Properties of Thermoplastic Polyurethane Elastomers Chemically Modified by Rosin

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ABSTRACT: Thermoplastic polyurethane elastomers (TPUs) are prepared including different amounts of rosin in their composition. Rosin is used either as an additive, mixed in the TPU solutions, or as a reactant in the chain-extension step of polymer synthesis. The properties of the materials are studied using solution viscosity measurements, size-exclusion chromatography, stress-controlled rheometry, differential scanning calorimetry, wide-angle X-ray diffraction, and contact angle determinations. Rosin as an additive does not markedly change the polymer properties. On the contrary, the use of rosin in the chain-extension step leads to sharp increases of viscosity and molar mass as well as improvements of rheological properties and changes in morphology: the crystalline regions are more affected (variations in the softening temperature and enthalpy) than the amorphous ones (quite constant glass-transition temperature). The conclusion is that rosin acts as an actual chain extender and that it modifies the organization of both the hard and the soft segments of the polymers. Furthermore, the TPUs are used as raw materials of solvent-based adhesives, which adhesion properties are characterized by T-peel tests of PVC/TPU adhesive joints. Rosin as an additive cannot improve the low tack (initial adhesive strength) of TPU, although as a chain extender or cochain extender (together with butane diol) rosin allows development of significant initial adhesive strengths, while keeping a high level of actual (maximal) adhesive strength. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 3402–3408, 2001

Key words: thermoplastic polyurethane elastomers; rosin; chain extension; polymer structure; chemical modification; initial (tack) and actual adhesion properties

INTRODUCTION

Thermoplastic polyurethane elastomers (TPUs) are generally prepared by reacting a diisocyanate, a long-chain macroglycol (polyester or polyether type), and a chain extender (i.e., glycol, diamine), although other additives, such as fillers, may also be included.[1,2] They are $(AB)_n$ alternating-type copolymers of soft and hard segments.[3] The soft segments, oligomeric macroglycol chains, are flexible and weakly polar. The hard segments, formed by reaction of isocyanate groups with the chain extender, are rigid and highly polar. The differences in polarity between hard and soft segments allow phase separation to occur in the TPU structure, generating microdomains[4] that determine the physical properties of the polymer.[5]

TPUs are versatile polymers used in many different applications.[1,2,6] For instance, they are common raw materials in the formulation of solvent-based adhesives, applied as contact adhesives in the automotive, footwear, and furniture

industries.[1,7,8] Typical TPUs used as adhesives have a reduced weight percentage of hard segments, and their properties are mainly determined by the soft segments. Therefore, these TPUs are elastic in the temperature range between the glass-transition temperature (T_g about −60°C) and the softening temperature (T_s about 60 to 100°C) of the elastomeric domains.[9]

One of the main problems regarding the application of TPUs as adhesives lies in the weak initial adhesive strength (green tack) developed in the substrate/adhesive/substrate system. Generally, it is necessary to wait for about 72 h until the adhesive strength reaches its maximum.[10,11] As a consequence, final manipulations of the bonded assemblies are delayed and industrial production rates are excessively lowered.

Many efforts are being devoted to solve this problem, especially focused in the use of such additives as fillers or tackifiers in TPU adhesive solutions.[12,13] However, no remarkable improvement has yet been achieved, probably because of the lack of compatibility of many additives with TPU solutions.

Even though a classic way to improve compatibility is the chemical association of additives with the polymeric chains, to our knowledge no studies have been published on the grafting of fillers or tackifiers on TPUs. Drawing on our own experience of the synthesis of TPUs,[9,14–16] we examined the possibility of grafting rosin-type tackifiers onto TPU chains and studied the influence of this chemical modification on the properties, especially adhesive ones, of the polymers. The aim of this study is to describe the results we obtained.

EXPERIMENTAL

Materials

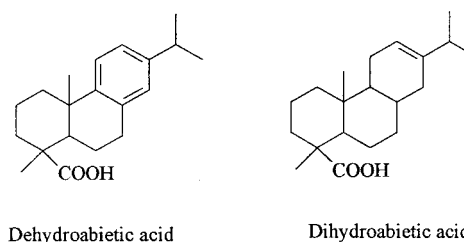TPUs were prepared from diphenylmethane-4,4′-diisocyanate (MDI, 98% purity; Aldrich Chemi-

Figure 1 Dehydro- and dihydroabietic acids, main components of disproportionated rosin.

cals, Milwaukee, WI), poly(ϵ-caprolactone) ($\overline{M}_n$ = 3000 g/mol) as macroglycol (Solvay Interox, Cheshire, UK), and controlled composition mixtures of 1,4-butanediol (chain extender, 99% purity; Aldrich) and disproportionated rosin (tackifier, mainly constituted of dehydroabietic and dihydroabietic acids [Fig. 1]; La Unión Resinera, Madrid, Spain). Moisture in the macroglycol was removed by heating overnight at 70°C under 0.7 MPa pressure. The NCO content of the prepolymer was obtained by titration with n-butylamine (ASTM D 2572-80).

Preparation of Polyurethane Elastomers

TPUs were prepared according to the prepolymer method. The prepolymer was obtained by reacting the macroglycol with MDI in excess (NCO groups/OH groups = 1.2), under stirring and at a temperature below 80°C. To complete the polymerization, the prepolymer was further reacted (12 h at 80°C in an oven, after mixing), with stoichiometric amounts (NCO remaining groups = OH + COOH groups) of rosin and/or 1,4-butanediol: COOH/OH = 0/100 (PU), 50/50 (PUR50), 75/25 (PUR75), and 100/0 (PUR100). Table I indicates the estimated rosin wt % in the different TPUs.

Adhesive solutions were prepared by dissolving 18 wt % TPU in 2-butanone using a laboratory mixer. The characterization of the TPUs was carried out using films prepared by slow evaporation of

Table I Nomenclature and Composition of TPUs

TPU	Reactant (with Prepolymer)	Rosin (wt %)	
		Mixed	Grafted
PU	1,4-Butanediol	0	0
PU + R	1,4-Butanediol	2	0
PUR50	50% Rosin/50% 1,4-butanediol	0	1.8
PUR75	75% Rosin/25% 1,4-butanediol	0	2.6
PUR100	Rosin	0	3.5

the solvent (to avoid the formation of bubbles) from 50-mL adhesive solution samples in flat molds.

To compare the tackifier grafting and mixing approaches, solutions and films (PU + R) were prepared by mixing (3 h stirring at 500 rpm) the solution of TPU 0 (no rosin grafted) with 2 wt % rosin (only one rosin wt % was selected because, even if the PU properties are modified by the presence of rosin, they do not seem to be markedly influenced by its actual wt %).

Characterization Techniques

Molecular and Nanometric Properties

Viscosity Measurements. Viscosities of TPU adhesive solutions were measured at 25°C using a Brookfield DV-I digital viscometer (Brookfield Instruments, Middleboro, MA). The results obtained were the average of the values obtained with spindle no. 4 at different speeds (0.3, 5, 10, and 20 rpm).

Molar Masses (and Distribution) Measurements. Absolute molar masses and their distributions were measured using a size-exclusion chromatography (SEC) unit consisting of a Varian model 9002 pump (Varian Associates, Palo Alto, CA), a Polymer Laboratories column set, and a twin detection system: Varian model RI-4 differential refractometer and multiangle laser light scattering detector (LLS Wyatt model DawnDSP [Wyatt Technology, Santa Barbara, CA], fitted with a laser photometer [λ_0 = 632.8 nm]). THF was used as the solvent and the flow rate was 1 mL/min for 10-μL injections of 1–4.2 g/L TPU solutions.

FTIR. IR spectra of TPU films were obtained in transmission mode using a Perkin–Elmer 1600 series FTIR (Perkin Elmer Cetus Instruments, Norwalk, CT). TPU films were prepared by spontaneous evaporation at room temperature of diluted (1/5) adhesive solutions deposited on a KBr crystal. There were 16 scans per experiment at a resolution of 4 cm^{-1}.

Wide-Angle X-Ray Diffractometry (WAXD). Diffraction patterns of TPU film samples (30 × 30 mm) were obtained on a Seifert JSO-Debyeflex model 2002 apparatus (Rich. Seifert & Co., Ahrensburg, Germany) in the range of Bragg's angle 2θ = 6–60°, using a monochromatic CuK$_\alpha$ radiation.

Bulk Properties

Stress-Controlled Rheometry. The rheological properties of the TPUs were measured using a Bohlin CS-50 rheometer (Bohlin Instruments, East Brunswick, NJ). Plate–plate geometry (upper plate diameter: 20 mm; gap between plates: 0.6 mm, settled at 200°C), 1 Hz shear frequency, and 0.05 target strain (region of linear viscoelastic response, as established by means of a stress sweep experiment at 100°C) were used. The temperature was varied from 200 to 30°C, at a cooling rate of 5°C min^{-1}.

Differential Scanning Calorimetry. DSC experiments were carried out on a Mettler DSC 30 apparatus (Mettler, Barcelona, Spain) to determine the glass-transition temperature (T_g), the softening temperature (T_s), and enthalpy (ΔH_s) of TPUs. Aluminum pans containing 5 to 10 mg of TPU films were heated, at a rate of 10° min^{-1}, from −100 to 100°C under nitrogen atmosphere.

Adhesion Properties

Contact Angle Measurements. Contact angle measurements were carried out on a Krüss system (Krüss Optronic GmbH, Wunstrof, Germany) according to the sessile drop method. Ethylene glycol was chosen as the test liquid. Single drops (2 μL) of ethylene glycol were deposited on the surface of the TPU films, and the contact angle at each side of the drop was measured. Although the values obtained were always reproducible, at least five measurements on the same film were achieved, with a standard deviation less than ±2°.

T-Peel Tests. T-peel tests were carried out between solvent-wiped (wiping was carried out with cotton immersed in 2-butanone, the solvent being allowed to evaporate for at least 30 min at room temperature) plasticized PVC samples (bonded area: 30 cm^2). Typically, 10 mL of adhesive solution was applied to each PVC strip to be joined, and allowed to dry for 30 min. The resulting adhesive film was heated to 80°C using infrared radiation, to facilitate the interlocking of the PU chains on the two PVC strips. The strips were quickly applied on each other and a pressure of 3.5 MPa was exerted for 10 s to achieve a suitable joint. The joints were kept at 23°C and 50% relative humidity for different times: 15 min to test the initial adhesive strength developed in the PVC/TPU adhesive/PVC system, and 72 h to test the maximal adhesive strength developed in the system (as stated elsewhere).[10,11] The T-peel test was carried out at 0.1 m min^{-1} peeling rate using an Adamel–Lhomargy (MTS) DY-25 test instrument (Adamel-Lhomargy, Paris, France). The val-
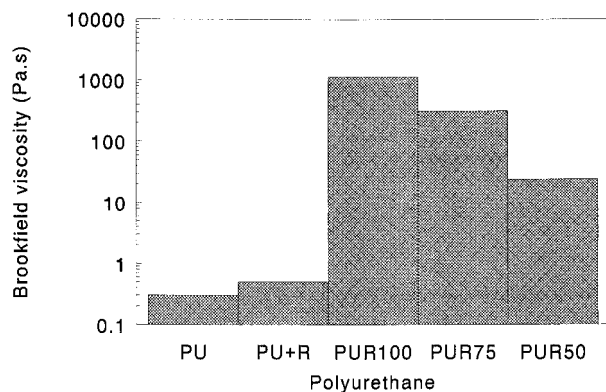
Figure 2 Viscosities of TPU adhesive solutions.

ues taken into account were the average of at least five experimental determinations with a standard deviation less than 10%.

RESULTS AND DISCUSSION

Chemical Structure of Modified TPUs

Figure 2 shows the variation of the Brookfield viscosity of adhesive solutions with composition of TPUs. Compared to PU solutions, viscosity increases slightly when rosin is added to the adhesive solution (PU + R), but it increases steadily when rosin is included as a reactant in the TPU formulation (PUR100, PUR75, PUR50); the larger the amount of rosin, the higher the viscosity of the solution. This can indicate that the molar masses are enhanced when rosin is used as a reactant, which suggests that rosin is not only grafted onto the TPU chains but also acts as a chain extender, either by itself (PUR100) or together with 1,4-butanediol (PUR75, PUR50). The values of TPU average molar masses (Table II) strengthen this assumption. Molar mass remains almost constant when rosin is mixed with PU solutions, but it increases steadily in the case of

Table II Average Molar Masses, in Number ($\bar{M}_n$) and Weight ($\bar{M}_w$) of TPUs

| TPU	$\bar{M}_n$ (g/mol)	$\bar{M}_w$ (g/mol)	$I^a = \bar{M}_w/\bar{M}_n$
PU	4.8×10^4	6.7×10^4	1.4
PU + R	4.4×10^4	6.0×10^4	1.4
PUR100	1.1×10^5	1.7×10^5	1.5
PUR75	1.0×10^5	1.5×10^5	1.5
PUR50	1.0×10^5	1.4×10^5	1.4

[a] Polydispersity index.
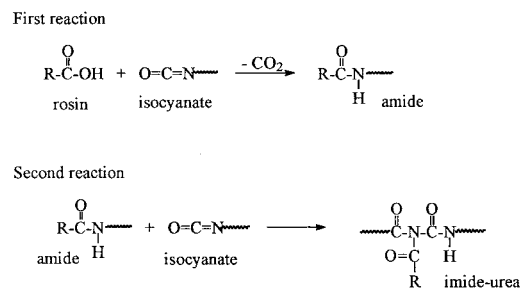
Scheme 1

PUR solutions, thus confirming the existence of structural changes in the TPUs when rosin is allowed to react with the prepolymer. It is worth noticing that the distribution of molar masses is not influenced by the nature of the prepolymer reactant. Its low 1.5 value (which can be explained by a limited extent of the chain extension reaction) is the same, regardless of whether butane diol, rosin, or their mixture is used.

Given the low quantities of rosin, its reaction with the prepolymer cannot be studied directly. However, using a model reaction, that is, MDI with rosin (in the same condition as for prepolymer and rosin), the formation of a polymer containing amide, imide, and urea functions (IR characteristic signals corresponding to N—H: 3305 cm^{-1} and C=O: 1800, 1640 cm^{-1}, versus NCO: 2300 cm^{-1} and COOH: 3300–2500 cm^{-1}) can be verified.

Scheme 1 proposes a possible pathway for the formation of amide and, further, imide and/or urea groups by reaction of isocyanate and acid functions. It assumes a bifunctional behavior of the rosin acid group, which is thus able to act as a chain extender. **Scheme 2** represents our assumption of a chain extension of the prepolymer
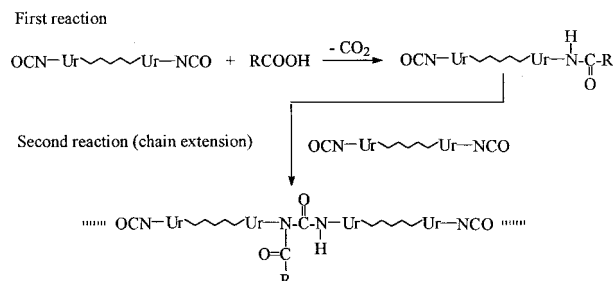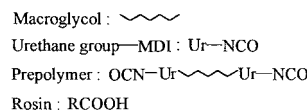
Scheme 2

Table III DSC Parameters of TPUs

TPU	T_g (°C)	T_s (°C)	ΔH_s (J/g)
PU	−57	51	73
PU + R	−57	55	80
PUR100	−56	48	69
PUR75	−57	47	67
PUR50	−55	46	69

by rosin and of the resulting close proximity of rosin and urethane units.

Morphology of Modified and Unmodified TPUs

Table III summarizes the results of DSC measurements of T_g, T_s, and ΔH_s in such a temperature range that softening concerns only soft segments. The glass-transition temperature remains constant regardless of TPU composition, indicating that rosin does not affect the amorphous regions. Regarding the softening temperature and enthalpy, their values increase when the PU is mixed in solution with rosin (PU + R) and, on the contrary, decrease when rosin is included in the TPU formulation (PUR100, PUR75, PUR50). Both T_s and ΔH_s are quite constant for PUR, regardless of the amount of rosin.

Because ΔH_s depends on the organization of the soft segments (i.e., on the interactions between TPU chains) the experimental data indicate that this structural organization decreases when rosin is present as a chain extender, but that it increases when rosin is mixed with PU solutions. Thus, the crystalline domains of the structure are affected by rosin. When it is mixed in solution with PU (PU + R), no interaction exists between the polymeric chains (mainly polar) and the rosin molecules (mainly nonpolar), resulting in a segregation of PU and rosin, which allows a reorganization of the polymeric chains and an increase in the effectiveness of the interactions between them. On the contrary, when rosin is grafted onto the polymeric chains, it causes important steric hindrances that worsen the organization in the structure of TPUs.

In summary, DSC data are in agreement with the presumed molecular structure and morphology of rosin-modified TPUs. Acting as a chain extender, rosin is grafted to the polymeric chains close to the urethane groups and indirectly affects the crystalline domains of the TPUs.

WAXD studies provide for a thorough characterization of TPU morphologies. As shown by Fig-
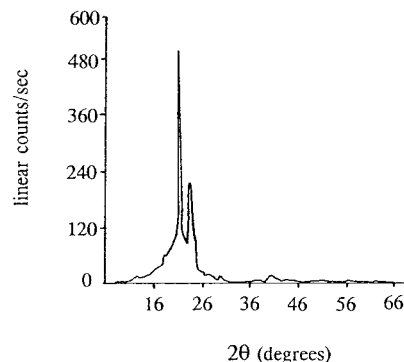
Figure 3 X-ray diffraction pattern of PU.

ure 3 (WAXD pattern of PU as a typical example) diffractograms of TPUs show two main peaks at 21 and 24°, which correspond, respectively, to the (110) and (020) diffraction in a linear polyester[17] and whose intensities are related to the crystallinity of the TPUs. The results of the studies are summarized in Figure 4. It can be observed that PU + R and PUR100 are more crystalline than other TPUs. The behavior of PU + R has been explained, however, by the enhancement of interactions in its structure, which gives a more ordered and crystalline TPU. Regarding PUR100 its proposed structure involves lesser interactions between the soft segments than those in PU or PU + R structures; therefore its high crystallinity could not be expected. A possible explanation is that the crystallinity of PUR100 is attributed not only to the soft segments but also to the hard segments. Because the chains have been extended with rosin, the high volume of hard segments is likely to render them unable to interact with each other unless they are reorganized. Such behavior has also been found in the case of TPUs whose hard segments crystallize when the materials are
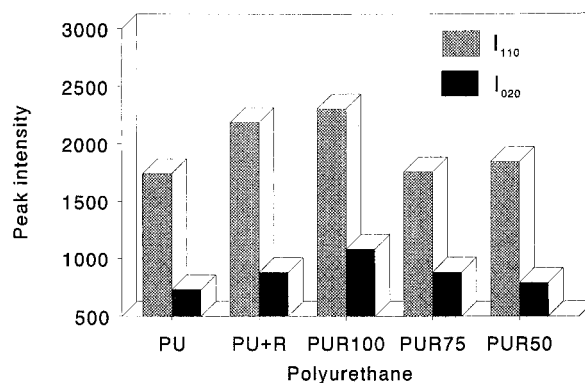
Figure 4 Variation of the WAXD peak intensities versus composition of TPUs.
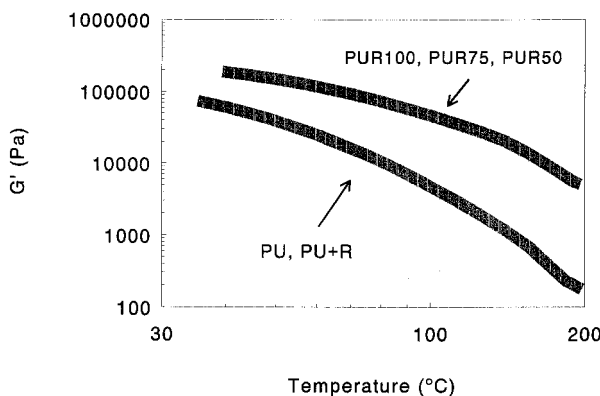
Figure 5 Tendencies of the variation of the storage modulus (G') versus temperature for modified and unmodified TPUs.

annealed.[17,18] We assume that the rosin–imide–urea fragments organize themselves in PUR100, thus increasing its crystallinity (this hypothesis is not at variance with the low values of T_s and ΔH_s of PUR100 because these concern only the organization of the soft segments); we refer to this as "extracrystallinity." Regarding PUR75 and PUR50, their low crystallinity can be explained by the lack of homogeneity of their hard segments (rosin and 1,4-butanediol are used together as chain extender), which decrease the effectiveness of the interactions between them, thus lessening their contribution to the crystallinity of the TPUs.

In summary, WAXD studies emphasize the conclusions of DSC studies. The classic distribution in soft and hard domains is changed by the rosin units in such a way that the overall crystallinity is enhanced in the presence of rosin, whether it is grafted or only mixed, unless rosin is used as a cochain extender together with 1,4-butanediol.

Bulk and Adhesive Properties of Rosin-Tackified TPUs

Figure 5 shows the variations with temperature of the storage modulus (G') of TPU samples, as obtained by DMA measurements. Two tendencies are observed. The modulus of grafted rosin TPUs (PUR100, PUR75, and PUR50) is higher than that of unmodified TPUs (PU, PU+R). On the contrary, when temperature increases its decrease is lesser. This indicates, on the one hand, that added rosin does not influence the cohesion of PU (i.e., the interactions between PU chains) and, on the other, that grafted rosin gives more resistant (i.e., with stronger interactions between chains) structures.

Concerning wettability, contact angle measurements were achieved to study the influence of rosin on the surface properties of TPUs. Table IV shows the contact angle values of ethane diol with TPUs and rosin. It is quite obvious that rosin does not influence the surface properties of TPUs, which could be explained by the very low quantities of rosin in the materials, but which is rather ascribed to the holding of rosin into the bulk of materials.

Finally, the influence of rosin on adhesive properties of TPUs was studied using the T-peel test in a PVC/TPU adhesive/PVC system. Figure 6 shows the variation of T-peel strength with composition of TPUs, 15 min (initial adhesive strength) and 72 h (maximal adhesive strength) after the adhesive joints were achieved.

For all TPUs, failure was 100% cohesive in the TPU film for the samples tested 15 min after being joined and more than 80% adhesive at the PVC/TPU interface for the samples tested 72 h after being joined. However, the behaviors of PU and PU + R, on the one hand, and of PUR50, PUR75, and PUR100, on the other, were completely different: the T-peel strength increased strongly with time in the case of unmodified TPUs, whereas it decreased more or less in the case of rosin-modified TPUs.

We assume that, after 15 min, the structure of PU is not organized and therefore that its cohesion and adhesive strength are very low. Mixed rosin (PU + R) does not influence the initial adhesive strength, as already determined. After 72 h, PU reaches its most stable configuration (crystallization of the soft segments) and hence achieves its optimal cohesion (and optimal T-peel strength). Mixed rosin exerts a somewhat negative influence, which leads to the conclusion that using rosin as an additive in TPU formulations is quite pointless.

Regarding PUR50, PUR75, and PUR100, the chemical modification by rosin causes an outstanding improvement of the initial adhesive strength. We assume that a phase separation occurs instantaneously, allowing the organization

Table IV   Contact Angle Values (Ethylene Glycol, 25°C) for TPUs and Rosin (R)

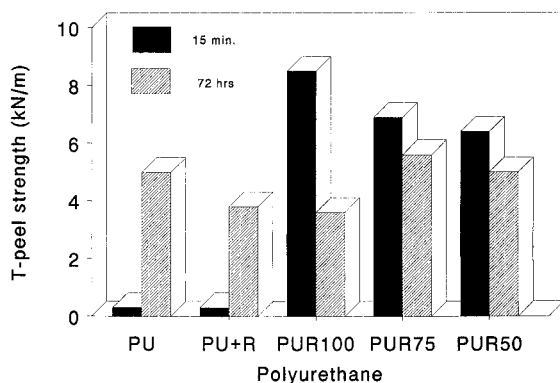| TPU or R	Contact Angles (Degrees)
PU	56
PU + R	59
PUR100	60
PUR75	61
PUR50	60
R	35

Figure 6 T-peel strength versus composition of TPUs, 15 min and 72 h after adhesive joining.

of the hard rosin-modified segments. As a consequence a fair cohesion is reached after 15 min, imparting suitable tack properties to PUR. The progressive crystallization of the soft segments (corresponding to the macroglycol) results in an overall drop of the T-peel strength. Because it is unlikely that the cohesion of TPUs can decrease, we assume that the progressive crystallization gives to PUR a somewhat brittle character and hence a lowered peeling strength (as could be expected, the highest decrease is observed in the case of TPU100, which is also the most crystalline TPU of the series).

CONCLUSIONS

1. The use of rosin mixed as an additive in TPU formulations does not affect the properties of the polymers, although as a reactant or co-reactant in the chain-extension step of polyurethanes' synthesis rosin imparts remarkable modifications. The increases in such characteristics as solution viscosity or molar mass can be explained by assuming that rosin acts as a bifunctional chain extender.
2. There are structural changes that can explain the rheological and thermomechanical properties of rosin-modified TPUs. Although the amorphous regions of the TPUs are apparently not concerned, the crystalline regions do change. Rosin-modified TPUs (PUR50, PUR75) are less crystalline than unmodified ones (PU, PU + R) and extracrystallinity can be afforded by the organization of the rosin-modified hard segments (PUR100).
3. Finally, the chemical modification of PU by

rosin results in outstanding improvements of the initial adhesive strength (tack), whereas the maximal adhesive strength is virtually unaffected. Thus, rosin-modified TPUs may be used as suitable heat-activated pressure-sensitive adhesives.

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