Macromol. Symp. **2003**, *198,* 271-281

Ternary Phase Separation in Polyurethane Elastomers with Immiscible Soft Segments

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Summary: Polyurethane elastomers with two immiscible hard-segment polyols have been synthesized from homogeneous prepolymer mixtures, to obtain incompatibility on a molecular scale from reaction driven phase separation. Miscibility of a series of different soft-segment polyols and of their prepolymers with 4,4'-diisocyanatodiphenyl methane (MDI) has been investigated by cloud point analysis. UCST-behavior was observed for all binary combinations of polyols and of prepolymers; prepolymer formation lowered UCST with respect to polyols with the option to adjust it by further addition of MDI. Polyurethane elastomers have been synthesized and characterized with respect to their thermal, mechanical and viscoelastic (DMTA) behavior. Broad temperature ranges of loss factor above 0.1 were observed from polyurethanes with two immiscible soft-segment polyols. Rebound resilience, however, was still significant at room temperature, because of the low transition temperatures of the polyols used. Introduction of a third partially miscible component, a hard-segment from tetraethyleneglycol and MDI gave materials with a loss factor above 0.1 over a temperature range from –50 to 120 °C and higher. The studies proved that the concept of intimate mixing of immiscible soft-segments in polyurethanes works for the design of viscoelastic materials with good damping properties.

Keywords: damping, PUR-elastomers, ternary phase separation, viscoelasticity

Introduction

The use of energy absorbing and vibration damping materials has been continuously growing in the last decades. Applications of these materials include insoles for athletic shoes,[1] seismic isolation pads to protect buildings from earthquake damage, shock-absorbing encapsulates for under water sonar devices, vibration insulating systems for high-speed railway trucks[2] and the damping of vibrations and noise from the moving parts of machinery.[3]

Damping performance is related to the structure and to the molecular weight of materials. One mechanism of damping is based on material that absorbs mechanical or acoustic energy and transforms it into thermal energy, which is dissipated into the matrix. This mechanism of energy absorption can be described by the relation $\tan \delta = E'' / E'$, where E'' is the loss

DOI: 10.1002/masy.200350823

modulus, E' the storage modulus and tan δ damping factor, dissipation factor or loss factor. At the glass transition condition, which involves both temperature and frequency effects, the cooperative molecular motion of chain segments transforms a maximum of mechanical energy into heat.

The damping temperature is defined as wide as the glass transition temperature of the polymer. Common damping materials are homopolymers or copolymers, which exhibit efficient damping in a temperature range of $T_g \pm 15$ °C.[4] The acoustic spectrum spans from 20 Hz to 20,000 Hz three decades of frequencies. For many polymers, according to the WLF-equation, the time-temperature equivalence is 6 °C to 7 °C per decade of frequency or about 20 °C for the acoustic range.[5] Thus polymers often suffice to damp the full acoustic range at one temperature, they fail, however, when temperature changes of more than 20 °C occur. Therefore, it is necessary to widen the temperature range of the glass transition.

One solution to this problem lies in selecting multicomponent polymers with a controlled degree of partial miscibility. Incompatible polymer alloys[6,7] display separated T_g's and therefore exhibit several damping ranges corresponding to the glass transition temperatures of the components. Homogeneous polymer alloys[8] show only one T_g, which may be slightly broader than that of the individual components. Semi-miscible polymer blends where mixing between the polymers is extensive, have a very broad damping range that covers a wider frequency and temperature range.

Semi-miscible polymer blends can be made by several methods among them formation of interpenetrating networks (IPNs). IPNs are intimate mixtures of two (or more) network polymers in which at least one of the networks is formed in the presence of another[9]. Ideally, bonding between the networks is absent, chains of one network are threaded through those of the second network; they are catenated. Advantages of IPNs over other multicomponent polymer blends are the forced miscibility and increased surface area. IPN's are one of the newer materials in energy absorption and vibration damping.[9-14] An approach, which has the advantages of IPNs, is the manufacture of a network structure from two different network polymers, which use the same branching units. These polymers should be miscible at the temperature of manufacture and undergo reaction driven phase separation to give a multiphase polymer blend with physical or chemical cross-links. This is schematically shown in Figure 1.

The present contribution reports on the synthesis and characterization of polyurethane elastomers made from two different soft-segment polyols that are inherently immiscible.

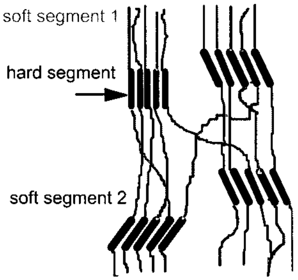
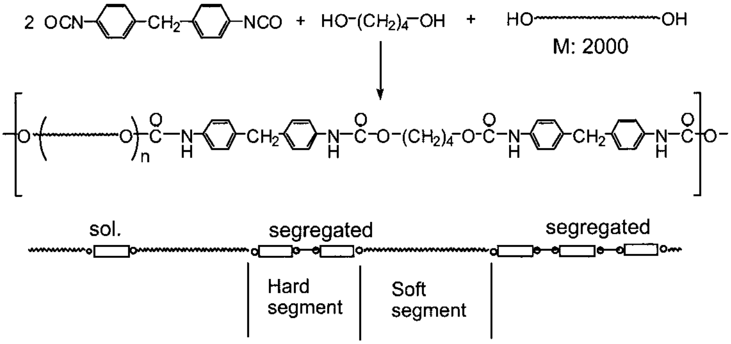


Fig. 1. Polyurethane with immiscible soft-segment polyols (schematic).

Results and Discussion

The strategy used in the present study is based on the synthesis of essentially linear multiblock polyurethane elastomers consisting of hard- and soft-segment blocks, which are immiscible at service temperature. The hard-segments are oligourethane units, e.g. from 4,4'-diisocyanatodiphenyl methane (MDI), and a "chain extender", e.g. 1,4-butanediol, the soft-segment blocks are α,ω-dihydroxy polyethers or aliphatic polyesters (cf. Scheme 1). The hard-segment domains are crystalline and function as multivalent branch points.

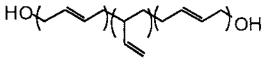
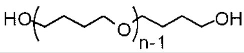
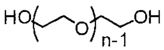
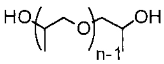
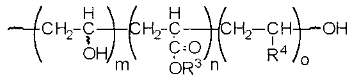


Scheme 1

Intimate mixing of incompatible soft-segment polyols, a prerequisite of good damping properties, should be possible with isocyanate terminated prepolymers of these polyols for the synthesis of polyurethane elastomers. Polyols, their structure and functionality are included in Table 1. As no literature data on miscibility of these materials was available, miscibility was studied measuring the cloud point upon cooling of homogeneous mixtures.

Miscibility of the polymethyl acrylate was observed with the polybutadienediol (PBDD), with polyoxypropylenediol (PPG), and with polyethylene glycol (PEG) above 185 °C. PPG is also miscible with polyoxytetramethylenediol (PTMO), while PPG and PEG are immiscible. All of the combinations studied over a wider range of composition showed typical upper critical solution behavior (UCST), which can be seen from cloud point curves in Figure 2.

Table 1. Miscibility of polyols (50 / 50 wt. %).

Polyol **(functionality)**	**PEG**	**PPG**	**PMA** H-4903	**PMA** H-4904	**PBDD** 
PTMO (2) 	>215 + <215 -	+	+	>190 + <190 -	>140 + <140 -
PEG (2) 		-	>185 + <185 -	-	-
PPG (2) 			+	+	+
PMA H-4903, H-4904 (2.5)  $-(CH_2-\overset{H}{C}(OH))_m-(CH_2-\overset{H}{C}(C{=}O)(OR^3))_n-(CH_2-CH(R^4))_o-OH$				+	-

+ means miscibility at 25 °C, - means immiscibility, numbers stand for temperatures

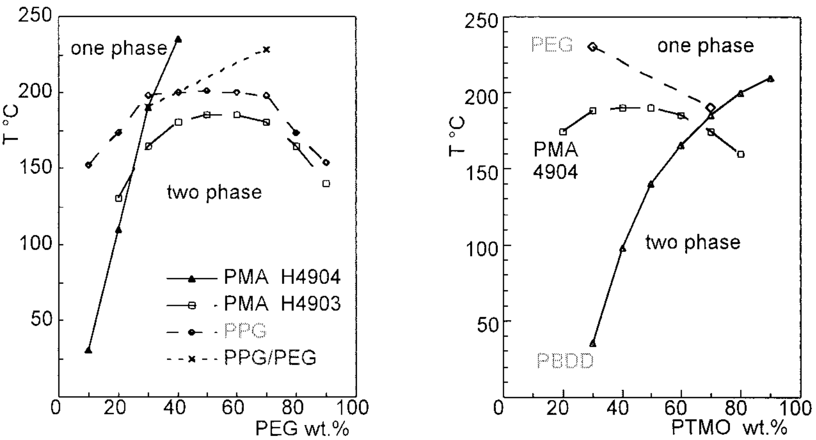


Fig. 2. Cloud point curves of mixtures of polyols with PEG (left) and PTMO (right).

Prepolymer formation, i.e. reaction of soft segment polyols with excess diisocyanate, adds identical MDI-monourethane units to the polyols, which should be a means to improve miscibility. Miscibility of prepolymers was studied as described for the polyols; the results are included in Table 2. Prepolymer formation has a huge effect on compatibilization in some combinations and almost no effect in others. PEG/PPG, which are miscible as polyols above 185 °C, become miscible as prepolymers above 95 °C, a temperature range that will be reached during elastomer formation. The same is true for PMA H-4904/PTMO (190 °C and 131 °C). On the other hand miscibility of PTMO/PEG is practically unchanged, even if a 1 : 8 ratio of polyol/isocyanate is used (215 °C vs. 197 °C).

Table 2. Miscibility of prepolymers (50 / 50 wt.%).

Polyol	**PEG**	**PPG**	**PMA H-4903**	**PMA H-4904**	**PBDD**
PTMO	1/8* >197 +	+	+	1/6* >131 +	+
PEG		>97 +	+	1/12* >182 +	-
PPG			+	+	+
PMA H-4903				+	1/6* >70 +
PMA H-4904	*: Molar ratio of polyol/MDI; (otherwise 1/4)				-

The effects of prepolymer formation and of further dilution with MDI are illustrated in Figure 3. Again UCST-behavior is observed and the strong decreasing effect of prepolymer formation on the UCST. Additional MDI, the amount of which is limited, however, by the desired hard-segment content of the polyurethane, is a method to adjust miscibility within a wide range. As the isocyanate is consumed during PUR-formation, reaction driven phase separation of the polyols is expected to occur.

Polyurethanes were synthesized to have a hard-segment content of 40 and 50 weight percent, respectively. PUR-elastomers with a single polyol were included for comparison. Prepolymers with the appropriate amount of MDI were mixed in a 1 : 1 ratio, heated to maximum temperature of 100 °C, the amount of chain extender was added sufficient to have a 2 percent excess of isocyanate groups (index 102). After homogenization, the mixture was transferred to a mold and cured at a temperature were initially homogeneous conditions were ensured. All molded sheets of 80 x 300 x 2 mm were annealed for 6 h at 120 °C to ensure comparable thermal history. To slightly enhance compatibility, apart from mixing prepolymers that had been separately synthesized, prepolymers were also made from the mixture of two polyols, which should give block-copolymers of the different polyols linked by a MDI unit.

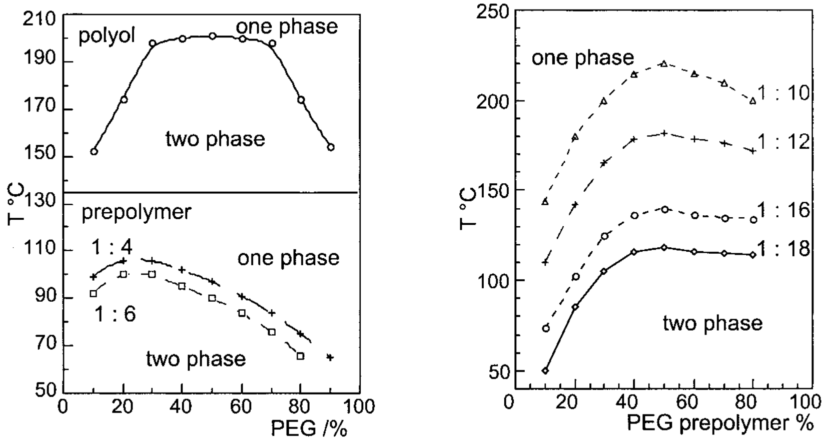


Fig. 3. Cloud point curves of mixtures of prepolymers from PPG / PEG (left), from PMA H4904 / PEG (right).

The PUR-elastomers were characterized by differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), tensile testing, and rebound resilience. In Table 3 properties of polyurethanes from a single polyol and of some binary combinations of these have been collected. In terms of elongation and tensile stress normal behavior is observed, only the rather small elongation at break of No. **103-2** does not fit. The result of mixed soft segments is a decrease in rebound resilience, which is to be expected. Somewhat surprising is the decrease of permanent set (permanent deformation) of the tensile specimen which is smaller for mixed soft segments than for the individual elastomers.

Glass transition temperatures from DSC are higher than those of the pure polyols, which indicates some phase mixing with the hard-segment blocks. DSC is not very sensitive to detect glass transition temperatures, in particular, there is a rather big difference between Tg from DSC and from DMTA, which was run at a frequency of 1 Hz. DMTA-values are by 20 K higher in some cases and almost equal in others. Tan δ values increase at the temperature of Tg from DSC, the maximum, which was taken as Tg, is at the temperatures given in column 8 of Table 3.

Table 3. Influence of soft segment composition on properties of polyurethane elastomers.

No.	**Polyol**	σ MPa	ε %	**Rebound resil.**[a] %	**Perm. set**[b] %	**Tg** °C DSC	**Tg** °C DMTA	**Tm** °C	**Tg** °C polyol
90-1	PTMO	43.0	510	53	120	-65	-61	229	-65
98-4	PEBA	25.5	475	39	115	-37	-17	201	-56
111-1	PPG	27.1	500	39	90	-47	-33	226	-66
110-2	PPG-PEBA	24.4	200	34	10	-48	-16	223	-66 -56
103-4	PEG-PPG	24.3	600	27	75	-46	-23	181	-46 -66
104-4	PEG-PTMO	38.8	525	46	105	-69	-58	226	-46 -65

All polyurethane elastomers have 50 % hard-segment content

a) rebound resilience according to DIN 53512

b) residual of 300 % elongation after 48 h

Table 4. Influence of the synthetic procedure on thermal properties of polyurethane elastomers.

No.	**Polyols** Method	HS %	σ MPa	ε %	Rebound resil. %	Perm. set %	Tg °C DSC	Tg °C DMTA	tan δ	tan δ > 0.1 (range)
103 -1	s	39	24.7	675	40	60	-46.7	-26.3	0.51	-52 – 1 (53)
-3	d **PEG**		25.7	700	34	50	-49.4	-25.4	0.46	-54 – 7 (61)
-2	**PPG** s	50	23.3	575	36	85	-47.4	-25.4	0.29	-53 – 5 (58)
-4	d		24.3	600	28	75	-46.4	-23.6	0.34	-50 –33 (83)
104 -1	s	39	36.7	550	57	50	-68.0	-55.5	0.27	-85 – 4 (89)
-3	d **PEG**		37.0	550	53	35	-69.0	-52.9	0.32	-81 – 1 (82)
-2	**PTMO** s	50	37.8	525	45	125	-58.8	-67.1 -26.6	0.12	-76 – -13 (63)
-4	d		38.8	525	47	105	-69.1	-58.9	0.19	-83 – - 1 (82)

s: prepolymer from mixture of two polyols

d: mixture of two prepolymers

PEG and PPG with weight ratio 1 : 4

PEG and PTMO with weight ratio 1 : 4

As mentioned above the method of synthesis, i.e. either from a mixture of two prepolymers or from a prepolymer made from a mixture of two polyols should have an influence on phase mixing or compatibilization of polyols in the final elastomer. Mixtures of PEG with PPG and of PEG with PTMO both with 75 wt. % PEG were used, because the prepolymer mixtures had suitable UCST (cf. Fig. 2). The mechanical and damping properties of this series of experiments together with the composition of the polyurethane elastomers are summarized in Table 4.

There is no influence of the synthesis on tensile strength or elongation at break in both series. Rebound resilience seems to be slightly lower for double prepolymer PUR with the exception of **104-2** and **104-4**, where they are equal within experimental error. Permanent set values are lower for the double prepolymer elastomers. Glass transition temperatures from DSC again are on average 20 K lower than those from DMTA for PEG/PPG (series **103**), while they are equal in the series **104** with the exception of **104-2**, where two maxima of tan δ are detected, one in the order of the DSC-value, the other with 26.6 °C as low as in the other series. The maxima of tan δ are in the range from 0.3 to 0.5 for PEG/PPG polyurethanes and from 0.12 to 0.32 for PEG/PTMO elastomers. The temperature range in which tan δ is larger than 0.1 is considered to be the range of damping. It is broader for the PEG/POTM series (approximately 80 K) and of the order of 60 for the PEG/PPG elastomers. This behavior is further illustrated by tan δ vs. time curves, which are shown in Figure 4.

The concept of immiscible soft-segment polyols obviously can be used to synthesize polyurethanes with good damping properties, a drawback of the materials used is the temperature range in which damping occurs. To introduce a further component in the polyurethanes that can contribute to damping at slightly higher temperature, tetraethyleneglycol was used as chain extender besides 1,4-butanediol. Again PUR-elastomers were made as described above.

From the data in Table 5 can be seen that the maximum of the loss factor in general is below 0.5. The only exception is the elastomer **113-1**, which is based on a polyesterdiol and tetraethyleneglycol. This sample has a maximum value of 0.90 for tan δ and in addition the damping maximum at room temperature, which also explains the very low rebound resilience of only 9 % for this sample.

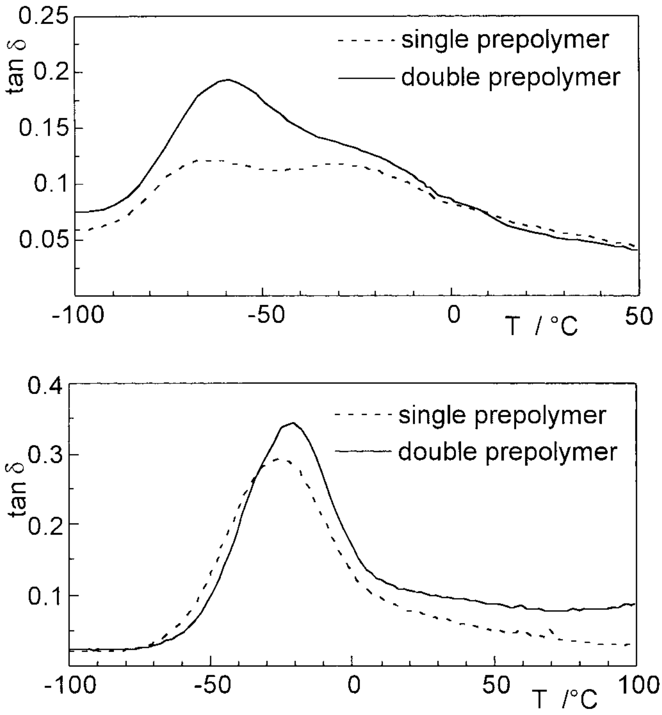


Fig. 4. Damping factor vs. temperature for elastomers 103-2 and -4 (left), for 104-2 and -4 (right).

Table 5. Influence of the hard-segment structure on viscoelastic properties of polyurethanes with immiscible soft-segments.

No.	Composition	tan δ max	tan δ > 0.1 °C	Range °C	Rebound resilience[a] %
106-1	PTMO-TEG	0.18 0.34	-73 – 200	273	44
90-1	PTMO-BDO	0.17	-85 – -4	81	53
113-1	PEBA-TEG	0.90	-8 – 200	208	9
98-4	PEBA-BDO	0.35	-36 – 23	59	39
110-2	PPG-PEBA-BDO	-0.28	-42 – 15	56	34
114-1	PPG-PEBA-TEG	0.38 0.47	-42 – 200	242	18
112-2	PO / EO-TEG	0.29 0.34	-70 – 119	189	34

TEG: tetraethyleneglycol; BDO: 1,4-butanediol
a) rebound resilience according to DIN 53512

The temperature range of damping (tan δ > 0.1) is very large for elastomers with TEG as chain extender (190 K and more), which can also be seen from Figure 5, where storage modulus and loss factor of a polyurethane based on PPG and polyester with TEG as chain extender are shown as a function of temperature. For this sample the loss factor is bigger than 0.2 from -40 °C up to the melting of the hard-segments near 200 °C.

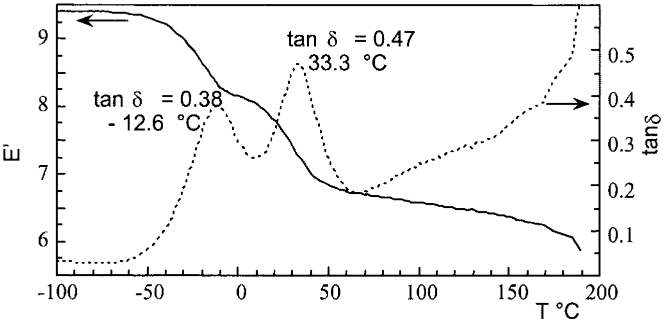


Fig. 5. DMTA of polyurethane 114-1 (frequency 1Hz).

Conclusions

The concept of immiscible soft-segment polyols in intimate contact has been applied to study polyurethane elastomers for mechanical and sound vibration damping. Synthesis from a homogeneous mixture of components proceeds via reaction driven phase separation to the expected morphology (cf. Figure 1). As glass transition temperatures of standard commercial soft-segment polyols are at low temperature, an additional phase to provide damping was introduced by means of a hard-segment consisting of oligourethanes from MDI and tetraethyleneglycol. This provided some phase mixing with increase of TG of the different soft-segment phases and a transition from the amorphous parts of the hard-segment. Efficient damping over a temperature range of more than 200 K was achieved by this method. The results prove that reaction driven phase separation has the same efficiency in terms of mixing of immiscible material on a nearly molecular level as IPNs. Work to extend this concept to polyurethane foams is under progress.

Acknowledgment

Financial support of this work from the Fonds der Chemischen Industrie gratefully acknowledged.

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