

Thermal and Mechanical Characterization of Maleimide-Functionalized Copoly(urethane-urea)s

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ABSTRACT: Maleimide functionalized copoly(urethane-urea)s were prepared by the reaction of a binary mixture of dibenzyl diisocyanate and 5-maleimidoisophthalic diisocyanate with a macrodiol (PEGA-2000), using diethylene glycol and trimethylolpropane as chain extender and crosslinkers in toluene-dichloromethane solutions at the ratio NCO/OH = 1.2. Structures of polymers were confirmed by IR spectroscopy and properties were studied by thermal and mechanical analysis (dynamic mechanical analysis (DMA), differential scanning calorimetry, thermogravimetric analysis, stress-strain) and

other physical methods. Maleimide modification increased the storage modulus and Young's modulus of copoly(urethane-urea)s, slightly increased their glass transition temperature from -10.6°C to -6.3°C . Copoly(urethane-urea) networks obtained by thermal polymerization of maleimide functions showed significantly increased of the mechanical properties. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3245–3254, 2009

Key words: functionalization of polymers; polyurethanes; mechanical properties; thermal properties; membranes

INTRODUCTION

Polyurethanes are some of the most versatile materials used in today's applications. Their many uses range from flexible foams in upholstery, to rigid foams as walls insulation from roofs and appliances to thermoplastic polyurethanes used in medical devices and footwear, coatings, adhesives, sealants and elastomers used on floors and automotive interior design.¹ Interest in functional polymers is steadily increasing due to their diverse uses as polymeric reagents and catalysts,^{2–4} polymer drugs,^{5,6} etc.

Incorporation of maleimide groups into polymers proved its efficiency in the increase of crosslinking density, enhancement of thermal stability, and improvement of flame retardancy.⁷ *N*-substituted poly(acrylamide)s⁸ and polymethacrylates⁹ with dimethylmaleimide groups has been used as photopolymers for microsystem applications. About 20 years ago, Mikroyannidis reported on his attempts to prepare polyketones containing maleimide group.¹⁰ Recently, Liu and Wang¹¹ reported on multifunctional maleimide oligomers, polyamides, polyaminoaspartimides,¹² and crosslinked epoxy materials exhibiting thermal remendability and

removability starting from multifunctional maleimide and furan compounds, and thermally reversible cross-linked polyamides and thermo-responsive gel by means of Diels-Alder reaction.^{13,14}

In this work, new functional copoly(urethane-urea)s having maleimide groups were prepared by polyaddition of a binary mixture of dibenzyl diisocyanate and 5-maleimidoisophthalic diisocyanate with a mixture of polyethyleneadipate glycol (PEGA-2000), diethylene glycol, trimethylolpropane (TMP), and water.

EXPERIMENTAL PART

Materials

Maleic anhydride (Aldrich), 5-aminoisophthalic acid (Aldrich), sodium azide (Aldrich), dichloromethane, dibutyltin dilaurate (Aldrich), 4,4'-dibenzyl diisocyanate (DBDI, local mark), trimethylolpropane (TMP, Aldrich), toluene, poly(ethylene glycol) adipate (PEGA-2000) with a molar weight of 2000 (Baxenden), diethylene glycol (DEG, Aldrich) were used as received.

Measurements

The Fourier transform infrared (FTIR) spectra were recorded on a Bruker Vertex 70 spectrophotometer.

The ¹H-NMR and ¹³C-NMR spectra were run on a Bruker 400 MHz spectrometer using DMSO-d₆ as solvent and tetramethylsilane as an internal standard.

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Melting and softening points were measured with a Gallenkamp hot-block melting point apparatus.

Stress-strain measurements were performed on dumbbell-shaped samples cut from thin films on a TIRA Test 2161 apparatus, Maschinenbau GmbH Ravenstein Germany. Measurements were run at an extension rate of 46 mm/min, at room temperature of 23°C. All samples were tested three times and the averages were obtained.

Thermogravimetric analysis (TGA) was performed under nitrogen flow (15 cm³/min) at a heating rate of 20°C/min, from 25 to 500°C, with a Mettler Toledo model TGA/SDTA 851 apparatus. The initial mass of the samples was 4–6 mg.

Dynamic mechanical experiments (DMA) were made using a Diamond PerkinElmer instrument that applies a sinusoidal stress to the sample and measures the resulting strain. The amplitude of the applied force used was within the linear viscoelastic range for all investigated samples. The thermo-mechanical properties were evaluated starting from the room temperature up to a temperature beyond the glass transition, at a heating rate of 4°C/min and a frequency of 1 Hz, under nitrogen atmosphere. The size of films was of 10 mm × 10 mm × 0.5 mm for the tension attachment.

Differential scanning calorimetry (DSC) measurements were done using a Mettler TA Instrument DSC 12E with a heating rate of 10°C/min, in nitrogen.

Atomic force microscopy (AFM) images were collected in semicontact mode with a Solver PRO-M, NT-MDT, Russia.

Dynamic contact angles were performed by the Wilhelmy plate technique, using a Sigma 700 precision tensiometer produced by KSV Instruments. The sample plate dimensions were 50 × 8 mm and rate of immersion emersion was 5 mm/min in water. Immersion depth was 5 mm in standard conditions. All measurements were obtained as the average of three measurements.

Monomers and polymers synthesis

5-Maleimidoisophthalic acid (**1**) was prepared from 5-aminoisophthalic acid and maleic anhydride according to the reported method,¹⁰ mp = 317–320°C.

5-(2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)isophthaloil dichloride (**2**) was prepared by the reaction of **1** with thionyl chloride in 1,2-dichloroethane (DCE). The product was separated by precipitation with *n*-pentane and then filtered. The white solid was recrystallized from ligroin and the final product was obtained in 85% yield, mp = 115–118°C [112–115°C]¹⁰.

5-(2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)isophthaloil diazide (**3**) was prepared by interfacial condensation of compound **2** in methylene chloride with a solution of excess sodium azide in water at 0–5°C for 5 h. The organic layer was separated and washed two times with 150 mL water and dried over anhydrous magnesium sulphate. The compound **3** was obtained by the evaporation of DCE and resulting in 83% yield, mp = 76–79°C (from ethanol).

FTIR (KBr, cm⁻¹): 3100, 2170, 1740, 1700, 1605, 1490, 1385, 1210, 1160, 840, and 620.

¹H-NMR (CDCl₃, TMS): δ = 8.61 (s, 1H, aromatic proton), 8.29 (s, 2H, aromatic protons), 6.94 (s, 2H, maleimide protons).

1-(3,5-diisocyanatophenyl)-1*H*-pyrrole-2,5-dione (**4**) was prepared by Curtius decomposition of monomer **3** in dry toluene, at reflux, for 5 h. The product was precipitated with *n*-hexane, resulting in 85% yield, mp = 119–120°C.

C₁₂H₅N₃O₄ (255.172): Calcd. C 56.48, H 1.97, N 16.46; Found C 56.42, H 1.83, N 16.08.

FTIR (KBr): ν (cm⁻¹) = 3100 (=CH), 2260 (NCO), 1728 (CO), 1600 (C=C of aromatic ring), 1377, 1148 (C–N–C), 840 (HC=CH of maleimide) and 698 (imide IV).

General procedure for the preparation of copolyurethanes C1–C5

Component I

PEGA-2000 (50 g, 25 mmol) and TMP (0.9 g, 9 mmol) were dehydrated at 120°C, for 4 h in vacuum, before use, they were dissolved in methylene chloride (46 g). To the solution diethylene glycol (3.5 g, 33 mmol) was added.

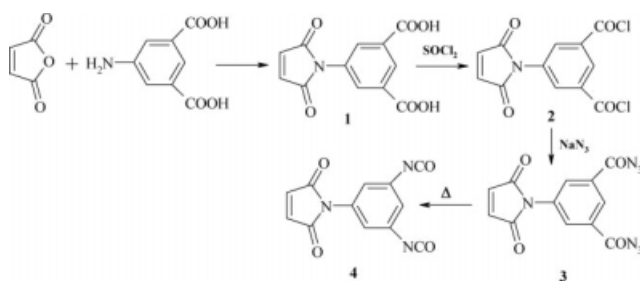
Component II

Mixture of DBDI and compound **4** in different molar ratios of 4.5 : 4.1, 5.5 : 3.1, 6.6 : 2, 7.5 : 1.1, and 8.6 : 0 were dissolved in the toluene-methylene chloride mixture (10 g), in a weight ratio of 1.8 : 8.2.

To a solution of component II, component I (10 g) and five drops of dibutyltin dilaurate as catalyst were added. The reaction mixture was stirred at room temperature for 2.5–3 h. The polyurethane solution was degassed in vacuum and then 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 it in cold water.

RESULTS AND DISCUSSION

A new diisocyanate monomer **4** (1-(3,5-diisocyanatophenyl)-1*H*-pyrrole-2,5-dione) was prepared by



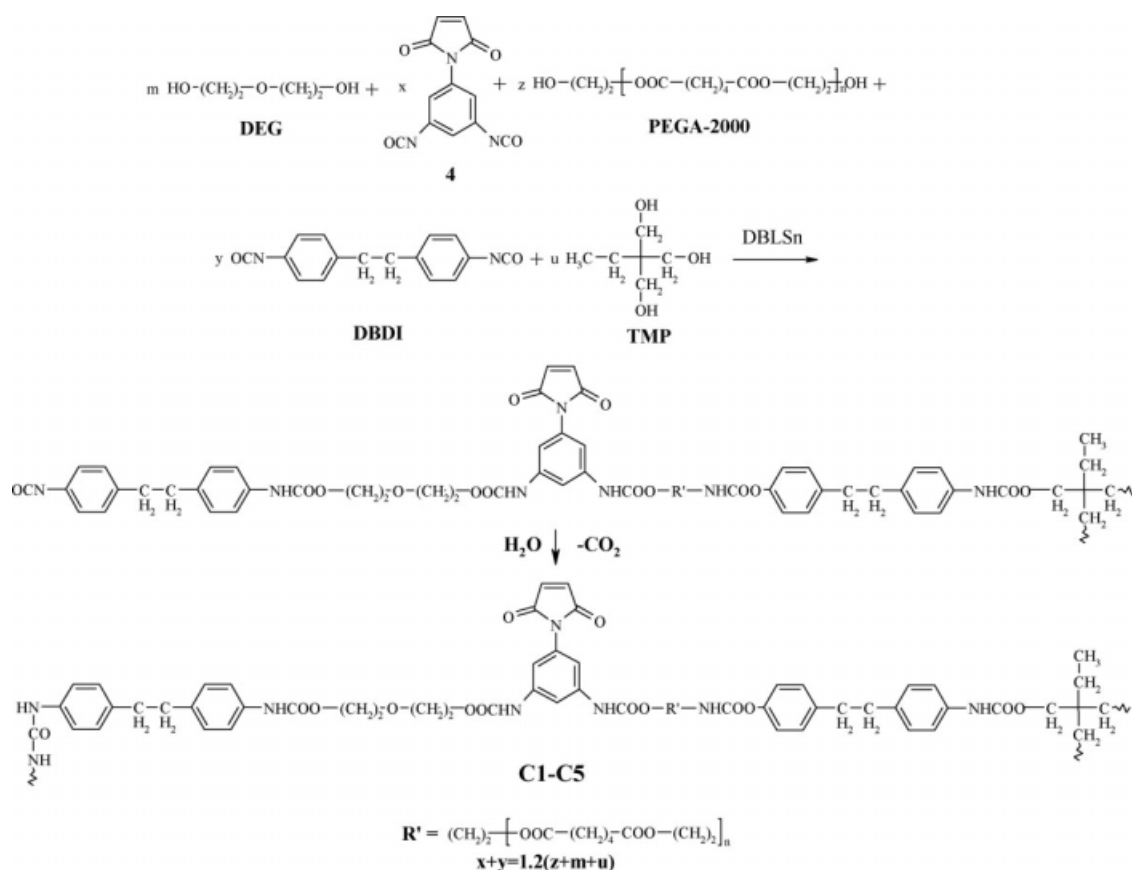
Scheme 1 Synthesis of diisocyanate monomer 4.

Curtius decomposition of monomer 3. Functional maleimides were prepared by the reaction of an equimolar mixture of maleic anhydride and 5-maleimidoisophthalic acid followed by the sequential transformation of COOH functional group in acid chloride, azide and isocyanate (Scheme 1). FTIR, $^1\text{H-NMR}$ and elemental analysis confirmed the obtained structures. FTIR spectra of compounds 2–4 presented absorption bands at 1710–1720, 1385–1400, 1155–1165, and 690 cm^{-1} (imide I-IV), 3100, 1605–1610 ($\text{C}=\text{C}$ double bond of maleimide), 3300–2800, 890, 2170, and 2270 corresponding to the functional groups COOH, COCl, CON_3 , and NCO, respectively.

The copoly(urethane-urea) varnishes C1–C5 were prepared by the reaction of two groups of reagents,

a hydroxyl-containing compounds mixture (PEGA-2000, DEG, and TMP) and a mixture of diisocyanates containing dibenzyl diisocyanate and monomer 4, in the presence of dibutyltin dilaurate, by one-step polymerization, at the ratio $\text{NCO}/\text{OH} = 1.2$, resulting in yield over 90%. The possible reactions and the possible structure of copolymers C1–C5 are presented in Scheme 2. The composition of copolyurethanes is presented in Table I. Structures of copolymers C1–C5 are confirmed by elemental analysis and ATR-FTIR spectra. Experimental elemental analysis data (N%) were in good agreement with the calculated values.

The ATR-FTIR spectra of copoly(urethane-urea) films C1–C5 are shown in Figure 1(a–c). As can be seen in Figure 1(a), the films presented the absorption bands at $1728\text{--}1712\text{ cm}^{-1}$ ($\text{C}=\text{O}$ bonds), $1614\text{--}1608\text{ cm}^{-1}$ ($\text{C}=\text{C}$ of maleimide and aromatic groups), $1532\text{--}1513\text{ cm}^{-1}$ (amide II and $\delta_{\text{C-N}}$), 1385 and 1168 cm^{-1} (C-N-C stretch of maleimide), 1217 and 1067 cm^{-1} (C-O-C stretch of ester and urethane groups), 699 cm^{-1} (maleimide ring deformation in-plane). The $\text{C}=\text{O}$ and $\delta_{\text{C-N}}$ stretch regions of films C1–C5 monitored by ATR-FTIR spectroscopy are reproduced in Figure 1(b,c). As can be seen from Figure 1(b), a fairly strong, free $\text{C}=\text{O}$ peak at 1728 cm^{-1} , which is present in the film C1 becomes



Scheme 2 Synthesis of copolymers C1-C5.

TABLE I
Composition and Elemental Analysis of Copolyurethanes C1–C5

Copolymer	<i>x</i>	<i>y</i>	<i>z</i>	<i>m</i>	<i>u</i>	Elemental analysis, <i>N</i>		Yield %
						Calculated	Found	
C1	0	8.6	2.5	0.9	3.3	3.10	3.23	91
C2	1.1	7.5	2.5	0.9	3.3	3.31	3.48	92
C3	2	6.6	2.5	0.9	3.3	3.47	3.53	92
C4	3.1	5.5	2.5	0.9	3.3	3.68	3.73	91
C5	4.1	4.5	2.5	0.9	3.3	3.86	3.95	90

smaller with the increases of maleimide content. On the other hand, strongly maleimide bonded C=O peak at 1712 cm^{-1} becomes stronger with the increases of maleimide content. Similar to carbonyl peaks, the peak of $\delta_{\text{C-N}}$ stretch at 1512 cm^{-1} becomes stronger with the increase of maleimide content [Fig. 1(c)].

The DSC measurements of copoly(urethane-urea) films are presented in Figure 2. The DSC curve of C1 (compound without maleimide) shows two exothermic peaks centred at 198 and 270°C, respectively, probably due to the complete reaction of NCO groups in excess, and an endothermic peak corresponding to the melting of hard segments. The

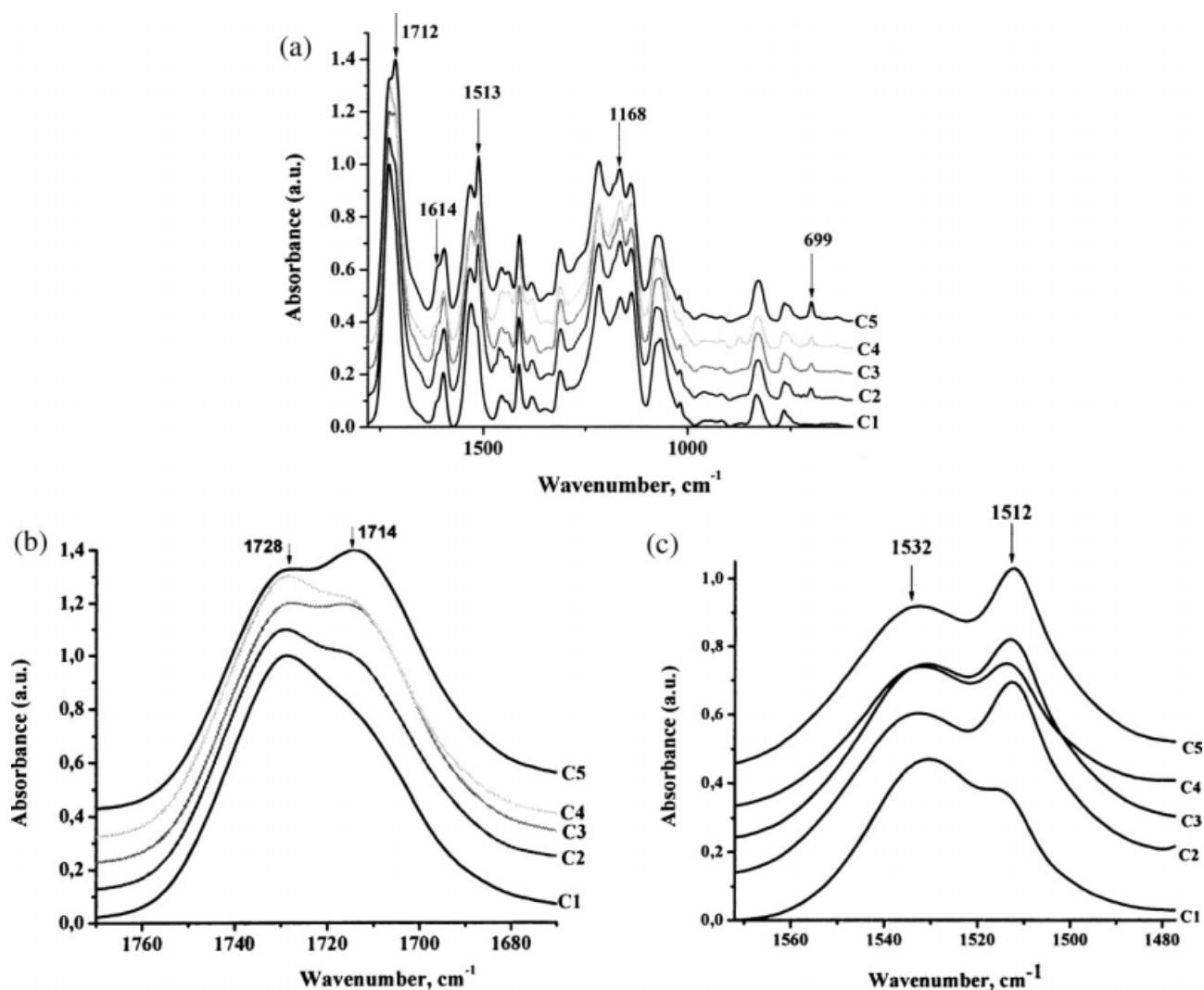


Figure 1 The ATR-FTIR spectra of copolyurethane films C1–C5 (a) and C=O and δ_{CN} regions (b and c).

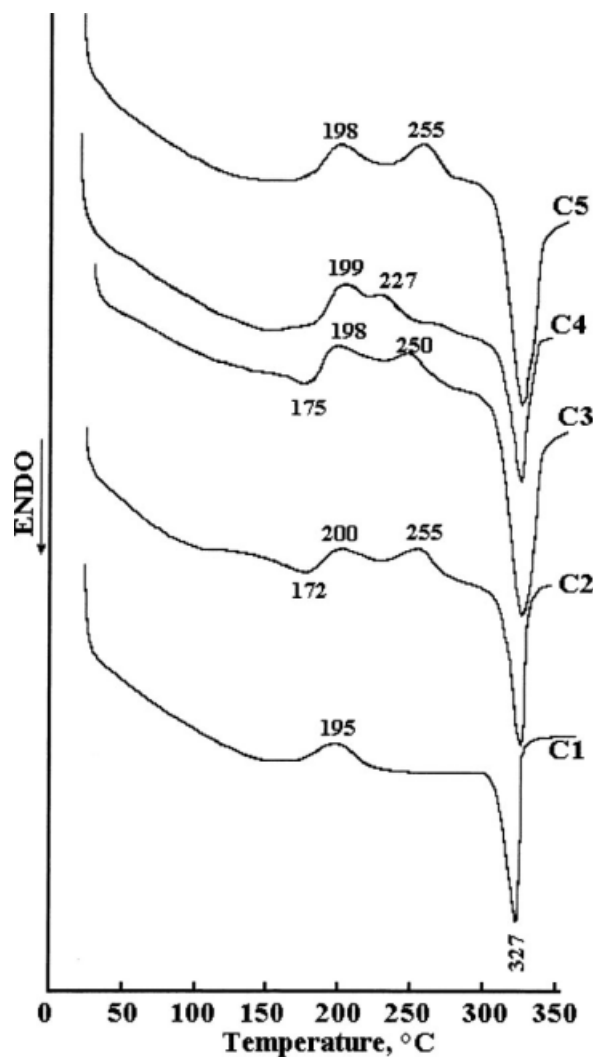


Figure 2 The DSC curves of copoly(urethane-urea)s.

DSC curves of **C2–C5** present two exothermic peaks at 198–199°C and 227–255°C attributed to the complete polyaddition of NCO groups and cure reaction of maleimide groups, respectively, and an endothermic peak at 327°C, corresponding to the melting of hard segments. The DSC curves showed a single inflection point in the second run, at negative temperature, corresponding to the glass transition temperature of soft segment of copoly (urethane-urea), that ranged between -14 and -6 °C (Fig. 3). T_g temperatures of soft segments increased with the maleimide content so that the copoly(urethane-urea) **C5** does not show T_g due to its high crosslinking density due to maleimide groups [Scheme 3(C)].

By processing TGA curves, thermal data presented in Table II resulted. It was observed that the copolyurethanes **C1–C5** presented two peaks and two maxima decomposition temperatures (PDT_{max1} and PDT_{max2}) corresponding to the two peaks (Table II). The first peak (PDT_{max1}) appeared between 339 and 341°C and is attributed to the depolymerization of the urethane bonds and soft segment decomposition, whereas the second peak appeared around 425–432°C indicating the hard segment breaking. The polymer having no maleimide diisocyanate (**C1**) presented PDT_{max1} and PDT_{max2} values at 340 and 425°C, respectively, and their corresponding weight losses of 12 and 60%, respectively. Polymers containing maleimide groups (**C2–C5**) showed PDT_{max1} and PDT_{max2} values ranging between 339–341°C and 426–432°C, respectively, and their corresponding weight losses were between 12.5–16% and 38–48%, respectively. The different values of PDT_{max} of copoly(urethane-urea)s **C2–C5** could be, probably,

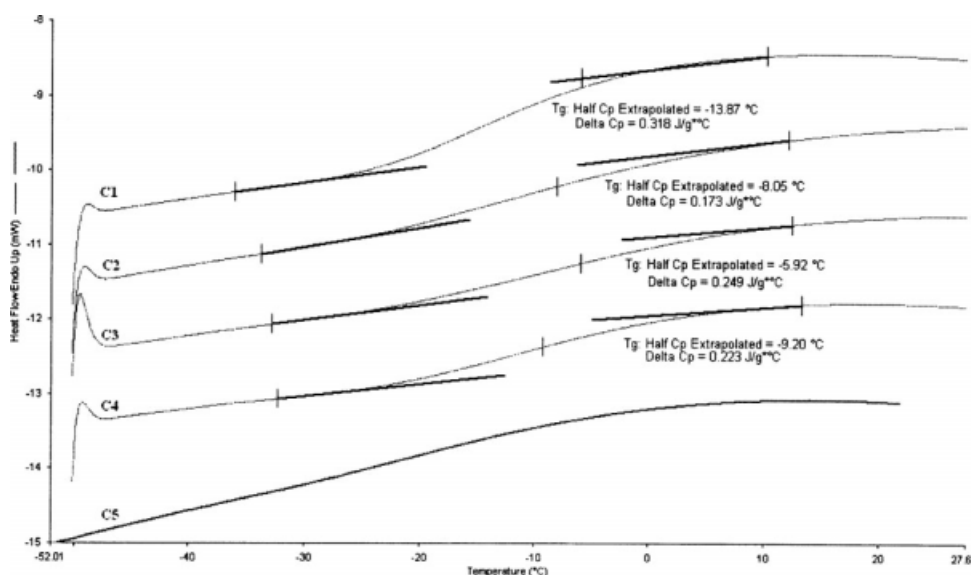
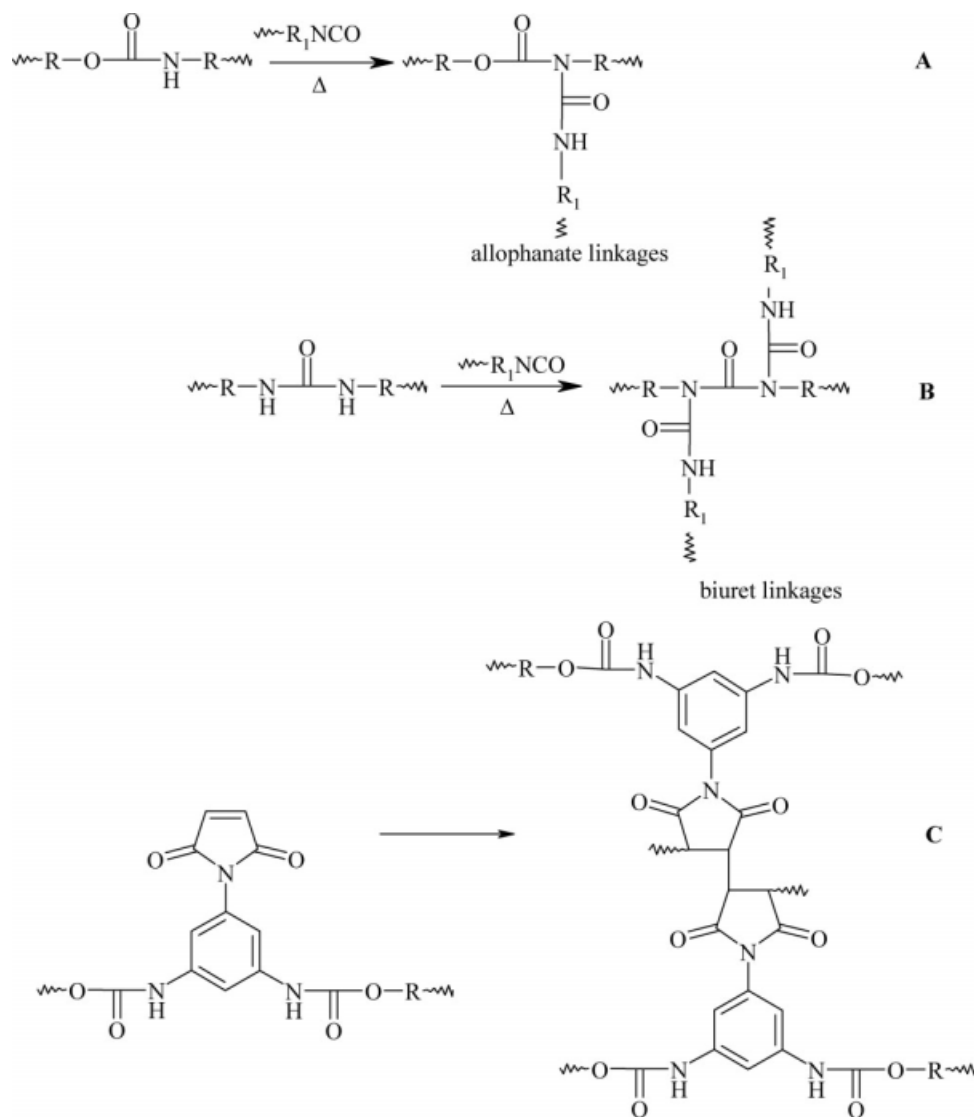


Figure 3 The DSC curves of copoly(urethane-urea) films at second heating cycle.



Scheme 3 The possible structures for non-polymeric tributyltin carboxylates in the solid state.

TABLE II
Thermal Stability of Cured Films

Sample	IDT ^a (°C)	Temperature (°C) for % weight loss ^b		PDT _{max1} ^c (°C)	PDT _{max2} ^c (°C)	Y _c ^d (%)
		T ₅	T ₁₀			
C1	260	320	335	340	425	3
C2	260	319	332	340	436	4
C3	260	318	328	339	427	6
C4	265	321	327	341	430	8
C5	270	322	325	340	432	11

^a Initial decomposition temperature.

^b Temperature for 5 and 10% weight loss.

^c Maximum decomposition temperature of cured film.

^d Char yield at 500°C.

TABLE III
Tensile Properties of Copoly(urethane-urea)
Varnish Films

Code	Tensile strength (N/mm ²)	Elongation at break (%)	Modulus (MPa)
C1	12.60	358.15	7.42
C2	24.64	174.84	16.86
C3	7.40	138.08	15.77
C4	8.87	198.20	16.72
C5	8.98	97.07	58.20
C1 ^a	11.71	346.97	5.51
C2 ^a	22.25	160.80	86.37
C3 ^a	23.86	132.72	89.47
C5 ^a	24.71	138.26	161.50

^a Films treated at 170°C for 1 h.

due to the high thermal stability of the three-dimensional structures of cured maleimide groups.

Mechanical properties

Mechanical properties such as tensile strength, elongation at break and modulus of copolyurethane varnish films are given in Table III. The stress-strain diagrams of maleimide functionalized copolyurethane varnish films C1–C5, maleimide crosslinked networks C1*–C5* obtained by thermal curing at 170°C for 1 h, and 250°C, C5**, were presented in Figure 4(a–c). The initial modulus increased with the increasing of maleimide content from 7.4 to 58.2 MPa for untreated films, but the tensile strength and elongation at break decreased from 12.6 to 8.8 MPa and from 358 to 138%, respectively [Fig. 4(a)]. By treating films at 170°C (C1*–C5*) the initial modulus and the tensile strength increased with the increasing of maleimide groups, but the elongation at break of films reduced. In the case of film containing 20% maleimide groups (C5), the initial modulus increased with the increasing of curing temperature from 58.2 to 303.3 MPa [Fig. 4(c)].

Dynamic mechanical properties

The storage modulus E' , loss modulus E'' and dissipation factor $\tan \delta$ of poly(urethane-urea) films C1–C5 are plotted as a function of temperature (Figs. 5 and 6) and the data of thermal transitions (T_g^s and T_g^r), glass storage modulus at -50°C , rubbery state modulus at 100°C and height of $\tan \delta$ peak are presented in Table IV. Dynamic mechanical curves ($E' = f(T)$) of films C1–C5 exhibited a high plateau corresponding to the glassy state modulus due to the elastic energy stored in the crystalline and glass state amorphous domains and another plateau attributed to the rubbery state modulus which is due to the en-

trophy elasticity owed to the two-phase structure of the material (Fig. 5)¹⁴.

The values of T_g^s of films C1–C5 corresponding to the relaxation associated with the glass transition of

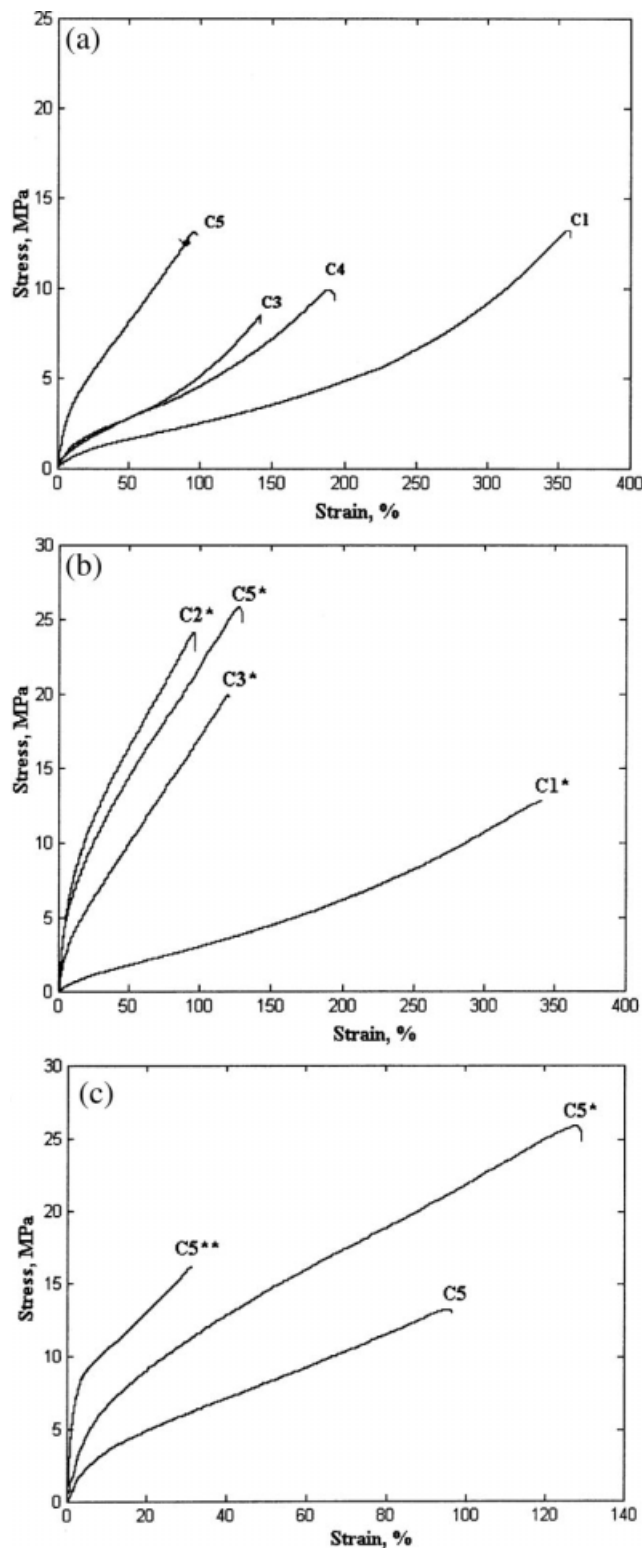


Figure 4 Stress-strain diagrams of copoly(urethane-urea) films untreated (a), treated at 170°C for 1 h (b), and treated at 250°C for 30 min (c).

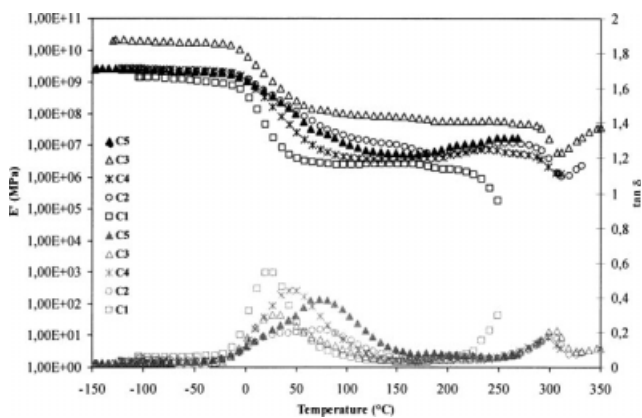


Figure 5 Storage modulus (black line) and $\tan \delta$ (grey line) profiles of copoly(urethane-urea) films.

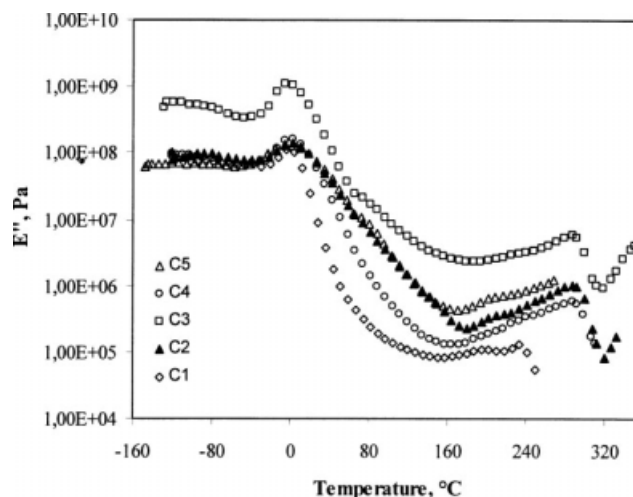


Figure 6 Loss modulus of copoly(urethane-urea)s.

the soft phase, determined by onset temperature of the decrease in E' , varied in the range of -10.3 and -6.3°C (the minimum value belongs to film C1). The storage modulus (E') of copoly(urethane-urea) films decreased from 1.0–17.3 GPa to 2.46–19.0 MPa in the temperature range of -50 and 100°C . As can be observed in Figure 5, loss factor ($\tan \delta$) exhibited one maximum peak for film C1 and other two peaks for films C2–C5 containing maleimide. The first maximum peak of $\tan \delta$ is stretched and shifted to higher temperature with the increases of the maleimide groups. So, the peak for film C5 is very large and starts at -15°C and stretches up to 150°C . The loss modulus of the copoly(urethane-urea) films as a function of temperature, determined by DMA, are displayed in Figure 6. The films C1–C5 exhibited two relaxations at around 0 and 300°C .

The glass storage modulus decreased after post-curing and the rubbery storage modulus increased with the maleimide content and curing temperature. So, E' (-50°C) decreased from 2.09 to 1.90 GPa for the film C5* and to 1.72 GPa for the film C5**. E' (100°C) increased from 10.80 to 29.80 MPa for the film C5* and to 46.20 MPa for the film C5**, simultaneously with the decrease of both height of $\tan \delta$ peak (from 0.389 at 0.160 mm) and T_g^α (from -8.1 to -26°C). A typical effect of thermal treatment of film C5 performed at 170°C for 1 h (C5*) and at 250°C for 30 min (C5**) is presented in Figure 7. The first treatment can induce two types of reactions, namely chain extension and crosslinking (through biuret or allophanate linkages) [Scheme 3(A,B)]. The second

TABLE IV
Dynamic Mechanical Analysis of Copoly(urethane-urea) Varnish Films

Sample	T_g^α ($^\circ\text{C}$) ^a	T_g^β ($^\circ\text{C}$) ^b	T_g^h ($^\circ\text{C}$) ^c	$E'(-50^\circ\text{C})$ ^e GPa	$E'(100^\circ\text{C})$ ^f MPa	Height of $\tan \delta$ peak	
						Soft phase	Hard phase
C1	-10.6	-13.9	233.5^d	1.00	2.46	0.555	–
C2	-6.3	-8.5	303	2.19	19	0.214	0.183
C3	-8.5	-5.9	303.5	17.30	102	0.305	0.237
C4	-9.3	-9.2	300	2.30	6.20	0.444	0.273
C5	-8.1	–	298.2	2.09	10.80	0.389	0.164
C1*	-13.5	–	228^d	1.60	4.15	0.682	–
C2*	-17	–	301	3.21	16.60	0.262	0.166
C5*	-20	–	295	1.90	29.80	0.205	0.152
C5**	-26	–	300	1.72	46.20	0.162	0.178

^a Glass transition temperature of soft segment of polymer by DMA measurement, corresponded to onset temperature of the decrease in E' .

^b Glass transition temperature of soft segment of polymer by DSC measurement.

^c Glass transition temperature of hard segment of polymer associated with the second maximum $\tan \delta$ peak.

^d Temperature corresponding to the second decrease of E' .

^e Glass storage modulus at -50°C .

^f Storage modulus at 100°C (rubber state modulus).

TABLE V
Water Contact Angle of Copoly(urethane-urea) Varnish Films

Sample	θ_{adv} (deg)	θ_{rec} (deg)	Hysteresis (deg)
C1	96.56 ± 1.01	28.25 ± 0.79	68.31 ± 0.79
C2	87.63 ± 1.08	39.42 ± 0.69	48.21 ± 0.69
C4	83.18 ± 1.13	41.35 ± 0.53	41.83 ± 0.53
C5	53.87 ± 1.08	45.67 ± 0.57	8.20 ± 0.57
C5*	88.52 ± 1.17	42.96 ± 0.87	45.56 ± 0.87
C5**	91.37 ± 1.13	39.13 ± 0.67	52.24 ± 0.67

treatment induced the thermal curing of maleimide groups [Scheme 3(C)]. In other words, postcuring at 170 and 250°C increased the rubbery modulus by forcing the reaction to its completion and creating some intermolecular linkages, as well as by reducing damping by improving the level of the microphase separation.¹⁵

The α relaxation of films C5* and C5** is very broad, as evidenced by the variation of $\tan \delta$, which ranges over >150°C with a maximum value between 10 and 30°C considering the film C5 and C1. The slope of curves $\tan \delta = f(T)$ (Fig. 7) are gradually decreasing with the treatment temperature and the values of $\tan \delta$ (Table IV) suggest an increase of crosslink density and microphase separation in the structure of the material. Finally, the glass storage modulus is generally lower (except C1*) after postcuring, and the rubbery modulus is overall higher.

Surface characterization of copolyurethanes

Figure 8 shows the three-dimensional AFM images of copoly(urethane-urea) film C5 before and after the thermal treatment. It can be noted that the sample treated at 250°C for 30 min presented changes in surface roughness. The average roughness decreased from 11.5 for untreated sample to 5.2 for treated sample.

Wettability could be estimated by the determination of the dynamic contact angle. Four samples were immersed and withdrawn into and out of the

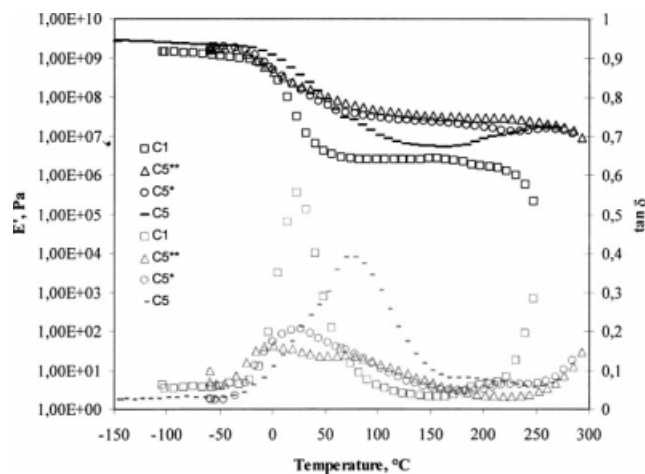


Figure 7 Variation of the storage modulus (black line) and $\tan \delta$ (grey line) with temperature for copoly(urethane-urea) films.

liquid simultaneously measuring the force acting on the samples. The advancing and receding contact angles were determined from the obtained force curve. Advancing and receding contact angle measurements on the casting films from polyurethanes based on monomer 4/dibenzyl diisocyanate/PEGA could provide more information on the hydrophilicity of films and hence their wetting ability (Table V). The advancing contact angle decreased with the increase of the amount of maleimidoisophthalic content (C1–C5) and increased with the increase of the cure temperature.

CONCLUSION

Novelfunctional copoly(urethane-urea)s with maleimide groups were synthesized. A typical effect of thermal treatment of copoly(urethane-urea) film performed at 170°C for 1 h and at 250°C for 30 min can induce in the first stage two types of reactions, namely chain extension and crosslinking (through biuret or allophanate linkages), and in the second step the thermal curing of maleimide groups.

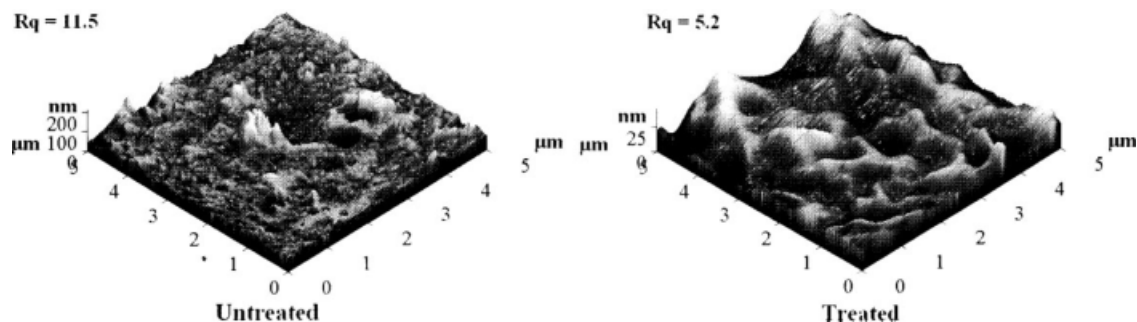


Figure 8 Three-dimensional AFM images of outer surface of copoly(urethane-urea) film C5 before and after thermal treatment at 250°C for 30 min. Roughness parameters (R_q) are added for each image.

All data obtained during characterization of these new materials are in good concordance with our expectations and with literature data.

Furthermore, these results open new prospective because these polymers can be thermal polymerized and used for synthesis of maleimide bioconjugate compounds by Michael polyaddition reaction to organic or biological compounds containing $-SH$ or NH_2 groups.

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