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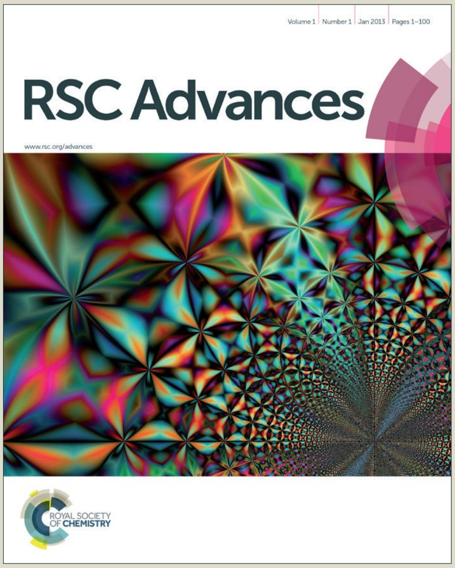

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Tailoring the hard domain cohesiveness in polyurethanes by interplay between the functionality and the content of chain extender

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Crosslinked polyurethane-ureas based on a mixture of 4,4’-dibenzyl diisocyanate, poly(ethylene adipate) glycol, diethylene glycol (DEG) and trimethylol propane (TMP) were synthesized with various ratios of DEG and TMP. The combination within the network structure of the chemical crosslinks generated by TMP and the cohesive strength of urethane and urea groups, which provide physical crosslinking points, plays a special role in the mechanical and thermal properties. Fourier Transform Infrared (FTIR) spectroscopy indicated the distribution of hydrogen bonds in these networks. The extent of crosslinking was monitored through dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC) and atomic force microscopy (AFM) and was found to be significantly influenced by the double function of TMP: plasticizer and crosslinker. The width and intensity of the glass transition region and the evolution of storage modulus on rubbery plateau region were analyzed in order to observe the trends in crosslinking and network homogeneity. The improved mechanical properties were generally accredited to the effect of crosslinking resulting from the high hydrogen bonding capability of the urea group in conjunction with the good rubber elasticity of network.

Introduction

The successful use of polyurethanes in coating application is mainly related to their unique molecular architecture from which interesting mechanical and thermal properties stem.[1,2] The distinguishing properties originate from the microphase-mixed morphology of a two-phase structure. Hard domains (HS) present high glass transition temperature (Tg) and provide high modulus, tensile strength and dimension stability, while the soft domains (SS) with lower Tg impart elastomeric properties to the material.[3,4]

Behind the dual phase morphology, the hydrogen bonding is a key parameter in determining the mechanical properties of the coating. The nature and type of interactions within the hard segment provide cohesion and rigidity, the structure of such a physical network being controlled by the strength of the hydrogen bond.[5] Nevertheless, the successful application of urethane coatings is often hampered by their susceptibility at elevated temperatures. Therefore, the performance of polyurethanes at elevated temperatures is dependent not only on the structure of the rigid segments, but also on their ability to remain associated at these temperatures. Only the presence of hydrogen bond physical network is not sufficient to provide the high temperature performance because these physical crosslinks deteriorate as the temperatures approaches 90°C and tend to disappear above 130°C.[6,7] Therefore, often above 130°C the mechanical properties are no longer acceptable, limiting their applicability.

Since the hardening of the hard domains is responsible for the modification of the mechanical properties, a special attention has been payed to the chemical crosslinking to modify the hard domain cohesiveness.

Chemical crosslinking has been accomplished in the hard segment in many different ways[8]: (i) by using an excess of isocyanate, which leads in the presence of a proper catalyst and at a particular temperature to the formation of allophanate and biuret bonds; (ii) by using multifunctional isocyanates; (iii) by using products of isocyanate dimerization or trimerization with proper catalysts; (iv) by using a chain extender with functionality higher than 2.

Considerable attention in the literature has been devoted towards understanding the changes in the structure–property relationship of polyurethanes by substituting a diol with a triol chain extender in order to increase the structural cohesion of molecular chains. Increasing functionality from 2 to 3 generated a three arm network junction considering that

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increasing the functionality will afford a higher degree of crosslinking.[9-11] The denser crosslinked network formed resulted in better mechanical properties and greater cohesion strength.

In addition to chemical crosslinking, increased hard segment cohesion can also be obtained by using hard segments with stronger non-bonded interactions, i.e., by improving the polarity of the hard domains. For example, significant improvements in many of the properties can be realized by introducing more strongly associated polar groups into the hard segments such as urea linkages.[12-14] Urea hydrogen bonds become more intensive at elevated temperatures and are strong enough to lead to self-assembly generating a three-dimensional hydrogen bonding network.

The experimental design in this study includes the incorporation of urethane and urea groups in a polymer in an optimum level, in order to combine their properties and generate a synergistic well-balanced property profile.

This manuscript reports a new family of polyurethanes-urea (PU) containing a mixture of a difunctional (DEG) and a trifunctional (TMP) chain extender in the structure of the hard segment. To our best knowledge, DEG and TMP as chain extenders and dibenzyl diisocyanate have not been simultaneously introduced into polyurethane to improve the corresponding network. If crosslinks are introduced via a combination of a diol and a triol, the effect of the chemical crosslinking is expected to be superimposed on the effect of the physical crosslinking, thus generating a complex behavior of the network. Particular attention has been paid to the trade-off between the thermo-mechanical properties and structural integrity of the hard segments of polyurethane networks chain extended with DEG and TMP of different contents. These networks were characterized by Fourier transform infrared spectroscopy (FTIR), atomic force microscopy (AFM), dynamic mechanical thermal analysis (DMTA) and differential scanning calorimetry (DSC).

Experimental

Materials

Poly(ethylene adipate) glycol (PEA) of molecular weight 2000 was purchased from Aldrich and was dehydrated at 120°C for 2 h before being used. The chain extenders: diethylene glycol (DEG) and trimethylol propane (TMP) and the catalyst – 1,4-diazabicyclo[2.2.2]octane (DABCO) were provided by Aldrich and were used as received. 4,4'-dibenzyl diisocyanate (DBDI) was supplied by the CICF Savinesti, Romania.

Synthesis of polyurethanes

A series of five polyurethane–ureas with a different chemical structure of the hard segment have been prepared starting from the same diisocyanate (DBDI) and the same polyesther polyol as macrodiol (PEA), in the presence of a catalyst (DABCO). The key variable was the chain extender used. Two kinds of chain extenders were used: DEG and TMP. The abbreviations of the polyurethane-ureas include the name of the chain extender: PU-DEG, PU-TMP, PU-DEG-TMP. The composition of the polyurethanes is listed in Table 1.

The polyurethanes were prepared by one step polymerization process according to the method described in a previous paper.[15,16] The synthetic route for the preparation of polyurethane–ureas is presented in Scheme 1. The synthesis is based on creating a hydroxyl and a diisocyanate solution, which are then mixed together in the presence of DABCO and allowed to react at room temperature. The one step method begins with the slightly favoured reaction between glycol and diisocyanate leading to the appearance of urethane groups. In the reaction system there is an excess of diisocyanate; side reactions may occur such as the formation of urea groups with atmospheric water.

Briefly, PEA dehydrated at 120°C and dissolved in methylene chloride was reacted with DEG and TMP and stirred for 15 min in order to obtain the hydroxyl containing compound. Then, DBDI dissolved in a toluene-methylene chloride mixture and filtered and DABCO were added to the hydroxyl solution and the reaction was stirred at room temperature for another 2.5-3 h.

Table 1. The composition of synthesized polyurethane-ureas

Sample	Polyurethane structure	Composition of polyurethane			
		DBDI [mmol]	PEA [mmol]	DEG [mmol]	TMP [mmol]
PU-DEG	DBDI-PEA-DEG	17	5	10	-
PU-TMP	DBDI-PEA-TMP	17	5	-	6.6
PU-DEG-1.8 TMP	DBDI-PEA-(DEG-TMP)	17	5	6.6	1.8
PU-DEG-2.6 TMP	DBDI-PEA-(DEG-TMP)	17.5	5	6.6	2.6
PU-DEG-3.4 TMP	DBDI-PEA-(DEG-TMP)	18.7	5	6.6	3.4

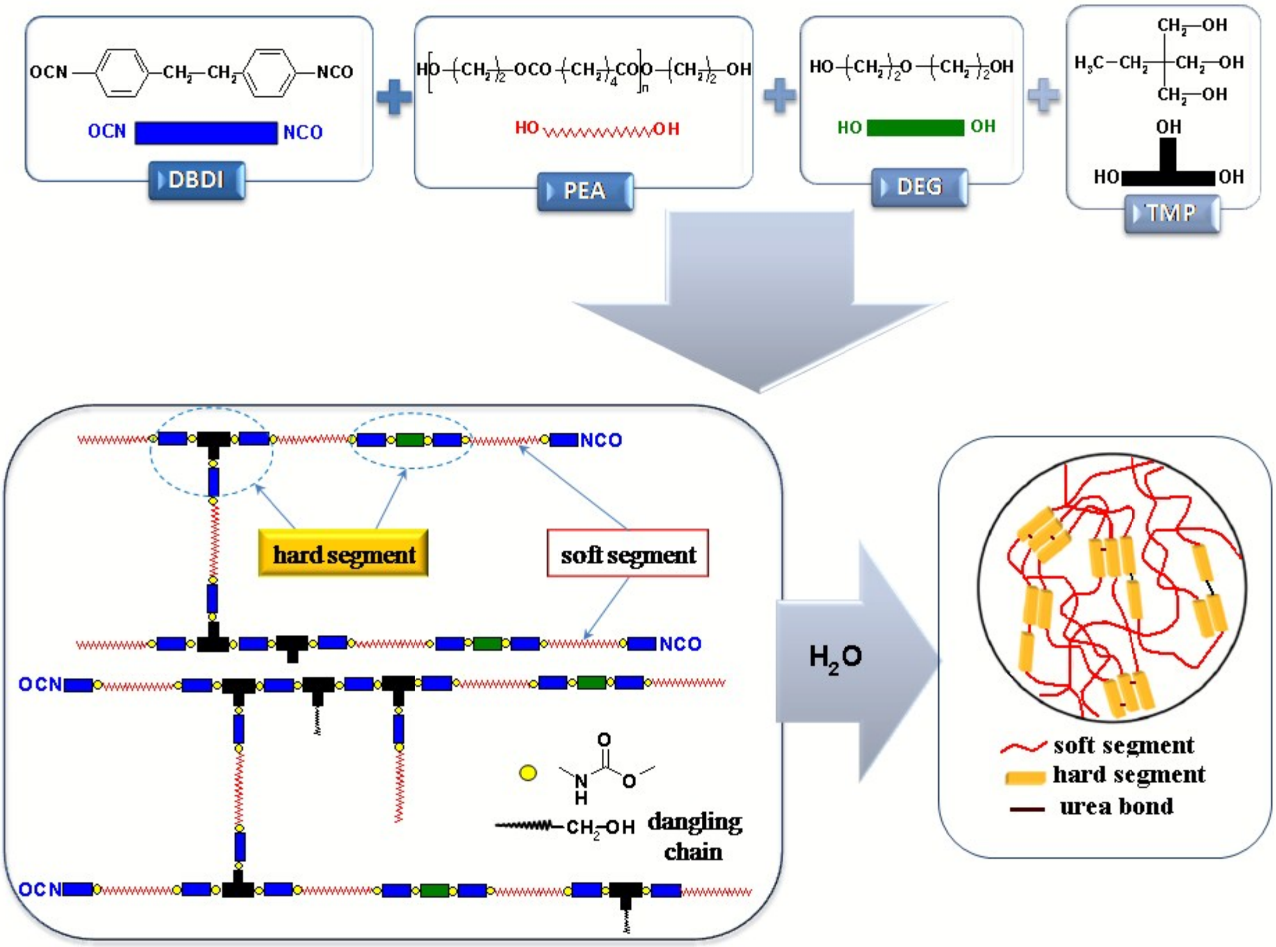
Preparation of polyurethane films

The resulted polyurethane solution was degassed in vacuum and quickly transferred to a glass plate using a doctor blade (e=2 mm). The solvent was evaporated in atmosphere, at room temperature, for 7 days. The film was removed from the glass plate by soaking in cold water and was dried at 40°C in a vacuum oven.

Characterization

Fourier transform infrared (FTIR) spectra were recorded on a Bruker VERTEX 70 Instrument equipped with a Golden Gate single reflection ATR accessory. The spectra were measured in the range of 4000-600 cm^{-1} with a nominal resolution of 2 cm^{-1} after 32 scans.

Differential scanning calorimetric (DSC) measurements of the synthesized materials were performed on a DSC 200 F3 Maia device (Netzsch, Germany). Two runs were performed for each sample in the range from -100°C to 260°C with a heating rate of 10 $^{o}C\cdot min^{-1}$. Tests were conducted on samples of about 10 mg that were gradually heated in order to observe the glass transition temperature. The DSC experiments were carried out with a liquid nitrogen cooler in a helium atmosphere.



Scheme 1. Synthetic route for the preparation of polyurethane-ureas

Dynamic mechanical analysis was performed with a PerkinElmer instrument using the tension mode. The temperature dependence of the storage modulus and loss factor of the rectangular samples with the length 10 mm, width 9.7 mm and thickness 0.5 mm was studied in the temperature range from -150°C to 250°C using a heating rate of 2°C·min^{-1}. Liquid nitrogen was used to achieve the subambient temperature. Relaxation temperatures were determined as the inflection point of the storage modulus as well as the maximum of tan δ peak. The apparent activation energies of the relaxations were calculated according to an Arrhenius-type equation, from the maximum values of the loss modulus at five frequencies (0.5, 1, 2, 5, 10 Hz).

The Young modulus and elongation at break of each sample were determined using the same PerkinElmer DMA. The experiments were carried out at various temperatures: -50°C, 20°C, 100°C, 150°C. The load was increased from 50 mN to 9800 mN (the limit of the instrument) with a rate of 50 mN·min^{-1}. The Young modulus was determined as the slope of the linear part of the stress-strain curve.

Atomic force microscopy (AFM) measurements of the topography of the samples were achieved at room temperature and ambient pressure, using a Scanning Probe Microscope SOLVER PRO-M AFM, NT-MDT (Russia). The images of the film surfaces were taken using the tapping mode with a rectangular shaped silicon cantilever. The average values of the AFM surface relief parameters were obtained from five different 5x5 µm^2 images.

Results and discussion

FTIR analysis

The use of the FTIR analysis was justified by the necessity of confirming the chemical structures of intended polyurethanes and understanding the type, extent and strength of the competitive hydrogen bonding in polyurethanes. The stretching vibrations of the N-H groups at 3330-3328 cm^{-1}, together with the carbonyl bands at 1730-1728 cm^{-1}, were indicative of the presence of urethane moieties (Figure 1).

The FTIR analysis confirmed the disappearance of the bands 2275–2250 cm^{-1}, which are the distinct characteristic peaks isocyanate groups, indicating the completion of the reactio between the diisocyanate and polyol. The analysis of the N stretching region is complicated. Many peaks coexist in thi region. Moreover, there are some disagreements regarding the frequency of the N-H stretching vibration.[17]

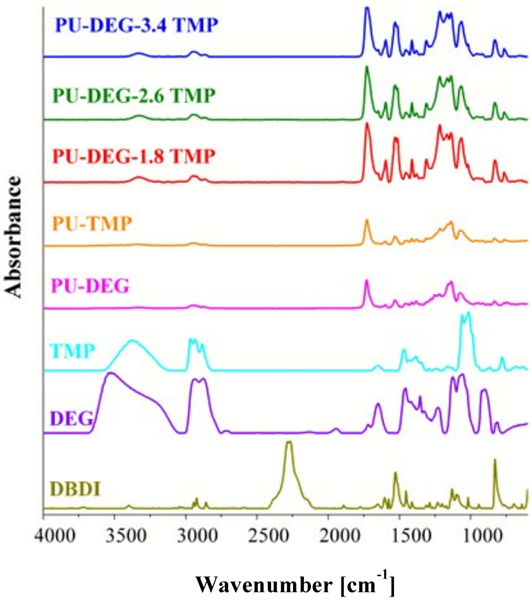


Figure 1. ATR-FTIR spectra of precursors and of polyurethanes containing DEG and/or TMP

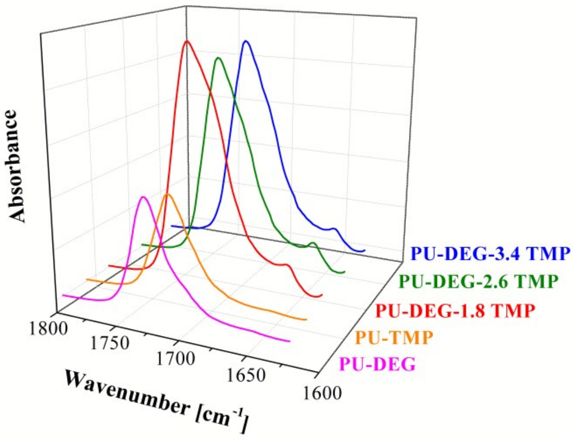


Figure 2. C=O stretching region of synthesized polyurethanes

Therefore, the extent and strength of hydrogen bonding in both hard-hard and hard-soft segments were discussed based on the analysis of the carbonyl band (Figure 2).

In order to obtain more insight into hydrogen bonding interactions, the carbonyl band was deconvoluted using a Gaussian function. This has been done by identifying and separating the contribution of free/hydrogen bonded C=O groups.[18,19] The deconvolutions were performed in 1800-1600 cm^{-1} region and the results are illustrated in Figure 3, for two polyurethanes: PU-DEG and PU-DEG-3.4 TMP.

The carbonyl stretching region comprises five absorption peaks. The peaks I and II are assigned to the stretching of "free" and hydrogen bonded urethane carbonyl groups, respectively. The free carbonyls give rise to hydrogen bonding between urethane (hard segment) and ester groups (soft segment). The hydrogen bonded carbonyls are formed by interurethane hydrogen bonding between the hard segments.[1,11,13,20]

The lower frequency peaks are due to urea with "free" (peak III), "monodentate" (peak IV) and "bidentate" hydrogen bonding (peak V). The last two peaks are present only in the hard segment.[14,21]

As schematically shown in Figure 4 the key difference between urethane and urea group is their hydrogen bonding aptitude.[22] Two different aspects can be remarked with adding TMP content. The peaks II and IV shift to a higher wavenumber. This frequency shift may be associated with a weakening of the strength of hydrogen bonds between the hard segments.[20] On the other hand, the peak V shifts to lower wavenumber and its intensity increases when both chain extenders were used. So, the increase in the TMP content also promotes the growing of the bidentate hydrogen bonding.[23] The effect of this increase in bidentate hydrogen bonding will be shown in the dynamic mechanical analysis.

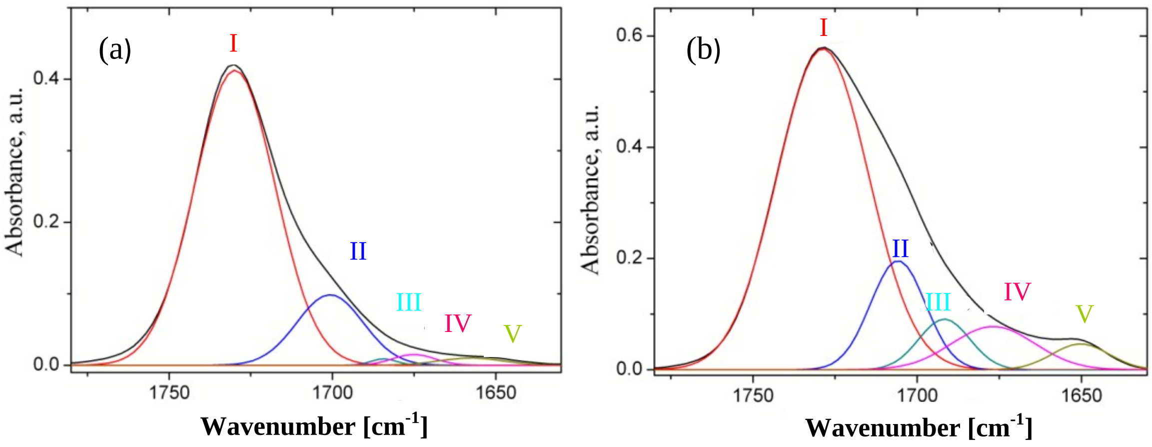
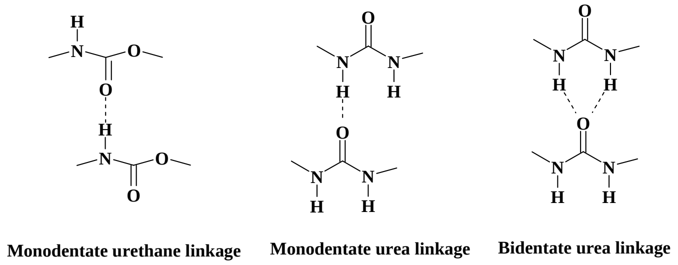


Figure 3. The deconvoluted curve of the C=O stretching zone of PU-DEG (a)and PU-DEG-3.4 TMP (b)



Monodentate urethane linkage Monodentate urea linkage Bidentate urea linkage

Figure 4. Schematic description of monodentate and bidentate hydrogen bonding between urethane and urea groups

Thermo-mechanical properties of polyurethanes

In order to understand the viscoelastic behavior of the more complex polyurethane structures (PU-DEG-TMP), that include both chain extenders (DEG and TMP), the viscoelastic behavior of the polyurethanes containing only one chain extender (PU-TMP and PU-DEG) is presented in the first instance. The results of the DMA experiment are presented in Figure 5 and 6 and the main viscoelastic characteristics are included in Table 2.

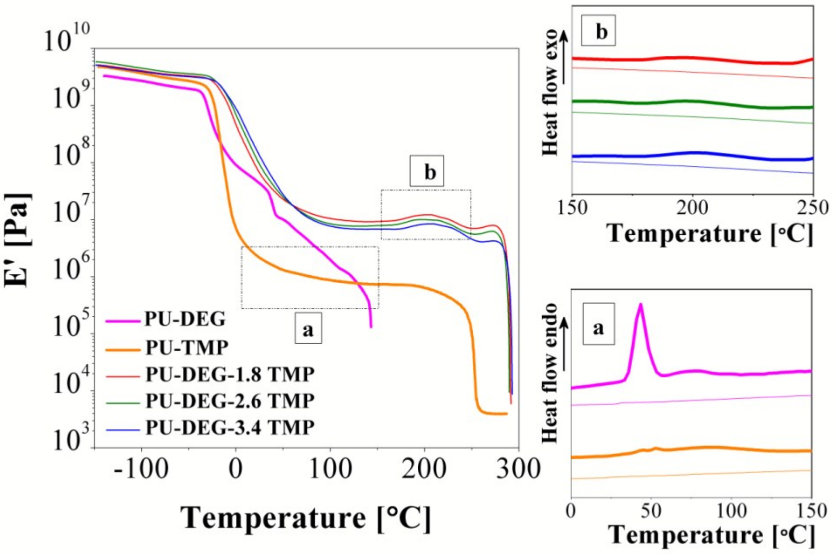


Figure 5. Variation of the storage modulus with temperature (2°C·min^{-1}, 1 Hz); DSC thermograms of the first heating (thick line) and second heating (thin line) of PU-DEG and PU-TMP (Figure a) and of PU-DEG-1.8 TMP, PU-DEG-2.6 TMP and PU-DEG-3.4 TMP (Figure b)

All the comments will be made by keeping in mind the particularities of the PU-TMP and PU-DEG structures. While PU-DEG has only one type of crosslinkings generated by hydrogen bonds, PU-TMP includes also chemical crosslinkings. Therefore, it is expected a stronger interconnectivity between chains in PU-TMP.[24] In the glassy region this is reflected in a higher E' modulus for PU-TMP (Table 2). In the same region, a gradual decrease of E' and the small peak on tan δ curve are attributed to the γ relaxation.

Table 2. Thermo-mechanical characteristics of synthesized polyurethanes

Sample	Glassy region					Glass transition region					Rubbery region
		γ relaxation				*α relaxation*					
	E' [GPa] -140°C	$T_{\tan\delta}$ [°C]	$h_{\tan\delta}$	Ea [kJ mol^{-1}]	R^2	T [°C] E'$_{onset}$	T [°C] tan δ	$h_{\tan\delta}$	Ea [kJ mol^{-1}]	R^2	E' [MPa] 150°C
PU-DEG	3.3	-82.5	0.04	76.18	0.98	-35.2	-24.1	0.29	305.1	0.99	-
PU-TMP	4.7	-82.7	0.04	61.81	0.97	-28.5	-8.17	1	319.5	0.99	0.73
PU-DEG-1.8 TMP	5.0	-85.3	0.05	43.30	0.99	-21.3	16.5	0.33	233.5	0.99	9.24
PU-DEG-2.6 TMP	5.7	-88.6	0.04	66.51	0.98	-17.8	25.1	0.33	324.6	0.99	7.85
PU-DEG-3.4 TMP	4.9	-87.5	0.04	46.60	0.99	-13.3	33.1	0.31	268	0.99	6.82

$h_{\tan\delta}$ – the maximum value of tan δ peak

Ea – activation energy calculated using the temperature of E'' peak

This relaxation appears practically at the same temperature for both samples (Tabel 2) and it is associated with the local motions of the $-CH_2-$ segments that belong to the soft domains.[25] The molecular origin of this relaxation was confirmed by the apparent activation energy value.

The beginning of the α relaxation, associated with the glass transition, is marked by the onset of the E' modulus drop. This takes place at a higher temperature for PU-TMP. However, the assessment of the glass transition temperature as a single value, considered to be the peak of tan δ, would mean to simplify too much the behavior of these polymers during the glass transition region. Nevertheless, these temperatures are included in Table 2, but it is important to underline that the glass transition is a range of temperature that spans between -50°C and 25°C.

The evolution of the viscoelastic parameters during the glass transition is unexpected at the first inspection. The decrease of E' modulus is faster for PU-TMP and gentler for PU-DEG. In the same time, the decrease of E' during the glass transition represents three orders of magnitude for PU-TMP and two orders of magnitude for PU-DEG. All these effects are also visible on tan δ peaks whose amplitude is much higher for PU-TMP (Figure 6). This behavior indicates that PU-TMP is more flexible than PU-DEG, contrary to what was enunciated in the glassy region. The variation of E' modulus with temperature in the glass transition region clearly displays that E'(PU-TMP) is higher than E'(PU-DEG) until -15°C, then the order is reversed.

In other words PU-TMP becomes more flexible during this region. How can be explained this inversion during the glass transition? Unlike the glassy region, where the structures are frozen, the glass transition involves long range coordinated molecular motions.

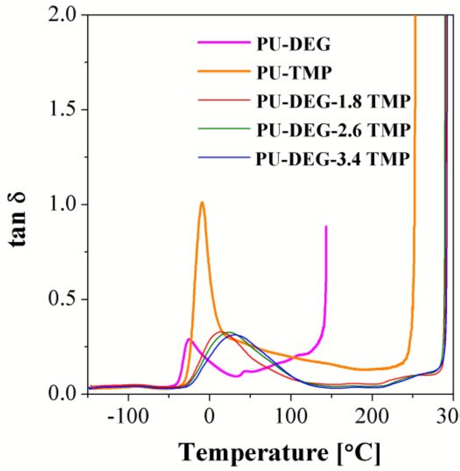


Figure 6. Variation of tan δ with temperature ($2^{o}C{\cdot}min^{-1}$, 1 Hz)

These motions impart some mobility to PU-TMP and its structure becomes more flexible than the one of PU-DEG during the glass transition. This can be explained by recalling some synthesis details.

Once the reaction components are mixed at room temperature, urethane links are formed statistically between the diisocyanate DBDI and hydroxyl groups of TMP and PEA. Despite the fact that DBDI is used in excess, the probability to react with all three hydroxyl groups of TMP is close to zero because the viscosity of the reaction medium increases as the reaction advances. Therefore, the chances of the hydroxyl groups to react completely with the isocyanate groups are reduced dramatically.[26-28]

In the structure of PU-TMP there are pendent methylol groups that become more flexible as the temperature is increased during the glass transition and they will function as internal plasticizer. The TMP reactant facilitates the formation of both chemical crosslinks and dangling hydroxyl ended chains. The chemical crosslink rules the behaviour in the glassy region, while in the glass transition region the influence of the internal plasticizer takes over.

On the rubbery plateau both effects dictates the viscoelastic response: the PU-TMP has a long (50°C-200°C) and stable rubbery plateau, despite the quite low E' modulus (< 10^6 Pa). The rubbery soft segment domains impart elastomeric properties. The more rigid hard segment domain held together by intermolecular hydrogen bonding and by crosslinks restricts the viscous flow and act as physical crosslinks for the rubbery soft segment. These can also explain the most remarkable mechanical properties of the elastomer: the high extensibility and low modulus. This will be explained in detail in the mechanical properties. This crosslinking allows the flexible segments to extend when the elastomer is stretched, but prevents the molecules from moving too far out of position, so the material has “memory” and reverts to its original dimensions when the force is removed.

As opposed to PU-TMP, the sample PU-DEG registers a continuous decrease of E' modulus. Moreover, the E' curve displays a small, but very steep decrease around 40°C, that corresponds to a peak on tan δ curve.

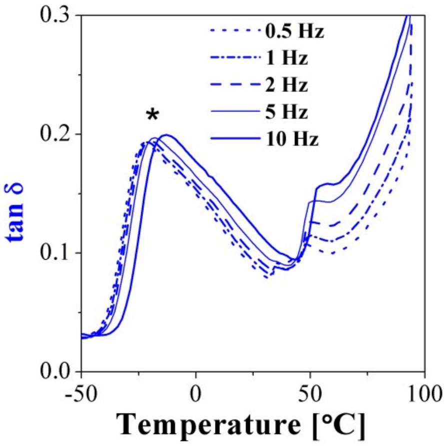


Figure 7. Variation of tan δ with temperature at five different frequencies (0.5, 1, 2, 5, 10 Hz) for PU-DEG

This tan δ peak does not have the characteristics of a relaxation[29]: the shift to higher temperature with increasing frequency and the inversion of the frequency curves as it is indicated by the star symbol for the α relaxation (Figure 7).

In this region the melting of the PEA segments takes place.[30,31] The sign on DSC thermogram for this melting is an endothermic peak around 43.4^{o}C (Figure 5a). The melting happens also in the case of PU-TMP, but its effects in the DMA are not so evident because of chemical crosslinks. A faint shoulder is barely distinguished after the glass transition, on tan δ curve. The presence of chemical crosslinks is also reflected in the DSC endothermic peak intensity (lower besides the one of PU-DEG) and broadness (20^{o}÷130^{o}C). As the hydrogen bonds start to loosen after 90^{o}C and thoroughly break after 130^{o}C, the hydrogen bonding network of PU-DEG loses the stability. The flowing of PU-DEG begins before 150^{o}C, E' modulus decreases abruptly, while tan δ increases steeply until the rupture of the film. The flowing of polymer segments for PU-TMP starts close to 250^{o}C, however the viscoelastic behavior has a different trend. The increase of tan δ and the decrease of E' is interrupted at 260^{o}C due to the existence of chemical crosslinks. They limit the flowing and maintain the elastic modulus E' at a constant, but very low value (under 10^4 Pa) at high temperature.

The evolution of the E' modulus and tan δ was also analyzed when the polyurethanes contain both chain extenders, in the samples PU-DEG-TMP. The breadth and the height of tan δ are the key criteria in interpreting the structural arrangement and the flexibility of polyurethane coating. The significant broadening of the tan δ peak indicates a less homogeneous structure than in the polyurethane containing only one chain extender. The glass transition temperature spans a very large temperature range, between -35^{o}C and 125^{o}C. In the same time, the smaller height of tan δ peak, as compared to PU-TMP, is the result of a higher degree of crosslinking, in all PU-DEG-TMP samples. The presence of DEG chains in the polyurethane network favours sterically the reaction of more OH groups of TMP with the isocyanate. In this way, less methylol groups are leaved as dangling chains and results in a higher crosslinking degree. The onset and the middle of the glass transition given by the E' drop and tan δ peak, respectively, are higher than in both single chain extended polyurethanes. When focusing only on the comparative behavior of PU-DEG-TMP samples, it is evident that higher TMP content slightly increases the glass transition temperature.

In the glassy and rubbery region the E' moduli for PU-DEG-TMP compounds are higher than both PU-DEG and PU-TMP. The values of the E' modulus registers also an inversion during the glass transition. Its values are higher for the higher content of TMP until 60^{o}C. Then, the order is reversed until the end of the experiment. As has been mentioned before, the mobility gained during the glass transition region makes the pendent methylol groups to act as internal plasticizer and as the content of the methylol groups is higher, the lower is the E'.

The increase in temperature above 180^{o}C brings additional rigidity. This is evidenced by the ascending trend of E' and the small tan δ peak. This supplementary increase in stiffness is frequency independent, so it cannot be considered as a relaxation. More probable this extra rigidity suggests the formation of more constraints, i.e. crosslinks. Two types of crosslinks are encountered in polyurethanes: (i) chemical crosslinks (allophanate, biuret) and (ii) intermolecular interactions between the hard segments via hydrogen bonding (inter-urethane, monodentate/bidentate urea hydrogen bonds).[32-34]

The formation of chemical crosslinking is not feasible because FTIR study confirmed the absence of free isocyanate. The interurethane hydrogen bonds and the monodentate urea hydrogen bonds disappear around 130^{o}C.[35]

More probable, as the temperature is raised and sufficient mobility is attained bidentate urea hydrogen bonds are capable of forming stronger hydrogen-bonding linkages with three-dimensional characteristics.[17,36] The formation of the three dimensional hydrogen bonding network may lead to a significant amount of interconnectivity between urea groups. This results into a shift of flowing to higher temperature. This shift to higher temperatures is likely due to the progressing hydrogen bond stability within the hard domains which lose their structural integrity at temperatures around 290^{o}C.

The origin of this increase in E' around 180^{o}C is closely connected with higher temperature DSC exothermic peak (180^{o}-230^{o}C) (Figure 5b). The exothermic process disappeared in the DSC second scan probably because it was not possible to reform hydrogen bonds during the relatively fast cooling of the sample in the calorimeter.[37]

Mechanical properties

The tensile tests were performed to note the extent of hard phase connectivity and mechanical performances with respect to tensile strength and elongation using different chain extenders.

The crosslinking is generally responsible for increasing tensile strength. In our case the use of TMP as chain extender does not strengthen but even lead to inferior tensile strength, a more flexible but less strong material being obtained (Figure 8).

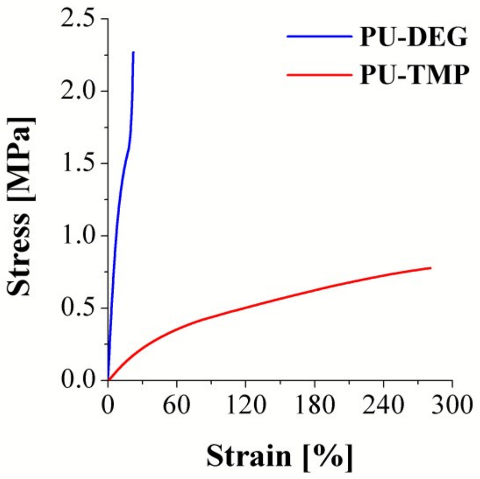


Figure 8. Stress-strain curves of PU-DEG and PU-TMP

The use of the triol leads to a defective network formation because of the incomplete crosslinking reaction generated by the lower reactivity of the second or third hydroxyl groups which act as internal plasticizer.

Changes in the mechanical properties did not show regularity as function of increasing TMP content (Table 3). The Young modulus did not increase as the TMP increased.

The simultaneous addition of DEG and TMP was beneficial for the phase mixing and resulted in the best mechanical properties. The higher moduli and tensile strength relative to PU-TMP are consistent with higher urea content, which results in more cohesive strength.

Table 3. Mechanical properties of polyurethanes

Sample	Young modulus [MPa]	Tensile strength [MPa]	Elongation [%]
PU- DEG	14.7	2.26	22
PU-TMP	0.79	0.77	280
PU-DEG-1.8 TMP	14.5	1.89	13
PU-DEG-2.6 TMP	12.3	2.22	21
PU-DEG-3.4 TMP	14.05	1.13	8

The decrease of elongation in all PU-DEG-TMP samples can be related to a more densely crosslinked structure, according to the changes observed in the DMA experiment. After the introduction of DEG and TMP, more crosslinks formed prevent the molecules from sliding past each other when the polymer is stretched.

A significant deterioration of the mechanical properties occurs as the working temperature increases as can be observed from the stress-strain curves of PU-DEG-1.8 TMP measured at different temperatures (Figure 9). The glass transition region obtained from the DMA starts at -21.3°C, which properly explains the distinct change of the stress-strain curve at 20°, 100° and 150°C.

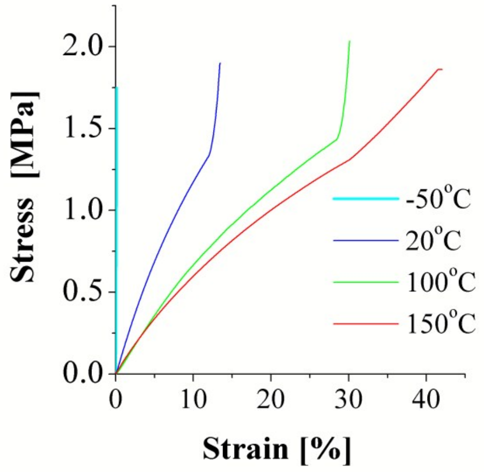


Figure 9. Stress-strain curves of PU-DEG-1.8 TMP measured at different temperatures (-50°C, 20°C, 100°C and 150°C)

The temperature dependence of the mechanical properties may be understood as a result of two processes occurring simultaneously taking into account that the soft and hard phases are covalent bonded and the deformation of one is impossible without the deformation of the other.[38]

When a stress is applied to polyurethane, the soft segments are oriented in the stretching direction causing a strain which then disrupts the structure and orients the hard segment according to Bonart model.[39] So, the first process is an ordering one and the second process is a disruptive one. The hydrogen bonds responsible for the domain cohesion start to break up as noted from previously DSC results.[40]

The breakage is followed by a reformation of hydrogen bonds during the application of stress, the greater conformational mobility of DBDI by the $-CH_2-CH_2-$ bridge allowing a higher tendency to self associate by hydrogen bonding. So, the restructuration of hard segments thought as a stress hardening phenomena is connected with the upturn in the stress-strain curve. The alignment of the polymer chains along the direction of elongation changes the degree of structural order, a greater molecular orientation of hard segment inducing stiffening.[41,42]

Morphology analysis

The changes occurring in the surface features of polyurethane films were monitored by AFM in tapping mode. Figure 10 reveals that the topography is determined by the structural peculiarities.

Usually, the morphological aspects can be correlated with the extent of crosslinking. Crosslinking can be used to enhance the mechanical stiffness and reduce the roughness as a result of the "tight" network formed.

The values depicted in Table 4 for average roughness (Sa) and root mean square roughness (Sq) parameters show that the most uneven surface appears in the case of DEG based PU. Replacing DEG with TMP is accompanied by a transition from a rough surface to a smooth and more homogeneous surface. It can be attributed to increased crosslinking.

Table 4. Roughness parameters of polyurethanes films

Sample	Surface roughness parameters	
	Average roughness Sa [nm]	Root mean square roughness Sq [nm]
PU-DEG	35.28	46.57
PU-TMP	5.06	8.09
PU-DEG-1.8 TMP	7.25	11.91
PU-DEG-2.6 TMP	0.71	1.36
PU-DEG-3.4 TMP	5.50	8.26

Rather different situation is observed when using both chain extenders.

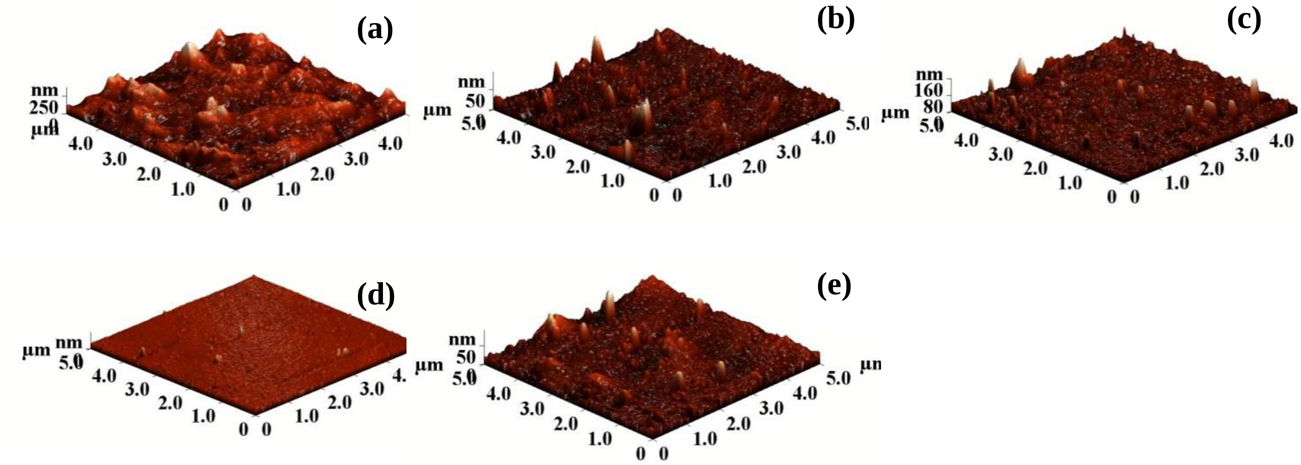


Figure 10. Tapping mode AFM 3D images of polyurethanes: PU-DEG (a), PU-TMP (b), PU-DEG-1.8 TMP (c), PU-DEG-2.6 TMP (d), PU-DEG-3.4 TMP (e)

The surface roughness of the film structure changes with increasing DEG/TMP ratio. The optimum ratio DEG/TMP, where the roughness is minimal, corresponds to the PU-DEG-2.6 TMP sample.

Generally, a smooth and homogeneous surface can be attributed to a “tighter” structure as a result of a higher extent of crosslinking. In this case, a higher content of TMP does not result in a tighter structure, as some TMP function as plasticizer.

Therefore, as concerning the roughness, there is a trade-off between the TMP that function as crosslink junctions and that one that functions as plasticizer.

Conclusions

The mechanical and thermal properties are determined by the functionality and the content of the chain extender added to the polymer. PU-DEG which is crosslinked only by hydrogen bonds has insufficient thermo-mechanical stability and is useless as a high performance coating.

An increase of TMP content has two opposite effects on the structure and properties of polyurethanes-urea. First, crosslinking just by TMP does not consolidate the macromolecular network as expected. The addition of the trifunctional agent resulted in disruption of hydrogen bonds patterns, thus destroying the organization of the hard segment and leading to compromising mechanical properties.

These relatively poor performances are the result of imbalance between the role of plasticizer and that of crosslinking agent.

Second, the combination of DEG and TMP in the hard segment enables the production of coatings with unique features. Controlled crosslinking through physical and chemical bonds leads to an improvement in what concerns the trade off between the thermal-mechanical stability and structural integrity of the hard segment. Moreover, this change in the chain extender plays a broad role in creating urea linkages which creates higher cohesive domains with improved mechanical properties. The presence of urea group and chemical crosslinking causes a microphase mixing generating more smooth networks. These morphological changes results in a shift of the glass transition to higher temperature and a broadening effect on the glass transition region with an increase of crosslinking.

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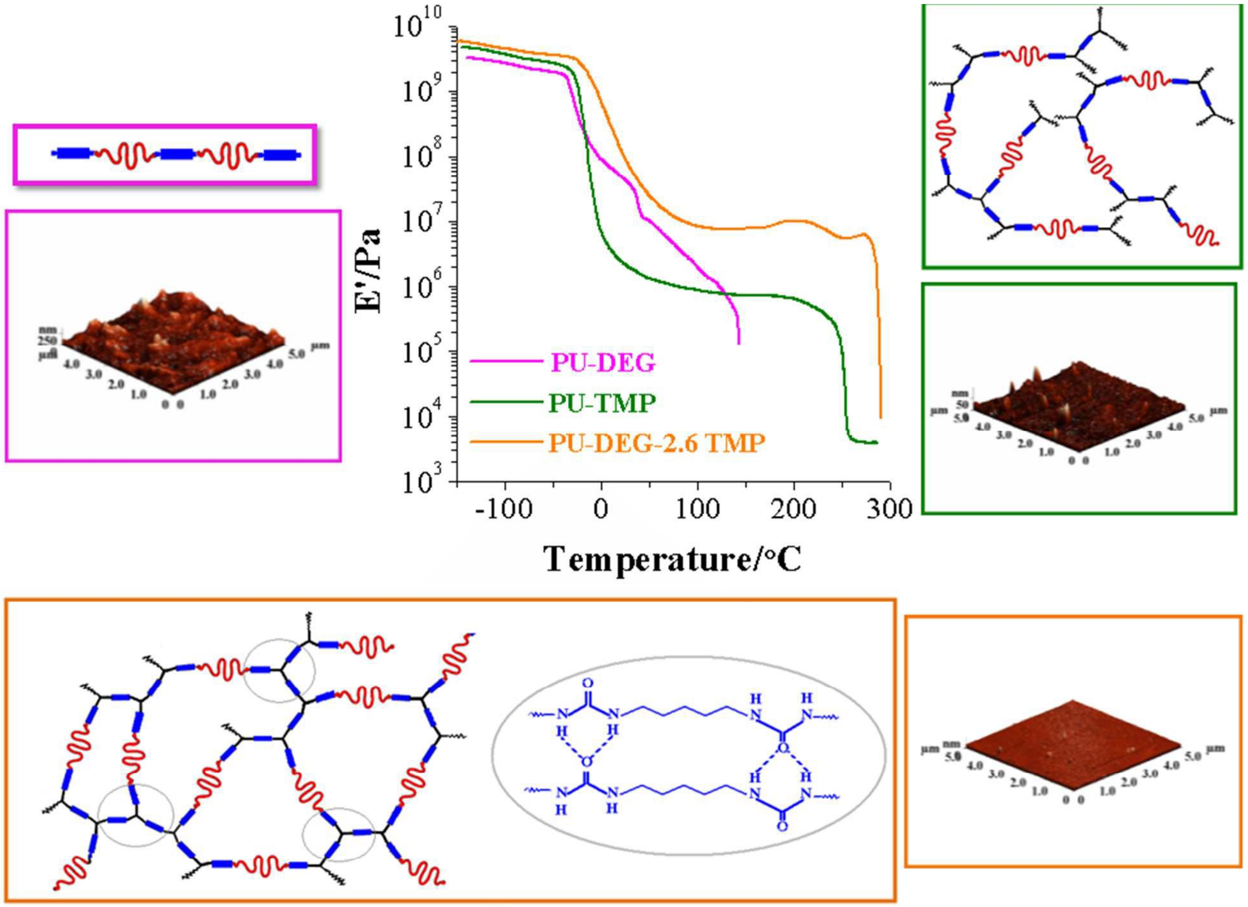

Thermo-mechanical behavior of polyurethanes with diol/triol chain extension is reflected in a particular behavior in the glass transition and rubbery region and is ruled by the functionality and content of chain extender.