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Use of new hydroxytelechelic cis-1,4-polyisoprene (HTPI) in the synthesis of polyurethanes (PUs): Influence of isocyanate and chain extender nature and their equivalent ratios on the mechanical and thermal properties of PUs

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Abstract: New segmented polyurethanes (thermoplastic-elastomers) based on previously described hydroxytelechelic cis-1,4-polyisoprene (HTPI), miscellaneous isocyanates and chain extenders at various equivalent ratios were prepared by the classical one-shot method. The influence of the nature of isocyanate and chain extender, as well as their equivalent ratios, on the mechanical and thermal materials behavior was investigated. Thus, a comparative assessment of material properties was performed. Microphase separation of hard and soft segments was observed by DMTA, DSC and AFM. Moreover, according to Thermogravimetric Analysis (TGA), linear relationships depending on the isocyanate and chain extender nature were found between the weight loss (%) and the percentages of hard segments. A classification of thermal stability in terms of weight loss was established. With the aim of a thermo-mechanical comparative study, polyurethane elastomers based on HTPI and isocyanates without chain extender, were also synthesized.

Introduction

Due to their versatility, polyurethanes are successfully employed as technological and specialty polymers in a large number of applications (shipbuilding, footwear, construction, cars, abrasion-resistant coatings, adhesives, fibers, biomaterials etc) [1, 2]. Moreover, improvement of their properties such as elasticity, dyeability, biocompatibility or shape memory effect is easily obtained by simple chemical modifications. This is particularly apparent for linear segmented polyurethanes [3-12] that are copolymers containing hard segments which present a melting point or glass transition temperature above ambient as well as soft polymeric segments which exhibit a glass transition and/or melting point considerably below room temperature. In these systems, the hard segments aggregate or crystallize to form distinct microphases and act as physical crosslinks for the soft phase, thereby imparting a rubbery character at room temperature. At elevated temperatures, the hard segments melt or soften and allow the copolymer to flow and to be processed like an ordinary thermoplastic resin. The hard phase is generally formed by an aromatic diisocyanate and an aliphatic diol, while the soft segment consists of an aliphatic polyol (mostly with polyether and polyester backbones). The synthesis of such polymers from renewable resources has attracted considerable attention from polymer scientists throughout the world because of their potential attributes as substitute petrochemical derivatives. With petroleum production facing exhaustion day over day, scientists and technologists focus their attention on renewable resources because these materials may act as potential raw materials for the manufacture of polymers in the 21st century [13, 14]. In this respect, Telechelic Liquid Natural Rubber (TLNR) represents a potent precursor of very wide range of polymers. The selective cleavage of high molecular weight polymers for the obtaining of Telechelic Liquid Natural Rubber (TLNR) and the chemical modification of such oligomers has been the center of lot of activities [15-17]. Strongly involved in chemical modifications of polydiene elastomers and Natural Rubber, our group focused its attention on selective degradation of cis-1,4-polyisoprene using well-controlled oxidative chain-cleavage of high molecular weight polyisoprene leading to new carbonyltelechelic cis-1,4-polyisoprene [18-20]. Chemical modifications of carbonyl end-groups and carbon-carbon double bonds at various ratios led to new hydroxy or aminotelechelic cis-1,4-polyisoprenes [20, 21]. Moreover, polyurethanes with different soft segment backbones based on these new oligomers were synthesized and their thermo-mechanical comparative study was investigated [21]. In this work, we report the synthesis of new segmented polyurethanes (thermoplastic-elastomers) obtained by reaction of new hydroxytelechelic cis-1,4-polyisoprene (HTPI) with several isocyanates and chain extenders (diols) at various equivalent ratios. The influence of hard segment nature on the mechanical and thermal properties of the materials was investigated. Furthermore, for a comparative mechanical and thermal study, polyurethane elastomers based on HTPI and several isocyanates, without chain extender, were also synthesized.

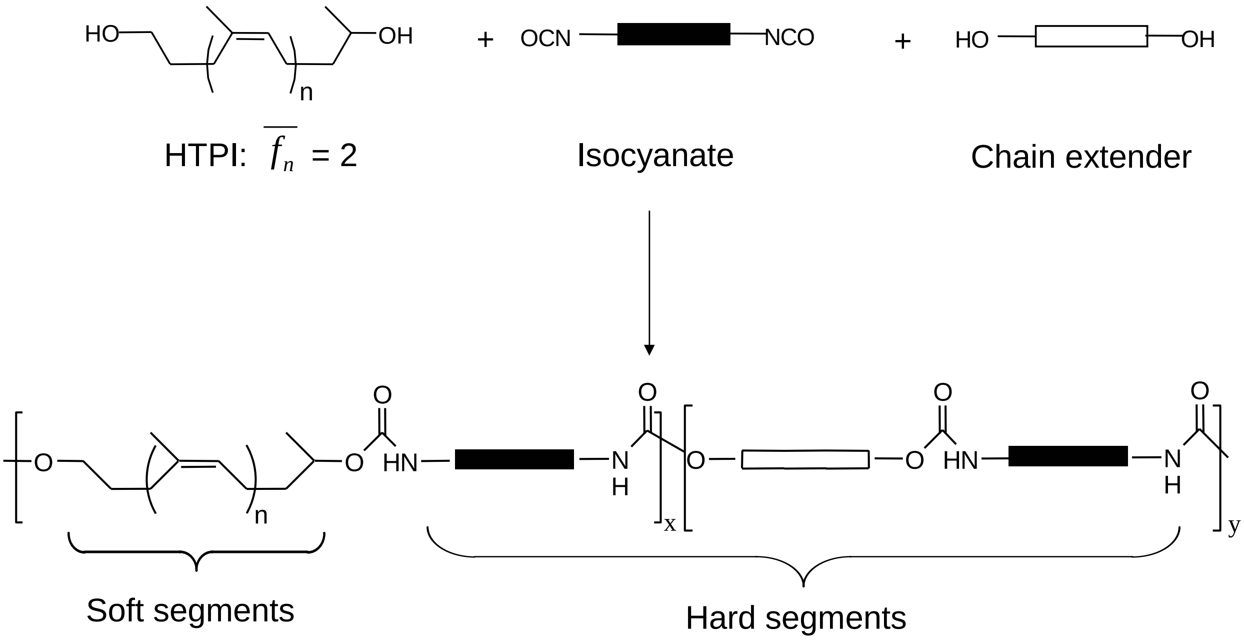
Results and discussion

Polyurethanes synthesis

Polyurethanes were synthesized by the classical one-shot method using solvent evaporation process under argon atmosphere at room temperature; materials obtained were next cured for 12 h at 60°C (Scheme. 1). Several isocyanates and chain extenders at various equivalent ratios (Tab. 1) were used to react with the hydroxytelechelic cis-1,4-polyisoprene (HTPI). For tensile tests, samples were prepared in bulk into a specific PTFE moulds.

Generally, all the obtained materials are yellowish, soft and transparent. When the $[OH_{ex}]/[OH_p]$ ratio is equal or is higher than 1.0, materials became hard and opaque due to, an increase in hard segments content and microphase segregation, respectively. Owing to a higher compact physical network, materials synthesized in presence of chain extender exhibit a density higher than 1.000. On the other hand, densities are generally lower than 1.000 for materials synthesized without chain extender.

Molar mass measurements could not be performed. Probably, this is due to the very high molecular weights of the obtained polyurethanes and possible secondary isocyanate reactions, such as allophanate formation. The solubility of the expected linear PUs, in some usual solvents (tetrahydrofuran, dichloromethane, chloroform, DMF, toluene) were found to be partial, despite improvement attempts by LiCl addition in order to break hydrogen bonds.



Scheme. 1. Synthesis of polyurethanes.

The FTIR spectra of all polyurethanes show the existence of absorption at approximately 3300 cm^{-1} and 1700 cm^{-1}. This, corresponds, respectively, to N-H and C=O stretching vibrations of urethane functions. After polymerization, no NCO absorption is observed at 2270 cm^{-1} which indicates that the reaction is completed. In addition, as expected, when the amount of hard segments increases (increase of chain extender equivalent ratios), the intensity of urethane band increases as well (Tab. 1: PU3-5, PU8-10, PU18-20, PU23-25).

Thermo-Mechanical behavior

The evolutions of E' and tan δ versus temperature for the synthesized polyurethanes are reported in Fig. 1 to Fig. 5; tan δ curves are presented below the E' curves. In all cases, whatever the nature of hard segments, the DMTA curves show a similar soft segment mechanical transition temperature (T_α = -42°C), which indicates a high microphase segregation and no interaction between hard and soft phases. Owing to experimental conditions, the T_α of hard segments is generally not observed, especially in the case of linear polyurethanes. Indeed, the increase of polymer softening with temperature increasing leads to material failure caused by the DMTA probe just before the hard segment T_α.

When no chain extender is used, diisocyanate nature (TDI, MDI, H_{12}MDI) has no notable influence on the behavior of PUs; thus, similar thermo-mechanical curves are obtained (e.g. Fig. 1a with TDI). On the contrary, when an isocyanurate (I-IPDI) is used in the same conditions ([NCO]/[OH] = 1.05), the material is crosslinked (thermosetting material) and furthermore the amount of hard segments is higher because of elevated I-IPDI molecular weight (Tab. 1). Thus, we observe an increase of E’ at the rubbery plateau and a decrease of tan δ_{max}. The material failure involved by the DTMA probe occurs at T > 170°C, i.e. after the hard segments mechanical transition temperature which appears at $T_\alpha = 65°C$ (Fig. 1b). In previous work [22-24], similar microphases segregation has been observed using a hydrogenated hydroxytelechelic polyisoprene (HHTPI) based polyurethane network.

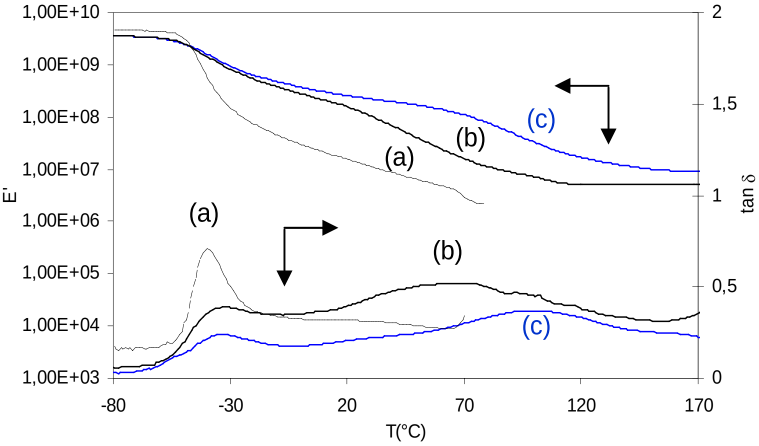


Fig. 1. Influence of the ratio [NCO]/[OH] = r on the thermo-mechanical behavior of synthesized polyurethanes: (a) PU1 (TDI, r = 1.05); (b) PU21 (I-IPDI, r = 1.05); (c) PU22 (I-IPDI, r = 1.75).

The increase of the isocyanate equivalent ratio ([NCO]/[OH] = 1.75) enhances the phenomenon whatever the isocyanate used (Fig. 1c and Fig. 2). Moreover, in the case of I-IPDI, we also observe an increase of the mechanical transition temperature of hard segments ($T_{\alpha\,(b)} = 94°C$) (Fig. 1c).

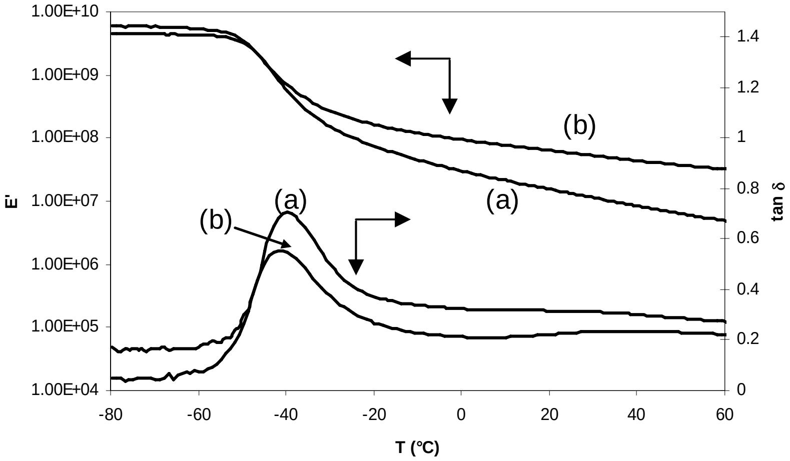


Fig. 2. Influence of the ratio [NCO]/[OH] = r on the thermo-mechanical behavior of synthesized polyurethanes: (a) PU1 (TDI, r = 1.05); (b) PU2 (TDI, r = 1.75).

On the other hand, when a chain extender is used, material based on TDI exhibits a lower E’ at the rubbery plateau and a higher tan δ_{max} compared to the others (Fig. 3). Furthermore, MDI exhibits the highest failure temperature. This behavior can be explained by a possible better aggregation of hard segments resulting from its aromatic structure, which enhances its mechanical resistance to failure.

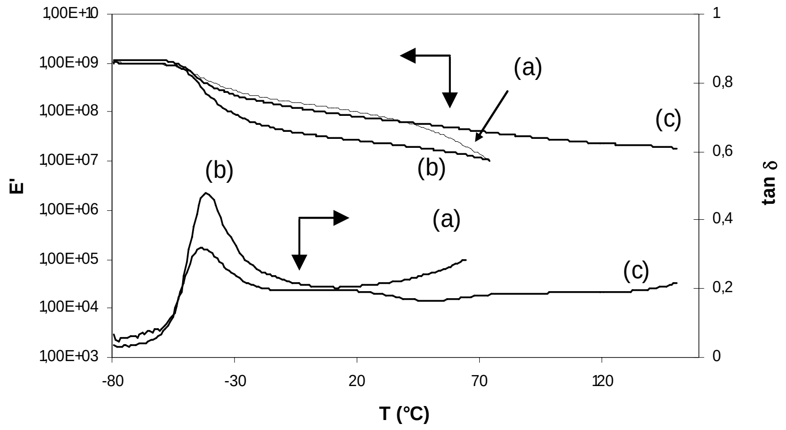


Fig. 3. Influence of diisocyanate nature in the presence of propanediol as chain extender using the ratio $[OH_{ex}]/[OH_p]$ = 2.00 on thermo-mechanical behavior of synthesized polyurethanes: (a) PU19 (H12MDI); (b) PU5 (TDI); (c) PU10 (MDI).

As expected, the increase of the chain extender equivalent ratio leads to an increase of E' at the rubbery plateau, an increase of length of the rubbery plateau, and a decrease of tan δ_{max} due to the increase of the hard segments ratio in the material (e.g. Fig. 4 for TDI and propanediol).

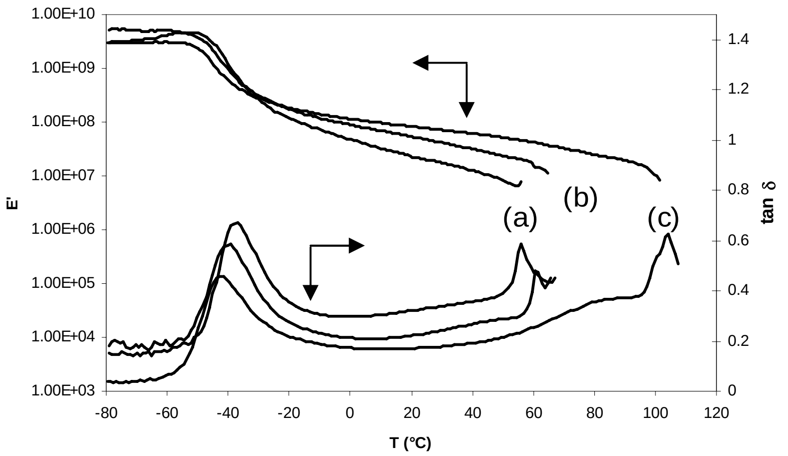


Fig. 4. Influence of chain extender concentration ($[OH_{ex}]/[OH_p]$ = r') on thermo-mechanical behaviour, e.g. for materials based on TDI and propanediol: (a) PU3 (r'= 0.50); (b) PU4 (r'= 1.00); (c) PU5 (r' = 2.00).

For the $[OH_{ex}]/[OH_p]$ equivalent ratio used (2.0), the increase of chain extender length does not exhibit a notable influence on the mechanical behavior except an increase of rubbery plateau length which may indicate an increase of hard segment mechanical transition temperature T_α (Fig. 5 a, b and c).

Compared to dihydroxy chain extenders, the use of trihydroxy analogues (glycerol) leads to a strong increase of the rubbery plateau length because of material crosslinking (thermosetting material) (Fig. 5e). Nevertheless, no notable change on E' and tan δ_{max} is observed owing to, approximately, the same weight percentage of hard segments in the compared materials.

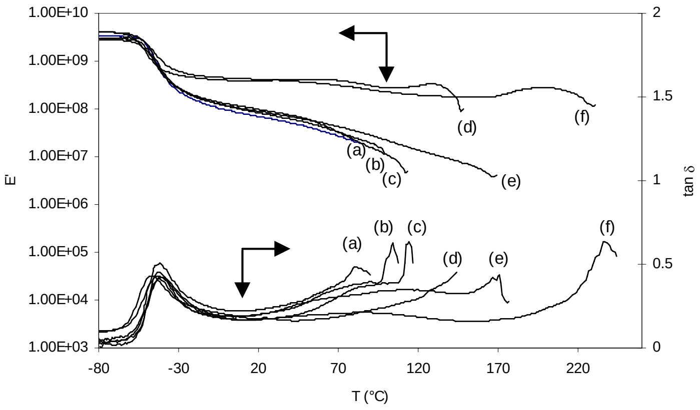


Fig. 5. Influence of chain extender nature on thermo-mechanical behavior, e.g. for materials based on TDI using the ratio $[OH_{ex}]/[OH_p] = 2.00$: (a) PU11 (ethanediol); (b) PU5 (propanediol); (c) PU13 (hexanediol); (d) PU25 (phenylenedimethanol); (e) PU14 (glycerol); (f) PU15 (tetraethyleneglycol).

Fig. 5 also shows the influence of the chemical structure of the chain extender on the mechanical behavior of materials at approximately, similar amount of hard segments (Fig. 5: (c) 1,6-hexanediol ; (d) 1,4-phenylene dimethanol ; (f) tetraethylene glycol). Compared to 1,6-hexanediol, higher values of E' at the rubbery plateau and failure temperatures are observed for tetraethylene glycol and 1,4-phenylene dimethanol. This can be explained by a decrease of flexibility due to aromaticity (ring rigidity and π-π interactions) in the case of phenylene dimethanol and due to polarity (hydrogen interactions) in the case of tetraethylene glycol.

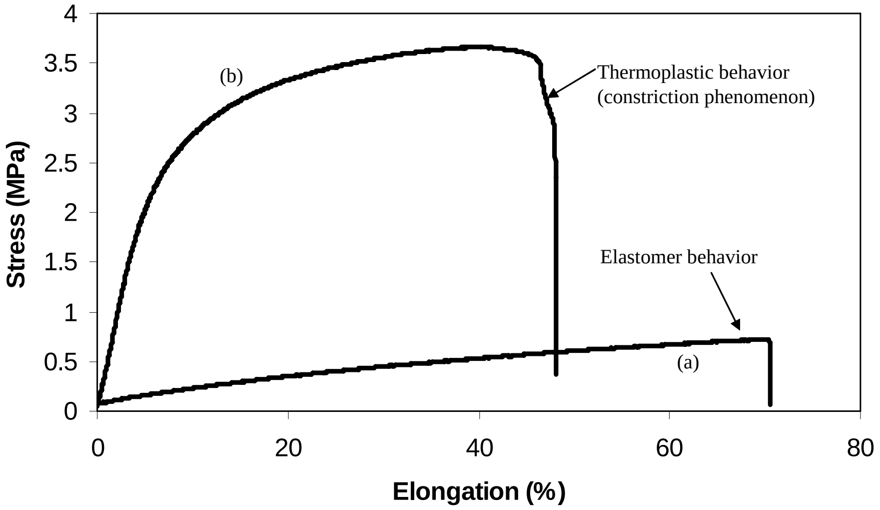


Fig. 6. Tensile test curves of: (a) PU16 (H_{12}MDI); (b) PU19 (H_{12}MDI and propanediol, $[OH_{ex}]/[OH_p] = 2.00$).

Fig. 6 shows an example of PU16 and PU19 tensile test curves which indicate that, for a small amount of hard segments (without chain extender), materials exhibit a typical elastomeric behavior, i. e. high elongation at break (70 ± 12 %), small ultimate stress (0.7 ± 0.1 MPa) and also a small Young modulus (2 ± 0.4 MPa). On the other hand, at higher amount of hard segments (i.e. with chain extender) materials exhibit thermoplastic behavior with relatively smaller elongation at break (48 ± 7 %), higher ultimate stress (3.7 ± 0.9 MPa), and a Young modulus (40 ± 3 MPa). In addition, a constriction phenomenon is experimentally observed just before breaking, confirming the thermoplastic behavior.

Thermal properties

DSC measurements performed on all different PUs yield similar results. Indeed, only one glass-transition temperature (T_g = -58°C) is observed, corresponding to the soft segments. This result confirms previous investigations performed by DMTA indicating microphases segregation.

Representative TGA curves of some prepared polyurethanes, which were obtained under an air atmosphere are shown in Fig. 7. For all tested polyurethanes, a three-step thermal degradation was observed. Weight losses and characteristic temperatures (T_{max}), were determined from the minima of the derived curve. The curves indicate that all polyurethanes remain stable up to 260°C, under the conditions used in the TGA, after which the first step of degradation occurs. More exactly, this temperature corresponds to the apparent temperature after which the sample starts to lose its weight, even if the cleavage of urethane bonds starts earlier. As demonstrated in our previous work [21], this first step corresponds mainly to the urethane degradation. Whatever the hard segment nature and content, same apparent end urethane degradation temperature was observed (345°C), thus, only comparative apparent thermal stability in terms of weight loss was evaluated. The second and the third steps correspond mainly to the soft segments degradation [21].

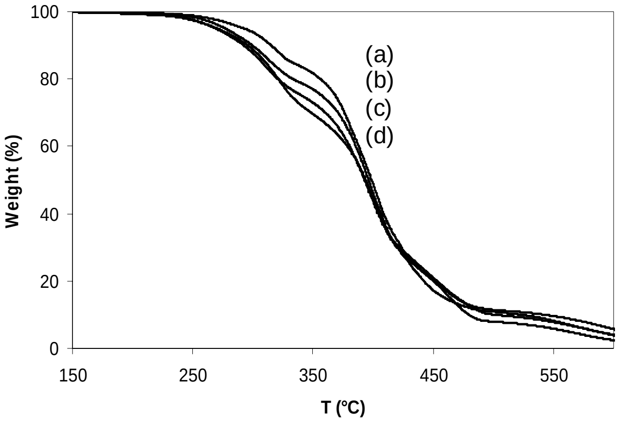


Fig. 7. Influence of chain extender concentration ($[OH_{ex}]/[OH_p]$ = r') on thermal degradation under air, e.g. for materials based on TDI: (a) PU1 (r'= 0.00); (b) PU3 (r'= 0.50); (c) PU4 (r'= 1.00); (d) PU5 (r'= 2.00).

Generally, the weight loss observed at the urethane degradation step is in consistency with the percentage of hard segments (Fig. 7). In fact, linear relationships, which depend to the isocyanate and chain extender nature (Fig. 8 and Fig. 9), were found between the weight loss and the percentage of hard segments. The dashed line in these figures corresponds to theoretical total degradation of hard segments. This theoretical curve includes a 6% contribution (observed from HTPI TGA curve [21]), that corresponds to the degradation of the polyisoprene backbone in this zone of temperature.

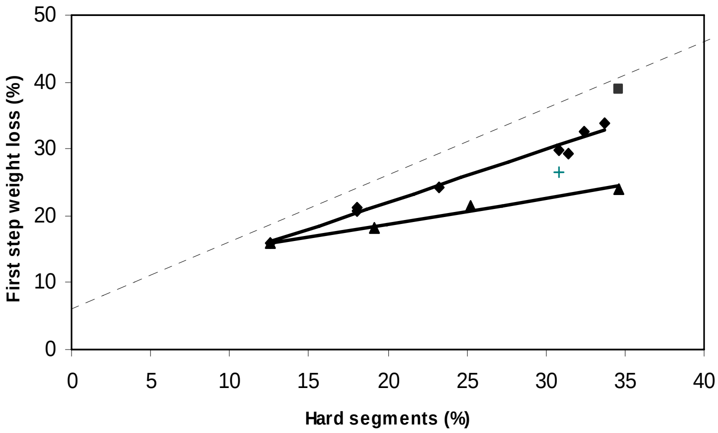


Fig. 8. Influence of chain extender nature on thermal stability in terms of weight loss, e.g. for materials based on TDI: (◆) n-alcanediol; (▲) phenylene dimethanol; (■) tetraethylene glycol; (+) glycerol; (-----) theoretical curve.

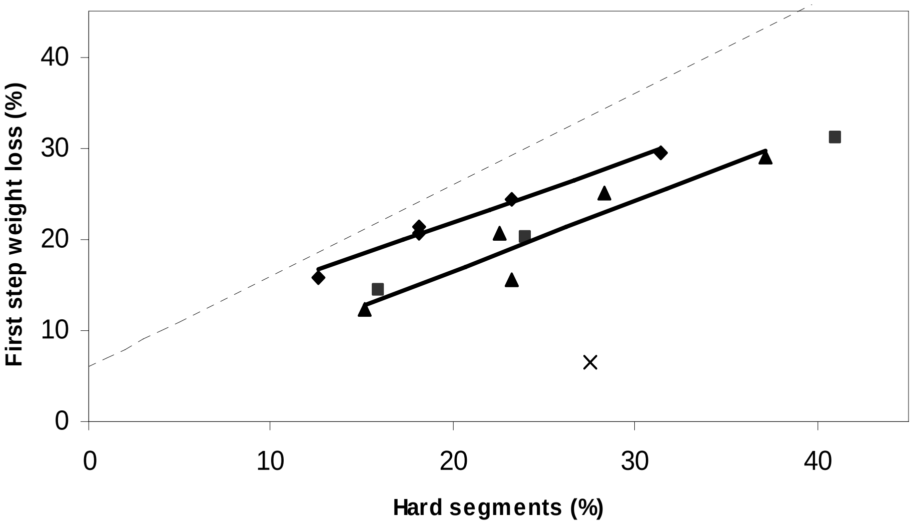


Fig. 9. Influence of isocyanate nature on thermal stability in terms of weight loss: (◆) TDI; (▲) MDI; (■) H_{12}MDI; (×) I-IPDI.

One can observe that the increase of hard segment content leads to a decrease of thermal stability in terms of weight loss (slope > 0) and a decrease of real hard segment contribution (increase of the difference between experimental and theoretical weight loss; slope < 1) at the first step degradation.

The linear curves which depend on the nature of the chain extender (Fig. 8), clearly show the following order of thermal stability: PUs (tetraethylene glycol) < PUs (n-alcanediol) < PUs (glycerol) < PUs (1,4-phenylene dimethanol). Similarly, the linear curves which depend on the nature of the isocyanate (Fig. 9) shows the following order of thermal stability: PUs (TDI) < PUs (H_{12}MDI), PUs (MDI) < PUs (I-IPDI).

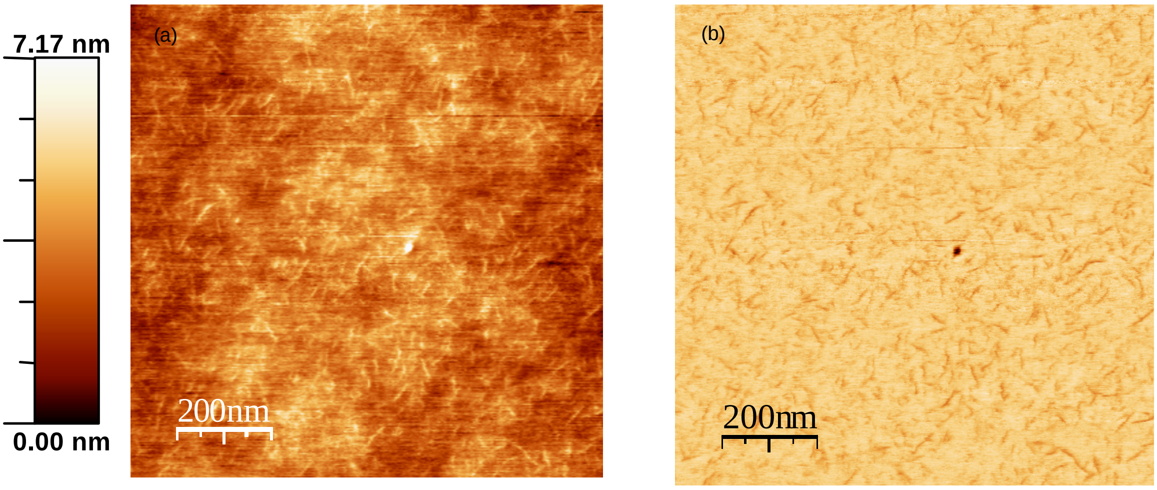


Fig. 10. AFM height (a) and phase (b) images of PU1 (TDI), roughness: 3.7Å.

Fig. 10 and Fig. 11 show AFM images for PU1 (12.6 % of hard segments) and PU5 (31.4 % of hard segments), respectively. The height images (Fig. 10a and Fig. 11a) enable the measurement of the roughness of such polymer surfaces. Roughness values are less than 5 Å, the surfaces are thus very smooth. The phase images (Fig. 10b and Fig. 11b) clearly show a two-phase morphology related to hard segment content; therefore, the microphases segregation is more pronounced for PU5 than for PU1. Hence, these results confirm our previous observations obtained using DTMA and DSC.

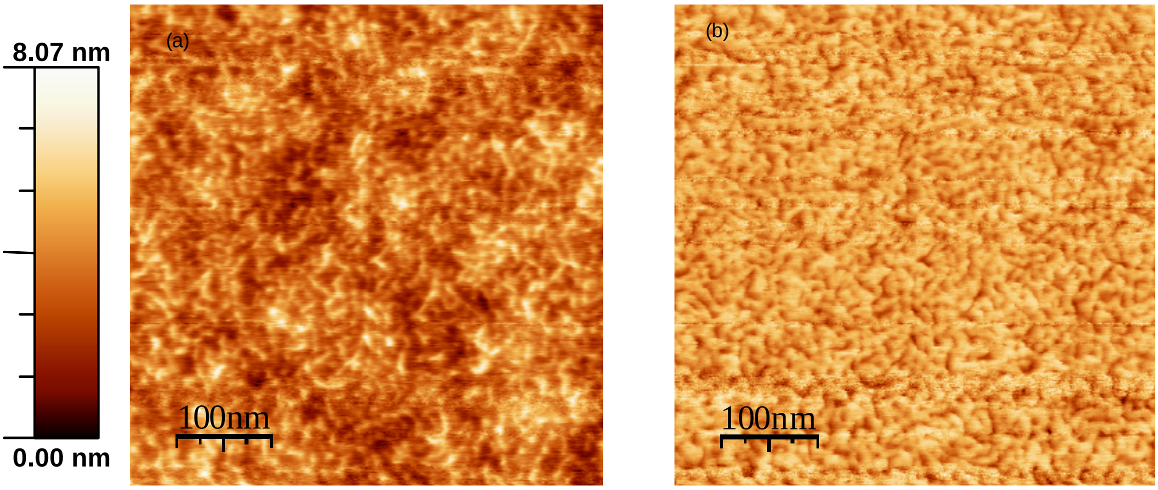


Fig. 11. AFM height (a) and phase (b) images of PU5 (TDI, propanediol), roughness: 5 Å.

Conclusions

In this work, we have synthesized new segmented polyurethanes and polyurethane elastomers from hydroxytelechelic cis-1,4-polyisoprene (HTPI) using several isocyanates and chain extenders at various equivalent ratios. Materials obtained were soft and no interactions between hard and soft phases were observed. Softening of thermoplastic materials was found to depend on the nature of the chain extender. Thermosetting materials were obtained with isocyanates or with chain extenders possessing functionality higher than 2. Modification of the nature of the hard segments as well as modification of the nature of the soft segments, by previously described chemical modification of HTPI backbone [21], offers a wide range of material properties. This leads to a large domain of potential applications for oligomers synthesized from Natural Rubber, a renewable resource.

Experimental part

Materials

Periodic acid (Acros, 99%), cis-1,4-polyisoprene (Acros, 98% cis, $\overline{M_w} = 800000$), meta-chloroperbenzoic acid (mCPBA, Janssen, 70% by titration), sodium borohydride (Acros, 98%), dibutyl tin dilaurate (DBTL, Aldrich), 4,4'-methylene bis(cyclohexyl isocyanate) ($H_{12}MDI$, $CH_2(C_6H_{10}NCO)_2$, Bayer), 4,4'-methylene bis (phenyl isocyanate) (MDI, $CH_2(C_6H_4NCO)_2$, Bayer), toluene 2,4-diisocyanate (TDI, $C_9H_6N_2O_2$, Aldrich, 95%), isocyanurate of isophorone diisocyanate (I-IPDI, VESTANAT® 1890/100, Degussa-Hüls, $\overline{M_n} = 825$, 16% NCO (w/w), $\overline{f_w}$ (NCO) = 3.43), ethylene glycol ($HOCH_2CH_2OH$, Prolabo), 1,3-propanediol ($HO(CH_2)_3OH$, Aldrich, 98%), 1,4-butanediol ($HO(CH_2)_4OH$, Acros, 99%), 1,6-hexanediol ($HO(CH_2)_6OH$, Acros, 99%), glycerol ($HOCH_2CHOHCH_2OH$, Prolabo), phenylene 1,4-dimethanol ($HOCH_2C_6H_4CH_2OH$, Acros, 99%), tetra ethylene glycol ($HO-(CH_2CH_2O)_4-H$, MERCK-Schuchardt, 97%), were used without further purification. Dichloromethane and tetrahydrofuran were purified by distillation according to conventional methods.

Methods

The polyurethane materials were characterized by the following methods:

- IRFT analysis

IR spectra were recorded on a FTIR (Perkin-Elmer spectrum 2000 FTIR), equipped with a diamond ATR device (Attenuated Total Reflection). Spectra were obtained from 10 scans in the 4000 to 500 cm^{-1} range.

- Dynamic Mechanical Thermal Analysis (DMTA)

The storage modulus (E') and loss tangent (tan δ) were measured using Dynamic Mechanical Thermal Analysis (DMA 7 Perkin Elmer) in compression mode with stainless steel parallel plate probe (1 mm diameter), at 1 Hz, and performed on small samples ($5 \times 5 \times 1.5$ mm^3) regularly taken from the polymer plate. The dynamic and static forces applied were 1000 mN and 1100 mN, respectively. Measurements were carried out in the range of -100 to 200°C, at a rate of 10°C/min. Standard calibration was performed with n-decane (T_m = -29.7°C) and indium (T_m = 156.6°C). The α transition, which can be understood as the mechanical manifestation of the glass transition phenomenon, was characterized by the T_α temperature taken at the maximum of the tan $\delta = f(T)$ curve.

- Room temperature uniaxial stress-strain analysis

Room temperature uniaxial stress-strain analysis was performed on at least three samples using an Instron table model tensile testing device at a cross-head speed of 2 mm / min using strength of 1N. Sample dimensions were about $30 \times 10 \times 3$ mm^3.

- Differential Scanning Calorimetric analysis (DSC)

Differential Scanning Calorimetry (DSC) determinations were performed on a Perkin-Elmer DSC-7 with a heating rate of 10°C/min under a nitrogen atmosphere. The sample weight was about 20 mg. Calibration was achieved with indium as reference material.

- Thermogravimetric Analysis (TGA)

Polymer thermal stabilities were checked by Thermogravimetric Analysis (TGA-7 Perkin-Elmer). Experiments were carried out in air (20 mL/min). A 50-750°C range was scanned at a heating rate of 20°C/min. For each weight loss, a characteristic temperature (T_{max}), which corresponds to the maximum rate of degradation, was determined from the minimum of the derived curve.

- Polyurethane densities determination

The density of the solid cast polyurethanes was measured using a specific gravity bottle.

- Atomic Force Microscopy (AFM)

AFM images were recorded with a near field “Pico plus” microscope from “Molecular imaging” company, in tapping mode (25°C, in air). The instrument was equipped to provide height and phase cartography. Images of different areas of each sample were recorded.

Synthesis of hydroxytelechelic cis-1,4-polyisoprene (HTPI)

Hydroxytelechelic cis-1,4-polyisoprene (HTPI) was obtained by selective reduction of carbonyltelechelic cis-1,4-polyisoprene resulting from controlled degradation of high molecular weight cis-1,4-polyisoprene according to a previously described method [19]. High molecular weight cis-1,4-polyisoprene was epoxidized by reaction of *m*-chloroperbenzoic acid leading to 5% epoxidized cis-1,4-polyisoprene. Cleavage of oxirane units was performed with periodic acid. Reduction of carbonyl end-groups was carried out with sodium borohydride to get HTPI of $\overline{M_n}$ = 1600 g mol^{-1}, Ip = 1.8 and T_α = -54°C.

The HTPI hydroxy index was calculated by the following relationship (1):

$$I_{OH} = (\overline{f_n} / \overline{M_n}) \times 0.76 = 1.42 \times 10^{-3} \text{ eq.g}^{-1} \qquad (1)$$

where:

- $\overline{f_n}$ is the HTPI average functionality, which is equal to 2.0 [20]. $\overline{M_n}$ is the average number molecular weight determined by SEC (calibration with polystyrene standards). 0.76 is a correction factor, due to the non absolute value of the HTPI molecular weight determined by SEC and corresponding to the titration of hydroxy groups by isocyanate functions. Indeed, there is a small difference between the real and the experimentally determined hydroxy indexes of the HTPI.

Synthesis of polyurethanes in presence of chain extender

Several chain extenders were used to react with TDI:
-1,2-ethanediol, 1,4-butanediol, 1,6-hexanediol, glycerol, tetraethyleneglycol with hydroxy concentration $[OH_{ex}] = 2\ [OH_p]$, where $[OH_p]$ is the hydroxy concentration of the HTPI.

-1,4-phenylene dimethanol and 1,3-propanediol were used at various equivalent ratios: $[OH_{ex}]/[OH_p]$= 0.5, 1 and 2.

Tab. 1. Composition and physical properties of the prepared polyurethanes.

polymer code	Isocyanate	Chain extender	$[NCO]/[OH_{ex}]/[OH_p]$	% hard segment (a)	% catalyst (b)	Appearance (c)	density
PU1	TDI	/	1.05/0/1	12.6	2.9	Y, S, T	0.994
PU2	TDI	/	1.75/0/1	18.1	2.8	Y, S, T	0.984
PU3	TDI	propanediol	1.57/0.5/1	18.1	4.0	Y, S, T	1.035
PU4	TDI	propanediol	2.10/1/1	23.2	4.9	Y, H, O	1.037
PU5	TDI	propanediol	3.15/2/1	31.4	6.7	Y, H, O	1.056
PU6	MDI	/	1.05/0/1	15.2	2.9	Y, S, T	1.034
PU7	MDI	/	1.75/0/1	23.2	2.6	Y, S, T	0.995
PU8	MDI	propanediol	1.57/0.5/1	22.5	3.9	Y, S, T	1.029
PU9	MDI	propanediol	2.10/1/1	28.3	4.8	Y, H, O	1.071
PU10	MDI	propanediol	3.15/2/1	37.2	6.1	Y, H, O	1.098
PU11	TDI	ethanediol	3.15/2/1	30.8	6.8	Y, H, O	1.058
PU12	TDI	butanediol	3.15/2/1	32.4	6.6	Y, H, O	1.054
PU13	TDI	hexanediol	3.15/2/1	33.7	6.5	Y, H, O	1.035
PU14	TDI	glycerol	3.15/2/1	30.8	4.9	Y, H, O	1.031
PU15	TDI	tetraethylene glycol	3.15/2/1	34.6	6.3	Y, S, T	1.078
PU16	$H_{12}MDI$	/	1.05/0/1	15.9	2.9	Y, S, T	0.897
PU17	$H_{12}MDI$	/	1.75/0/1	24.0	2.7	Y, S, T	0.840
PU18	$H_{12}MDI$	propanediol	2.10/1/1	29.1	4.6	Y, S, T	1.008
PU19	$H_{12}MDI$	propanediol	3.15/2/1	38.2	5.7	Y, S, T	1.015
PU20	$H_{12}MDI$	propanediol	4.20/3/1	41.0	6.3	Y, H, T	1.010
PU21	I-IPDI	/	1.05/0/1	27.5	2.5	Y, S, T	0.990
PU22	I-IPDI	/	1.75/0/1	38.7	2.1	Y, S, T	1.015
PU23	TDI	1,4-phenylene dimethanol	1.57/0.5/1	19.2	4.1	Y, S, T	1.011
PU24	TDI	1,4-phenylene dimethanol	2.10/1/1	25.2	5.0	Y, H, O	1.021
PU25	TDI	1,4-phenylene dimethanol	3.15/2/1	34.6	6.3	Y, H, O	1.060

(a) % hard segment = 100 [wt. of (isocyanate+chain extender)]/ total wt.
(b) % catalyst = (100 wt. of catalyst)/ total wt.
(c) Y: yellowish ; S: soft; H: hard; O: opaque; T: transparent

The HTPI (1 g/mL) and the chain extender were dissolved in THF after drying at 60°C under vacuum. The catalyst (DBTL) was then introduced to the solutions in the ratio of [DBTL]/[OH] = 0.045. Finally, TDI was added with a ratio of [NCO] = 1.05 [OH]. The different solutions were cast in PTFE moulds under an argon atmosphere for 2 h. The films formed after solvent evaporation were cured for 12 h at 60°C. Composition and physical properties of the prepared polyurethanes are depicted in Tab. 1 (PU3-5, PU8-15, PU18-20, PU23-25).

Synthesis of polyurethanes without chain extender

Different isocyanates were used: TDI, MDI, H_{12}MDI and I-IPDI. The HTPI was dissolved in THF (1 g/mL) after drying at 60°C under vacuum. The catalyst (DBTL) was added to the solutions with a ratio of [DBTL]/[OH_p] = 0.045. Finally, the isocyanate was added with a ratio of [NCO] = 1.05 [OH_p]. The different solutions were cast in PTFE moulds under argon atmosphere for 2 h. The films that formed after solvent evaporation were cured for 12 h at 60°C. Composition and physical properties of the prepared polyurethanes are shown in Tab. 1 (PU1-2, PU6-7, PU16-17, PU21-22).

Synthesis of polyurethanes in bulk

Two samples were prepared with or without chain extender (1,3-propanediol). The HTPI and the mixture HTPI/1,3-propanediol ([OH_{ex}]/[OH_p]= 2) were first stirred, dried and degassed at 60°C under vacuum until complete disappearance of bubbles. H_{12}MDI was then added in a ratio of [NCO]/[OH] = 1.05. The catalyst (DBTL) was subsequently added in a ratio of [DBTL]/[OH] = 0.045. The mixture was stirred, cast in a PTFE mould and placed in a vacuum oven at 30°C until bubbles disappear. Then, the vacuum was broken and the mould was placed under an argon atmosphere until the mixture became solid. The material formed was cured at 60°C for 2 h.

Sample preparation for AFM imaging

Thin polymer films were cast on freshly cleaved glass substrates using dilute solutions of the polymerization reagents in THF (2 mg ml^{-1}). The solvent was slowly evaporated during 1 day at room temperature under an argon atmosphere. The films were observed by AFM in height and phase mode.

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