frequency sweep: effect of soft block.

Table 5. Dynamic mechanical properties—frequency sweep*: effect of soft block backbone.**

Sample #	G' Range, 10 ⁷ Pa	G'' Range, 10 ⁵ Pa	Tan δ Range	Tan δ at 10 Hz
A	1.1	4.0–7.7	0.035–0.06	0.048
B	1.1	2.8–7.4	0.026–0.058	0.041
D	0.7	2.1–4.2	0.033–0.053	0.045

*Frequency range: 0.1–100 Hz.

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Table 6. Physical properties: effect of soft block backbone.*

Property/Sample #	A	B	C	D	E
Hardness, Shore A	80	81	84	82	91
Resilience, %	56	61	68	57	47
Split tear, lbf/in.	132	130	116	105	292
Die C tear, lbf/in.	421	450	452	444	440
Ultimate elongation, %	684	700	409	520	612
Tensile strength, psi	3612	2620	3435	3501	6534
Stress @ 100%, psi	574	742	767	711	579
Stress @ 200%, psi	775	907	1050	934	706
Stress @ 300%, psi	1003	1095	1583	1224	1100
Compression set, %	19.5	36.5	36	30.3	69.9
CLD: 2%	36	42	22	44	48
CLD: 15%	384	432	429	410	534
CLD: 50%	1800	1900	1906	1972	2015
Taber abrasion, mg/1000 cycles	3.8	4.8	0.4	7.7	4.6
NBS abrasion, index	79	77	—	77	42

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Table 7. Physical properties: comparisons—quasi-prepolymers vs. conventional prepolymers, C3-PPG-based systems.*

Property/Sample #	A Quasi-	B Quasi-	Conventional	Conventional Baytec MP-090
Extender	PTMEG/BD	PTMEG/BD	PTMEG/BD	BD
NCO, %	23	23	8.3	9
Viscosity @ 25°C, mPa·s	145	146	7500	7600
Hardness, Shore A	80	81	78	85
Resilience, %	56	61	61	20
Split tear, lbf/in.	132	130	102	60
Die C tear, lbf/in.	420	451	383	360
Ultimate elongation, %	685	700	918	410
Tensile strength, psi	3610	2620	1600	5000
Stress @ 100%, psi	575	742	590	990
Taber abrasion, mg/1000 cycles	3.8	4.8	55	90
Ratio A:B, isocyanate:polyol	66/100	70/100	100/22.2	100/9.6

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Table 8. Physical properties: comparisons—quasi-prepolymers vs. conventional prepolymers, C4-PTMEG-based systems.*

Property/Sample #	C Quasi-	D Quasi-	Conventional Baytec ME-040
Extender	PTMEG/BD	PTMEG/BD	BD
NCO, %	23	23	4.8
Viscosity @ 25°C, mPa·s	430	330	Solid
Hardness, Shore A	84	82	79
Resilience, %	68	58	65
Split tear, lbf/in.	116	105	—
Die C tear, lbf/in.	456	444	340
Ultimate elongation, %	409	520	480
Tensile strength, psi	3435	3500	4200
Stress @ 100%, psi	767	711	600
Ratio A:B, isocyanate:polyol	52/100	60/100	100/22.2
Taber abrasion, mg/1000 cycles	0.4	7.7	12

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Table 9. Physical properties: comparisons—quasi-prepolymers vs. conventional prepolymers, ester-based systems.*

Property/Sample #	E Quasi-	Conventional Baytec MS-080
Extender	Desmophen 2502/BD	BD
NCO, %	23	8
Viscosity @ 25°C, mPa·s	401	Solid
Hardness, Shore A	91	90
Resilience, %	47	50
Split tear, lbf/in.	292	320
Die C tear, lbf/in.	440	600
Ultimate elongation, %	612	470
Tensile strength, psi	6540	7000
Stress @ 100%, psi	580	1110
Taber abrasion, mg/1000 cycles	4.6	15
Ratio A:B, isocyanate:polyol	34/100	8.2/100

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Table 10. Physical properties: effect of postcuring.*

Property/Sample #	B	B Post-Cured	D	D Post-Cured	E	E Post-Cured
Hardness, Shore A	81	83	84	82	94	91
Resilience, %	61	56	58	57	48	47
Split tear, lbf/in.	129	123	85	113	312	292
Die C tear, lbf/in.	451	439	379	423	486	440
Ultimate elongation, %	700	636	449	533	568	612
Tensile strength, psi	2617	3080	1853	3720	5590	6534
Stress @ 100%, psi	742	678	664	612	702	579
Stress @ 200%, psi	907	892	868	833	825	706
Compression set, %	36.5	26.9	31.4	30.3	41.0	69.9
CLD: 2%	42	38	51	34	91	48
CLD: 5%	—	122	139	92	305	187
CLD: 15%	19	396	422	292	753	380
CLD: 50%	1900	1972	2009	1583	2290	2015
Taber abrasion, mg/1000 cycles	4.8	4.5	4.2	7.7	8.8	4.6
NBS abrasion, index	77	88	92	77	59	42

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In spite of high terminal unsaturation, which generally leads to poor physical properties, these elastomers show performance similar to that exhibited by the C4-PTMEG systems (Table 6). Very encouraging are the low abrasion and low compression sets. Chain extension in all ether-based systems has been with a blend of the 1000 MW PTMEG/BD. It is highly likely that the contribution of the C4-PTMEG soft segment from the chain extension process compensates for the C3-PPG soft segment created during the quasi-prepolymer preparation. Furthermore, higher molecular weight species involved during initial soft block formation helps in enhancing some of the physical properties. Nevertheless, the contribution to the soft block from the C3-PPG polyol is 18%.

In general, polyester polyol-based elastomers exhibit significantly better tensile properties in contrast to polyether-based elastomers, and this holds true for quasi-prepolymer elastomers with the 2000 molecular weight ester as the soft segment.

Ester soft segments in quasi-prepolymer systems improve tensile and tear properties but negatively impact resiliency and compression sets. Modulus development is similar in all quasi-prepolymer systems till 300% elongation. However, tensile strength of the ester-based elastomers is significantly higher, (6535 psi), alluding to greater strain-induced crystallization under stress, especially at extensions greater than 300% (Table 6).

Comparisons with conventional prepolymers based on C3-PPG polyether polyols (Table 7), C4-PTMEG polyether polyols (Table 8), and a 2000 MW polyester polyol (Table 9) demonstrate the possibility of substituting quasi-prepolymers for the conventional prepolymers. In all ether quasi-prepolymers, the hard block content is maintained between 31–35% with elastomers cast at similar hardness, between 78–84 Shore A (Table 1).

The contributions of both the soft and hard blocks are correlated to the properties observed. The soft rubbery block primarily affects resiliency, wear, tear, compression set and low-temperature properties, while the hard block governs hardness, modulus and tensile properties [3]. All the quasi-prepolymers tested showed excellent abrasion resistance.

The mobility of the molecular chains depends on the nature and chain length of the soft segment. From the DMS results we observed that elastomers based on quasi-

prepolymers had low T_g 's and relatively amorphous nature, contributing to their superior elastomeric properties (Table 7–9). Additionally, with higher chain lengths (MW \geq 2000), high linearity and a high soft block (>60%), crystallinity is favored and this, subsequently, improves some properties but also induces opaqueness and cloudiness in the final elastomer.

Speed is a consequence of the frictional force overcome during skating. The lower the coefficient of static and kinetic friction, the lower is the resistance to movement. Elastomers based on C4-PTMEG quasi-prepolymers (sample C) showed lower values of both static (24% lower) and kinetic (14%) coefficient of friction as compared to those based on C3-PPG quasi-prepolymers, when tested on cement. Values for static and kinetic coefficient of friction are 0.307 and 0.267, for elastomers based on C4-PTMEG quasi-prepolymers.

Among the ester systems, higher tensile strengths and tear strengths were observed with the Baytec MS-080 system (conventional 8% NCO prepolymer from Bayer Corporation). This can be attributed to the relative higher hard block content (40.4%), as chain extension is purely by 1,4-butanediol in this system.

Effect of Postcuring

Postcuring at temperatures slightly below the onset of melting helps to relieve irregularities, especially in the hard segment. This improves certain properties like tensile strength, compression sets and elongation (Table 10). In contrast, samples cured at 25°C for two weeks show small increases in the tear and resiliency over samples postcured at higher temperatures. All other properties are observed to be similar. Therefore, a two-to-four week cure at 25°C is in many respects similar to a high-temperature (60–110°C) cure, the decision to cure resting on time and energy criteria.

CONCLUSIONS

Novel isocyanate-terminated quasi-prepolymers with 23% free NCO have been developed that are liquid and stable at 25°C. Elastomers cast with these quasi-prepolymers show superior physical and dynamic properties making them suitable for use in various applications.

By prereacting the monomeric MDI (Mondur M) down to 23% free NCO with long-chain polyether or polyester polyols, formation of segmented structure is maintained at processing ratios closer to one-shot systems. Carbodiimide addition also helped in liquefaction. Subsequently, the quasi-prepolymers can be processed with conventional one-shot processing equipment. Processing advantages over conventional prepolymers can be realized with greater control over segregation, reactivities and homogeneity of castings as compared to one-shot systems.

The effect of the type of soft block, high temperature post-curing and isocyanate modification was observed on the physical and dynamic properties at constant hardness (or hard block content). Of special interest is the performance of elastomers based on C3-PPG polyols that combine property benefits and offer cost/performance advantages. Quasi-prepolymers based on C3-PPG polyols and C3-PPG blends had low viscosities and elastomers based on these quasi-prepolymers exhibited properties similar to C4-PTMEG-based systems.

Elastomers cast from C4-PTMEG-based quasi-prepolymers demonstrated low heat buildup, high heat dissipation and higher resiliency. Additionally, blends with higher molecular weight C4-PTMEG polyols in the soft segment improved the physical and mechanical properties.

As expected, elastomers cast from ester-based quasi-prepolymer systems were superior in tensile properties but showed lower resiliency and higher compression sets. Within the normal temperature range, dynamic properties were observed to be lower than in the ether-based systems.

In summary, these novel, shelf-life-stable, liquid quasi-prepolymers offer significant processing advantages with properties equivalent to conventional prepolymers. The study showed that elastomers with low abrasion, high resiliency and good tear resistance can be cast with quasi-prepolymers based on monomeric MDI (Mondur M) and C3-PPG, C4-PTMEG or adipate polyester polyols. The property advantages make these systems ideally suited for use in in-line skate wheels—with the polyether polyol based-systems more appropriate for roller hockey, recreational and fitness skaters, and the polyester-based systems more suited for aggressive skaters.

ACKNOWLEDGEMENTS

The authors would like to thank Jason Gyimesi, William Lawrence, and Diana Mullen for their help in preparing the elastomer samples. We also thank the following for the material analyses and subsequent discussions related to them: George Pastor and Farhad Cama for the DMA profiles, Joe Martin for the physical property results and Keith Wilson for the DSC spectra.

REFERENCES

- Chen, A. T. et al. 1993. *Polyurethane World Congress*, p. 388.
- Kogelnik, H.-J. et al. 1990. *Polyurethanes*, p. 207.
- Oertel, G. 1993. *Polyurethane Handbook: Chemistry—Raw Materials—Processing—Application—Properties*, Hanser Publishers.
- Goering, H. et al. 1985. *Plaste. Kautsch*, 32:14.
- Hwang, K. K. et al. 1984. *Polymer*, 25:947.
- Chang, Y. P. et al. 1975. *J. Poly. Sci.*, 13:455.
- Rabek, J. F. 1980. *Experimental Methods in Polymer Chemistry*, John Wiley & Sons.
- Hespe, H. et al. 1972. *Colloid. Poly. Sci.*, 250:792.
- Prolingheuer, E. C. et al. 1991. *Polyurethane World Congress*, p. 464.

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A Development Scientist in the Polyurethane Specialty Elastomers group, Polymers Division of Bayer Corporation, Dr. Madan is responsible for product development of one-shot elastomers, prepolymers and elastomeric composites. After receiving his B.Tech degree in Chemical Engineering from the Indian Institute of Technology, Kanpur, India, and a Ph.D. in Polymer Engineering

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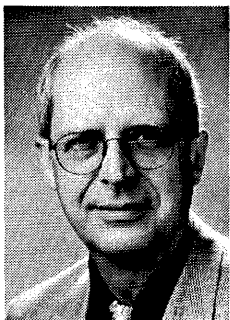
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Klaus Recker joined Bayer A.G. in 1973 after receiving his Ph.D. degree in Organic Chemistry from the University of Cologne, Germany. He spent one year in the Polyurethane Research Department working on cold-curing systems. Then he joined the Elastomer Group of the Polyurethane Applications Development Department where he was responsible for the development of cold- and hot-curing elastomeric systems.

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