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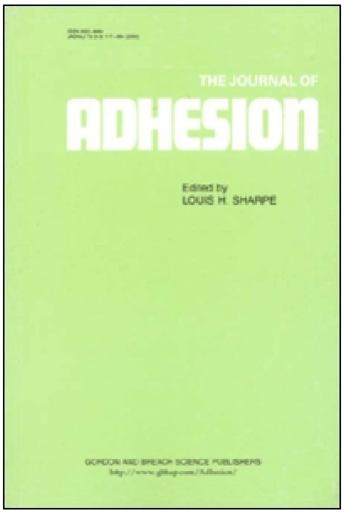

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Adherence of Liquid Crystalline TDI-Polyurethanes to Steel*

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Linear liquid crystalline polyurethane (LC-PU) were synthesized by the reaction of 2,4-toluene diisocyanate (TDI), 4,4'-bis-(6-hydroxyhexoxy)biphenyl (BHHBP), and poly(butylene adipate) (PBA). The BHHBP as mesogenic unit was incorporated into the hard segment formed by the reaction with the TDI. The hard segments are incompatible with the PBA soft segments. The mesomorphic behaviour is influenced by both the soft segment length and the hard segment concentration.

The adhesion of such polyurethanes used as primer in composites based on steel as substrate and alkyd melamine resin as coating is dependent on the polyurethane structure, the thickness of the polyurethane layer and its drying conditions. The highest wet adhesion stability is achieved by the hard-segment-type polyurethane composed of TDI and the mesogenic unity BHHBP. Partial substitution of BHHBP by 2,2-bis-(hydroxymethyl)propionic acid (BHMPA) in this LC polyurethane enhances the effectiveness of the primer.

KEY WORDS: Main-chain liquid crystalline polyurethanes; primer on steel; pull-off test; wet adhesion of alkyd melamine resin; mesogenic unit; glass transition temperature; hard segments; soft segments.

INTRODUCTION

The adhesion of an organic coating to steel is reduced under humid conditions, if water can penetrate through the polymeric layer to the substrate. The water accumulates in the interlayer between the organic coating and the substrate and weakens the interfacial bonds.[1–4] Highly ordered polymers hinder the penetration of low molecular mass molecules such as water.[5] As a primer they should increase the wet adhesion stability of a polymeric coating on steel.

While liquid crystalline polyesters and polyamides have been well known for more than 30 years, liquid crystalline polyurethanes (LC-PU) are a relatively "young" group of polymers: the earliest study about LC-PU was published by Iimura *et al.* in 1981.[6]

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Most publications dealing with main-chain LC-PU refer to hard-segment-type polyurethanes. Generally, mesogenic diisocyanates and/or mesogenic diols are used for the synthesis of polyurethanes with mesogenic properties of the hard segment phase.[7–15]

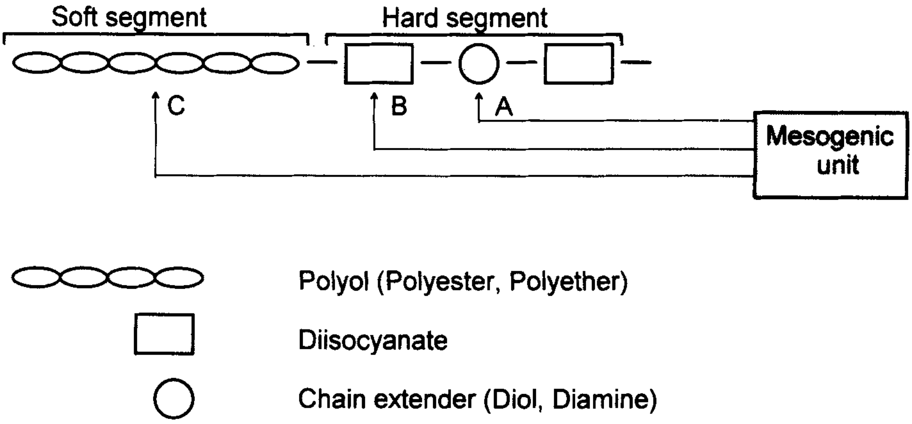
The object of our work was the preparation and characterization of LC-PU based on 2,4-toluene diisocyanate and the well-investigated mesogenic diol 4,4′-bis-(6-hydroxyhexoxy)biphenyl (BHHBP) and its modification by incorporation of poly(butylene adipate)s (PBA) of different molecular weight as soft segments in the main chain.[16] The general structure of a segmented polyurethane and the possibilities for incorporating the mesogenic units in the main chain are shown in Scheme 1. In our work only procedure (A) was used, *i.e.* incorporation of the mesogenic diol into the hard segment.

Referring to Funke *et al.*,[4] who had shown that carboxylic groups are excellent adhesional moieties for a composite with steel, we incorporated different amounts of 2,2-bis-(hydroxymethyl)propionic acid (BHMPA) into the hard-segment-type LC-PU as chain extender to achieve an increased specific interaction of the LC-PU with the oxidic steel surface. Polyurethanes obtained in this way were also applied as primer in a composite consisting of steel as substrate and an alkyl melamine resin as coating. The wet adhesion stability of the polymeric coatings was investigated.

EXPERIMENTAL

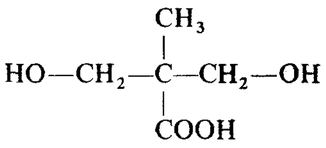
Dioxane (BASF) was dried by refluxing over 4,4′-diphenylmethane diisocyanate (MDI, BASF Schwarzheide) for 5 h, distilled and stored over activated 3–4 Å molecular sieves. N,N-dimethylformamide (DMF, Merck) was dried and stored in the same manner but it was distilled under vacuum.

2,4-Toluene diisocyanate (TDI, Merck) was used as received and stored at 0°C. 1,4-Butanediol (BD) was purified by vacuum distillation and kept dry by storage over activated molecular sieves.



SCHEME 1 General structure of segmented polyurethanes and possibilities for the incorporation of mesogenic units into the main chain.

2,2-Bis-(hydroxymethyl)propionic acid (BHMPA, Fluka)



$$\mathrm{HO{-}CH_2{-}\underset{\displaystyle \mathrm{COOH}}{\overset{\displaystyle \mathrm{CH_3}}{\overset{|}{\underset{|}{C}}}}{-}CH_2{-}OH}$$

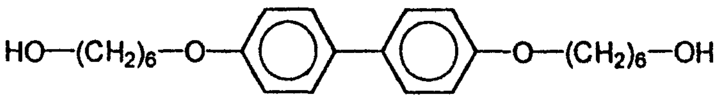
was used as received.

The PBA's were products of BASF Schwarzheide. The exact molecular weights were estimated by endgroup titration:

PBA 2000 (BA 20):	1860
PBA 600 (BA 6):	650.

Before use, the polyesters were heated under vacuum for 1 h at 160°C in a rotary evaporator. The water content was found to be $< 0.05\%$ by Karl-Fischer titration.

The mesogenic diol 4,4'-bis-(6-hydroxyhexoxy)biphenyl (BHHBP)



was prepared in a similar manner as reported by Stenhouse *et al.*[12]

The LC-PUs with OH-end groups were synthesized by a two-step prepolymer process in dioxane as solvent.[16] The LC-PU with carboxylic and hydroxylic groups were obtained in analogy to Yang[17] as follows:

BHHBP and the calculated amount of 2,4-TDI were reacted to an NCO-containing prepolymer in dioxane as solvent in the presence of 0.05% dibutyl tin dilaurate as catalyst at 80°C for 2 h. In a second four-necked flask, equipped with mechanical stirrer, gas inlet, condenser with drying tube and dropping funnel, BHMPA was dissolved in DMF at 60°C. The hot BHHBP/TDI-prepolymer solution was added to the BHMPA-solution in DMF and reacted at boiling temperature for 5 h. The polymer solution was poured in water and the precipitated polymer removed by filtration. The filtrate was extracted in a Soxhlet extractor for 2 h using water and then for 2 h using methanol as the solvent. The molecular weights were estimated by Size Exclusion Chromatography to be between 10000 and 15000. The concentration of the OH groups in the presence of the COOH-groups was estimated in DMF as described by Krüger and Gnauck.[18] The acid number was determined by titration with KOH in DMF solvent.

Films of 70–100 μm in thickness were obtained by casting the polymer solution on glass plates and evaporating the solvent under vacuum at 80–120°C, depending on the solvent. The polyurethanes were characterized by differential scanning calorimetry (DSC), polarizing microscopy and dynamic mechanical analysis (DMA).

For the adhesion measurements an adhesive tape pull-off test was used taking into account DIN 53232 (ISO 4624). The arrangement of the sample for the pull-off test is shown in Figure 1. The primer layers on the steel surface (St 1405) were obtained by

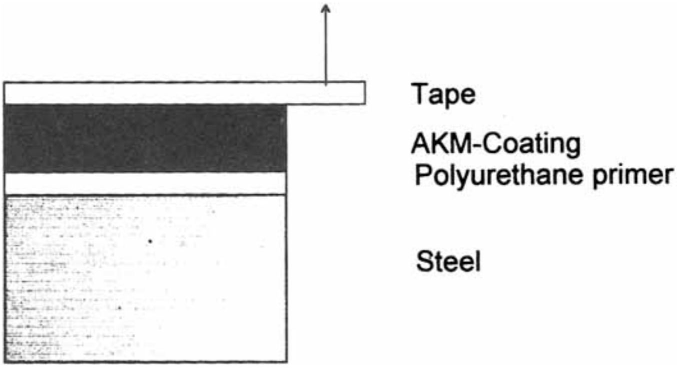


FIGURE 1 Sample for the pull-off test.

adsorption from differently concentrated polyurethane solutions for some days and dried at different temperatures. The prepared primer layers were overcoated with an alkyd melamine resin (AKM) with a thickness of about 50 µm by centrifugal casting and cured for 20 min at 140°C. The AKM-system consisted of 64 wt-% Alkydal F251 (Bayer) and 27 wt-% Maprenal MF800 (Casella), with xylene and ethylene glycol as solvents.[4] The coating was scratched down to the substrate. An adhesive tape (Tesaband 4651, Beiersdorf) was pressed on the AKM surface with a steel roller using 20 N/cm. For measuring the adhesion before and after storage in distilled water the tape was pulled off jerkily. If more than 10% of the organic layer was removed at the scratch, it was considered that the adhesion had failed.

RESULTS AND DISCUSSION

The composition of the investigated polyurethanes and the results of the Size Exclusion Chromatography (SEC) are summarized in Table I. The lower molecular weight of the

TABLE I
Composition of the LC-Polyurethanes without Carboxylic Groups; Results of Size Exclusion Chromatography (SEC)

PUR-Symbol	Hard segment content [weight %]	SEC Solvent: DMF Temperature: 25°C		
		Mn	Mw	[η] (dl/g)
T/BH	100	26700	33700	0.19
T/BA20	7.2	41300	58200	0.28
T/BA20/BH(1/1)	25.9	33700	41700	0.39
T/BA20/BH(1/4)	53.4	39000	51000	0.39
T/BA6	30.4	38000	62500	0.340
T/BA6/BH (1:1)	53.2	55600	80800	0.585
T/BA6/NH (1:4)	79.0	35600	106000	0.37

Abbreviations: T: 2,4-TDI; BH: BHHBP; BA20: PBA 2000; BA6: PBA 600
In parenthesis: Ratio PBA/BHHBP
All polyurethanes were synthesized as OH-terminated products.

unsegmented polyurethane T/BH may be caused by a limited solubility of the polymer in cold DMF.

The thermal behaviour of the polyurethanes was investigated by Differential Scanning Calorimetry (DSC) using the Perkin Elmer DSC-7 instrument with heating and cooling rates of 20°K/min, respectively.

The DSC thermogram of the unsegmented LC-polyurethane T/BH exhibited the following thermal behaviour (Fig. 2):

The heating curves showed the glass transition temperature (T_g) at 84°C. The T_g region was followed by a broad exotherm due to postcrystallization, with a peak at 117/120°C, and two sharp endotherms appearing at 157 (Tm1) and 169°C (Tm2). As reported by Smyth *et al.*,[19,20] these two endothermic peaks are associated with crystal melting but not with the crystal-mesophase and the mesophase-isotropic transitions, respectively. Upon cooling, the exotherms at 123 and 105°C are associated with the isotropic-mesophase and the mesophase-crystal transition, respectively.[12,19,20]

The thermal behaviour of the segmented polyurethanes with the mesogenic unit in the hard segment is characterized by three temperature ranges:

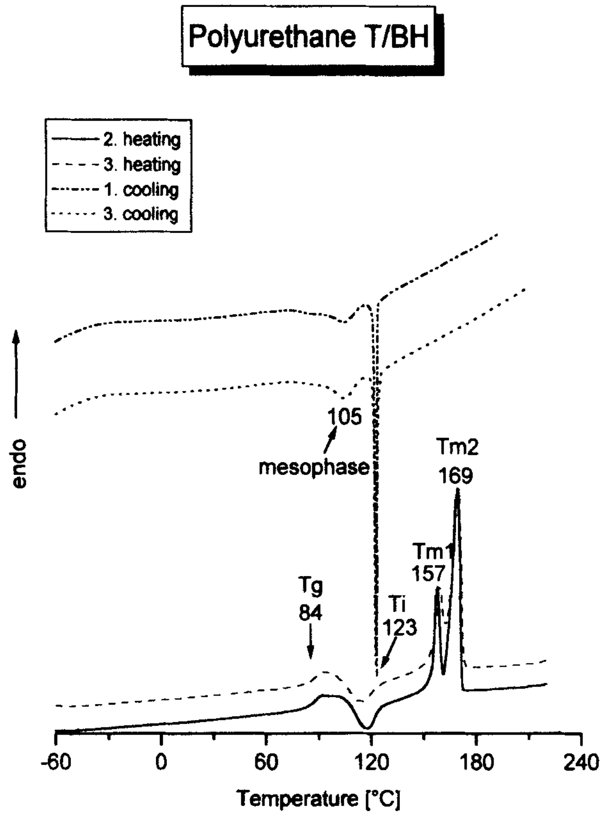


FIGURE 2 DSC thermogram of the unsegmented LC-polyurethane based on 2,4-TDI and BHHBP.

- The T_g region of the soft segment appearing in the temperature range from — 50 to 40°C.
- The temperature interval from 40–100°C, which includes the crystal melting of the soft segment phase and other physical phase transitions not clear up to now.
- The temperature Tm1 (130–150°C) and Tm2 (150–170°C) resulting from the transitions of the mesogenic hard segments.

Depending on the molecular weight of the applied polyester diol, pronounced differences of phase behaviour were observed.

While the T_g of polyurethanes based on PBA 2000 remains nearly constant, the polyurethanes with PBA 600 exhibit increasing T_g's with growing hard segment content (Fig. 3). This indicates a forced partial miscibility of hard and soft segments caused by the relatively short soft segment length. With PBA 2000 as soft segment, in the first DSC run melting of the crystalline soft segment phase is observed at about 50°C. The forced miscibility of PBA 600 soft segments with the BHHBP/TDI hard segments causes a lowering of the transition temperatures Tm1 and Tm2 of the mesogenic hard segments (Fig. 4). While products based on PBA 2000 exhibit LC-properties at hard segment contents >40%, the miscibility between hard and soft

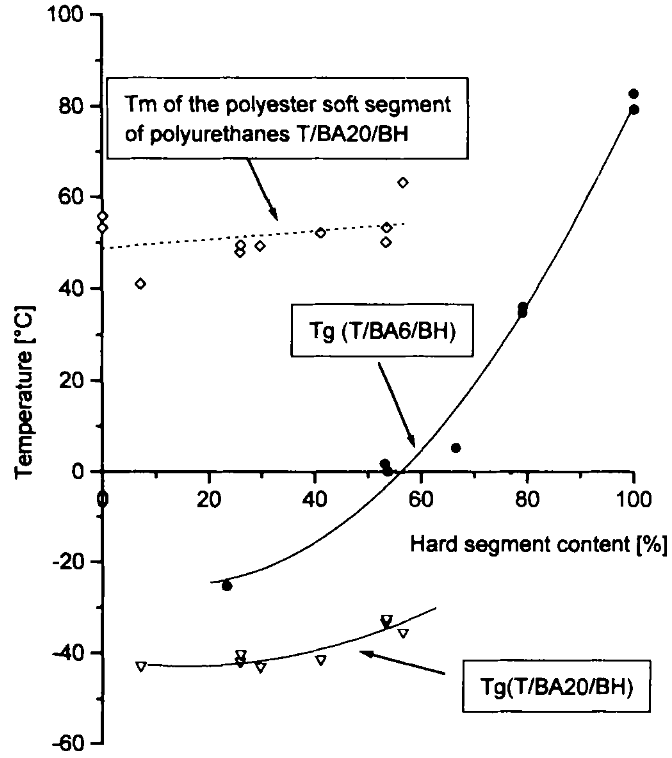


FIGURE 3 Glass transition temperature of segmented BHHBP polyurethanes and melting temperature of crystals of the PBA 2000 soft segment as measured by DSC.

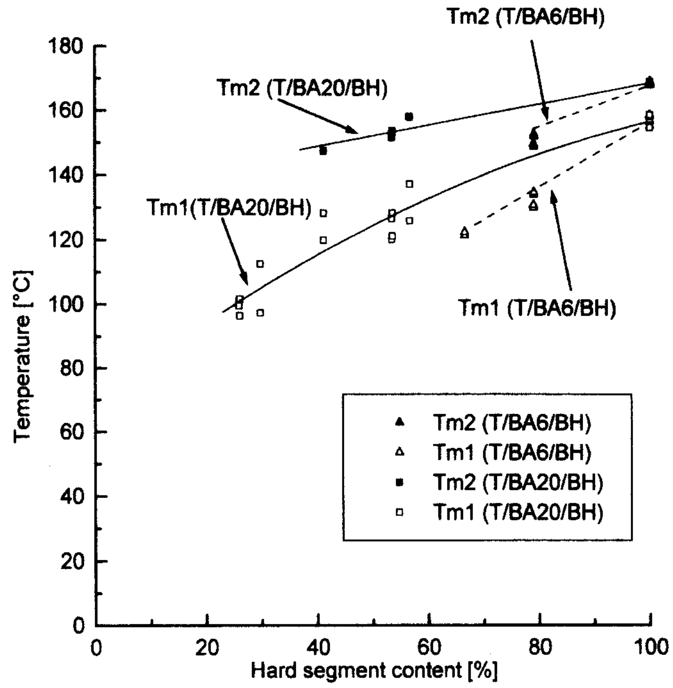


FIGURE 4 Dependence of the temperature position of the two melting peaks, Tm1 and Tm2, on the hard segment content for segmented polyurethanes based on PBA 600 and 2000.

segments suppresses the formation of the mesophase in polyurethanes with PBA 600 at hard segment contents below 60%. DMA measurements confirm that conclusion on the morphology of the investigated polyurethanes.[16]

The results of wet adhesion in the composite composed of steel as substrate, the mesogenic polyurethane as primer, and an alkyd melamine resin as coating are summarized in Table II. It is shown that the effectiveness of the polyurethane primer is

TABLE II
Wet Adhesion of AKM Coatings on Steel with Mesomorphic Polyurethanes as Primer

PUR type	Primer (PUR solution) (%)	Thickness of the primer layer (μm)	Drying temperature (°C)	Wet adhesion (days)
T/BH	0.2	~0.10*	70	1
T/BH	1.0	~0.25*	70	1
T/BA20/BH(1/4)	1.0	~0.40*	70	1
T/BH	15.0	8.0**	160	70–84
T/BA20/BH(1/2)	15.0	10.0**	160	28
T/BD[1]	15.0	10.0**	160	28–35

[1] 1,4-Butanediol as chain extender in comparison with a non-mesogenic unit
* By electron microscopy
** By electromagnetic induction (Permascope)

dependent on the structure of the polyurethane, the thickness of the primer layer, and the drying temperature of this layer. If the primer layer is thinner than 1 µm, the adhesion time after storage in water does not exceed one day. In this case, the formed layer was incomplete and defects were shown by optical microscopy. The coverage of the steel surface was comparable with islands. For a better (that means more durable) wet adhesion, a primer thickness of 5–10 µm and drying near the melting temperature, Tm1, of the mesogenic hard segment unit is necessary. The thicker layer was found to be without defects.

The highest wet adhesion of about 70 days could be achieved with the unsegmented polyurethane composed of TDI/BHHBP. This polyurethane represents a system with the most ordered morphology. In comparison, for the equivalent lower-ordered T/BD-polyurethane the wet adhesion durability is reduced by one-half.

A further increase in wet adhesion stability was observed using LC-PU's with carboxylic groups. Therefore, the T/BH-polyurethanes were chain extended with BHMPA as a COOH-containing diol. The composition of the investigated polyurethanes, their acid number and the results of wet adhesion are summarized in Table III. The drying temperature was 160°C. The carboxylic groups strongly influence the wet adhesion. With a primer layer thickness of about 2 µm, the wet adhesion was stable for more than 84 days. Not enough samples were available for proving further long-term wet adhesion tests. In comparison, with the T/BH-primer a better film formation without defects was observed at a lower layer thickness. Funke[2,3] has shown that an optimal adhesion will be reached if the adhering macromolecules have a stiff chain structure and a sufficient number of polar groups. With the introduction of carboxylic groups in the main chain of the liquid crystalline polyurethane, such a wet-adhesion-promoting structure was realized. At present, the question cannot be answered whether the improved adhesion with the inclusion of carboxylic acid groups is simply an additive or synergistic effect. To get more information on the dependence of the wet adhesion on the COOH-concentration of the polyurethanes, further investigations are necessary.

TABLE III
Wet Adhesion of AKM Coatings on Steel with Mesomorphic Polyurethanes Containing Carboxylic Groups as Primer (Drying temperature of the primer layer: 160°C)

PUR type	Acid number	Primer solution (%)	Thickness of the primer layer (µm)*	Wet adhesion (days)
T/BH/PA 40/36/5	13	0.2	< 1	1
T/BH/PA 40/36/5	13	1.0	< 1	2
T/BH/PA 40/36/5	13	5.0	2 ± 1	21–56
T/BH/PA 39/32/8	22,2	0.2	< 1	3–7
T/BH/PA 39/32/8	22,2	1.0	< 1	28–70
T/BH/PA 41/28/14	39,6	0.2	< 1	3
T/BH/PA 41/28/14	39,6	1.0	< 1	28–35
T/BH/PA 41/28/14	39,6	5.0	2 ± 1	> 84

* Thickness measured by electron microscopy
PA = BHMPA

SUMMARY AND CONCLUSIONS

Polyurethanes based on TDI and BHHBP as mesogenic unit are highly ordered polymers with LC properties. Incorporation of poly(butylene adipate)s as soft segments reduces the morphological order in the hard segment fraction of the polyurethane, depending on the chain length of the polyester. The wet adhesion stability was increased by applying LC-PU's as primer layer in a steel composite coated with an alkyd melamine resin. The wet adhesion is strongly increased at a primer layer thickness of about 10 μm and a drying temperature of this layer of 160°C. A further increase in wet adhesion (> 84 days) is observed by incorporation of carboxylic groups into the LC-PU. The concept of using a highly-ordered interlayer, realized by a LC-PU primer, to increase the wet adhesion stability of polymeric coated steel turns out to be successful.

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