

# Grafting of Polyurethane Surfaces with Poly(Ethylene Glycol)

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## SYNOPSIS

Films of a commercial poly(ether urethane), Pellethane 2363-80AE, were prepared through solvent casting from dimethyl formamide. The films were grafted with poly(ethylene glycol) (PEG) by a two-step procedure. In the first step, the film surfaces were treated with hexamethylene diisocyanate in toluene in the presence of triethylamine as a catalyst. In the second step, PEG 1500 was allowed to react in toluene with surface bound isocyanate groups. It was shown by ATR-IR, XPS, and contact angle measurements that the grafted surfaces were mainly composed of PEG, and that they were strongly hydrophilic. It was also shown that unreacted PEG was entrapped in the material, which influenced its mechanical and thermal properties. Extraction of the films with toluene eliminated the entrapped PEG, and the hydrophilicity as well as the PEG coverage of the surface decreased. However, a subsequent treatment with aqueous NaCl solution induced a molecular restructuring of the surface, increasing the amount of grafted PEG at the surface to a value close to the original one. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Linear, segmented poly(ether urethane)s are utilized in a large number of biomedical applications because of their comparatively high tissue and blood compatibility. The structure of the polymers may be varied within wide limits, and a range of materials with excellent mechanical and physical properties can be produced.<sup>1</sup> In blood contacting applications the surface properties are especially important, and it is therefore of interest to surface-modify polyurethanes in order to increase their blood compatibility, and at the same time retain their excellent mechanical properties.

Many studies have been performed aiming at producing hydrophilic surfaces by grafting of polymer surfaces with poly(ethylene glycols) (PEG).<sup>2-8</sup> It is believed that the PEG chains present at the polymer surface can reduce protein adsorption as well as platelet adhesion by an excluded volume ef-

fect, and by the dynamic motion of the water soluble PEG chains grafted to the surface. Han et al.<sup>9</sup> and Park et al.<sup>10</sup> have reported grafting of PEG and heparin onto surfaces of polyurethanes and polyurethaneureas by the use of diisocyanate coupling agents or by isocyanate end-capped PEG prepolymers. A decreased platelet adhesion to the surfaces after hydrophilization was reported.

Desai and Hubbell<sup>11</sup> have prepared hydrophilic surfaces by entrapping high molecular weight PEG and other water soluble polymers into polyurethane film surfaces. Most organic solvents swell the polyurethanes, and dissolved PEG may easily diffuse into the swelled polymer material. When swelled films containing absorbed PEG then are immersed in water, or dried, the swelled polymer structures collapse, and PEG will be entrapped in the material. The authors reported that after one week's extraction in water the surface still contained PEG and was hydrophilic. Also, platelet adhesion and adsorption of albumin was reduced as compared to unmodified material.

In the present work, PEG of relatively low molecular weight was grafted onto film surfaces of a commercial poly(ether urethane), Pellethane 2363-

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80AE. The grafting was carried out in toluene solution, which swells the polyurethane and allows diffusion of PEG into the film surfaces. The surface properties of the grafted films were accordingly dependent partly on grafted PEG and partly on entrapped PEG. The leaching of entrapped PEG by solvents, and the long-term properties of the modified surfaces in contact with water were investigated.

## EXPERIMENTAL

### Materials

Pellets of Pellethane 2363-80 AE (Dow Chemical) were extracted with ethanol during 3 days to remove processing agents and low-molecular weight components. The pellets were dried in a vacuum oven at 40°C and then dissolved in dimethyl formamide (DMF, Merck, p.a.) to a 12.5% (w/w) solution. The solution was cooled to 5°C and filtered under N<sub>2</sub> pressure through a 5- $\mu$ m Teflon filter (Millipore) to give a clear solution.

Pellethane films were prepared by solvent casting onto thoroughly cleaned petri dishes. The films were cast in two layers with evaporation of the solvent between each casting (24 h at 60°C). Before use the films were dried under vacuum at 60°C during 24 h.

Toluene (Merck, p.a.) was dried over molecular sieves (Union Carbide 5 Å). PEG,  $M_n = 1500$  (Berol Nobel AB, Sweden) was dried under vacuum at 60°C for 24 h. Hexamethylene diisocyanate (HDI, Merck, p.a.) and triethylamine (Jansen Chimica) were used without further purification.

## Methods

### Grafting of PEG Onto Polyurethane Surfaces

PEG,  $M_n = 1500$ , was grafted onto polyurethane surfaces in two steps (Fig. 1). Polyurethane films were immersed in a toluene solution containing 7.5% (w/v) HDI, and 2.5% (w/v) triethylamine as a catalyst. The reaction was allowed to take place at 50°C for 10–120 min under N<sub>2</sub> atmosphere. The films were then rinsed with toluene before immersion in a toluene solution containing 10% (w/v) PEG for 24 h at 40°C. After the reaction the films were rinsed with toluene to remove unreacted PEG and HDI from the surfaces. The films were characterized on the air-facing side (see above, Materials section) after being dried under vacuum at 20°C for 24 h.

### Solvent Extraction of Grafted Polyurethane

Film specimens containing surface grafted and entrapped PEG were weighed and immersed in toluene. The leaching of entrapped PEG from the films was registered as a weight loss after different leaching times in toluene at room temperature, and subsequent drying (see below). The toluene extracts were evaporated, and the residues weighed and analyzed by GPC. Grafted films, toluene leached as well as unleached, were also immersed for different periods of time in physiological NaCl solutions (0.9% w/w aqueous NaCl) at room temperature in order to examine the hydrolytic stability of the grafted layers, as well as the leaching out of entrapped PEG. The weight loss was determined as described above.

The leached films were dried under vacuum at

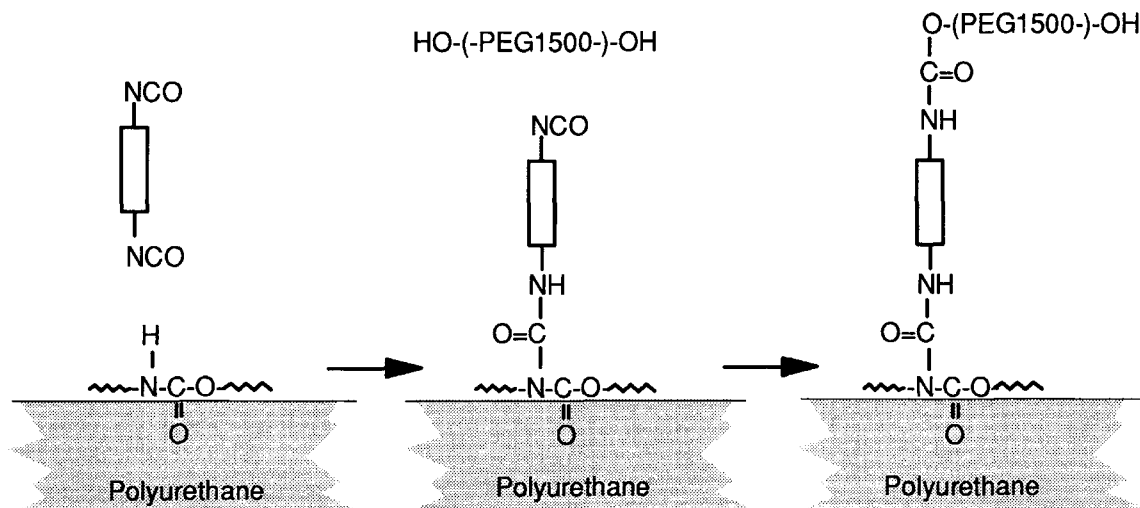


Figure 1 Reaction scheme for grafting of PUR surfaces with PEG.

20°C for 24 h and characterized in the same way as the unleached grafted films.

### Characterization of Grafted Films

**X-Ray Photoelectron Spectroscopy (XPS).** XPS spectra were obtained using a Kratos XSAM 800 spectrometer. The surfaces were examined before and after the grafting procedure, and after leaching with toluene and physiological NaCl solutions. The excitation X-ray source was Mg-K $\alpha$ , (1253.6 eV). The operation conditions were set at 12 kV and 24 mA. High resolution spectra of C1s, N1s, and O1s were run. C/O and C/N ratios were calculated, and the different band areas normalized by using Scofield crosssection factors, C1s = 1.00, N1s = 1.80, and O1s = 2.93.<sup>12</sup> The C1s peak was resolved by computer simulation into its constituent peaks: aliphatic C at 285 eV, ether C at 286.5 eV, and carbonyl C at 289.2 eV.

**Contact Angle Measurements.** Unmodified and modified polyurethane surfaces were analysed by measuring contact angles with water, using the pendant drop method. Milli-Q water, 3  $\mu$ L (Millipore) was placed on the polymer surface by means of a motor-driven syringe, and the advancing angle ( $\theta_{ADV}$ ) and receding angle ( $\theta_{REC}$ ) were obtained by increasing and decreasing the drop volume at a constant rate. The contact angles were monitored by a video camera, and evaluated from printouts of the video screen. The hysteresis in the wetting angles was calculated as the difference of  $\theta_{ADV}$  and  $\theta_{REC}$ .

**Attenuated Total Reflection-IR (ATR-IR).** ATR analyses were performed by means of a Perkin Elmer IR 881 infrared spectrometer equipped with an ATR attachment. The spectra were recorded at an incident angle of 45° using a KRS-5 crystal, giving an analysis depth of 1–2  $\mu$ m.

### Bulk Characterization

**Differential Scanning Calorimetry (DSC).** The thermal properties of modified and unmodified materials were determined with a Mettler TA 3000 System equipped with a low temperature cell. DSC traces were run twice between –150°C and +150°C at a heating rate of 20°C/min, with cooling between runs at the same rate.

**Tensile Testing.** Film specimens (10  $\times$  70  $\times$  0.5 mm) were tested on a tensile testing machine (J J In-

struments T 30K) equipped with a 100 N load cell at a strain rate of 50 mm/min. Reported values are averages of 5–7 samples.

**Torsional Pendulum.** Dynamic mechanical measurements were made at 1 Hz with a Brabender Torsionautomat, Lonza system, using film specimens (10  $\times$  50 mm) with thicknesses ranging from 0.8 to 2.1 mm. The temperature was swept between –150°C and +120°C at a rate of 1°C/min.

## RESULTS AND DISCUSSION

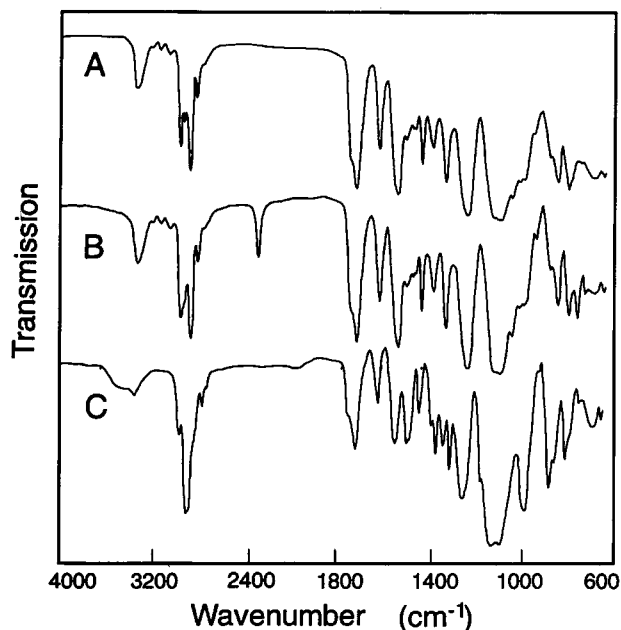
As mentioned in the Introduction, surface properties are very important for the performance of an artificial material in a biological environment. By surface grafting, blood and tissue compatibility may be changed without changing the overall mechanical properties of the material.

We have grafted PEG onto surfaces of polyurethane films by a two-step reaction presented in Figure 1. In the first step, HDI was allowed to react with urethane bonds at the surface in an allophanate reaction in order to functionalize the surface with isocyanate groups. The free isocyanate groups were then utilized in a second step for binding of PEG.

### Grafting of PEG onto Polyurethane Surfaces

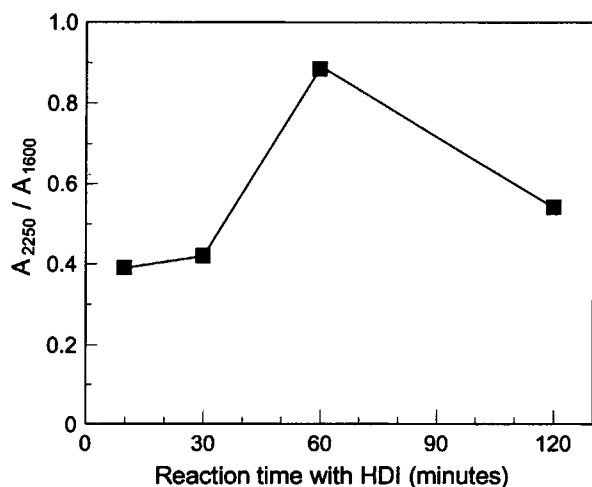
Diisocyanates have been used for activating polyurethane surfaces for a subsequent grafting operation.<sup>9,10</sup> Formation of allophanates from urethane and isocyanate groups generally do not occur below 100°C; but in the presence of a catalyst the reaction can take place at lower temperatures.<sup>13</sup> We used triethylamine as a mild catalyst for the reaction of HDI with polyurethane (PUR) films at 50°C in toluene. The reaction was relatively slow as compared to the rate obtained using more active catalysts, for example, cobalt salts,<sup>13</sup> but an active catalyst made the reaction more difficult to control. If the reaction was run too far, crosslinked brittle films were obtained, and the number of free NCO groups decreased.

The extent of the reaction was followed by ATR-IR. In Figure 2, ATR-IR spectra of untreated PUR and HDI grafted PUR are shown. After reaction with HDI a sharp band at 2250  $\text{cm}^{-1}$ , characteristic of NCO groups, appeared in the PUR spectrum [Fig. 2(b)]. The number of free NCO groups changed with the HDI reaction time. From the ATR-IR spectra the ratio between the absorption band at 2250  $\text{cm}^{-1}$  (NCO) and the band at 1600  $\text{cm}^{-1}$  (ar-



**Figure 2** ATR-IR spectra of PUR surfaces: (a) untreated PUR; (b) HDI grafted PUR; and (c) PEG grafted PUR.

omatic band) in the spectrum was calculated, and reported in Figure 3 as a function of the reaction time with HDI. As seen in the figure, a maximum number of free NCO groups was obtained after a reaction time of 60 min. The observed decrease in the number of free NCO groups at longer reaction times may be a result of ring formation through di-



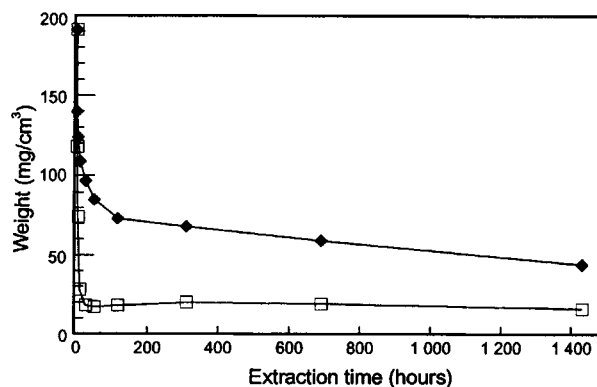
**Figure 3** Extent of reaction of HDI with PUR surfaces, measured from ATR-IR spectra as the ratio of the NCO absorption at  $2250\text{ cm}^{-1}$ , and the phenyl group absorption at  $1600\text{ cm}^{-1}$ .

merization of NCO groups and/or allophanate reactions.

In the second reaction step, hydroxylic groups of PEG were allowed to react with the free NCO groups at the surface (see Fig. 1). The presence of PEG at the surface after the reaction was evident from the ATR-IR spectra [Fig. 2(c)]. However, the PUR absorbs about 80% by weight of toluene during the grafting procedure. HDI as well as PEG can diffuse into the swelled material, allowing NCO groups and PEG to react in the bulk in the same way as at the surface. Consequently, the grafting will not be located entirely at the surface. Furthermore, an excess of PEG that has not reacted with isocyanate groups will be physically entrapped in the material on drying when the swelled gel-like structure collapses. After drying, the glass transition temperature of the PUR is substantially lower than  $0^\circ\text{C}$ , and due to the chain mobility in the system, entrapped PEG migrates to the film surface and crystallizes, giving rise to a characteristic spherulitic structure that makes the surface opaque and rough. The entrapped PEG consequently has a major effect on the surface properties, as well as on the mechanical behaviour.

#### Leaching of Grafted Polyurethanes

In order to investigate the influence of the covalently bonded PEG on the properties of the PUR surfaces, the entrapped PEG in the grafted films had to be removed. In order to evaluate the leaching of PEG from grafted films, samples were immersed in toluene and in physiological sodium chloride solution (0.9% NaCl in water), respectively, and the weight of the samples registered at different times. As seen in Figure 4, the rate of leaching is quite high in toluene, which is a swelling agent for PUR. After 50 h



**Figure 4** Extraction of PEG grafted PUR films in toluene (□), and in 0.9% aqueous NaCl (◆).

the weight of the films reached a steady-state value, and the surfaces became clear and the surface properties stable. When the grafted films were immersed in physiological NaCl solution (0.9% NaCl in water) instead of toluene the swelling was negligible. The weight loss curve, as shown in Figure 4, was similar in shape to the curve for toluene leaching, but the diffusion of PEG was slow, and a large amount of PEG was still entrapped in the film after 1400 h leaching.

GPC analyses of the toluene extract showed a big, narrow peak identified as PEG 1500. The extract also contained small amounts of low molecular weight urethane oligomers, as shown by GPC and IR spectra. When analyzed by DSC, films containing entrapped PEG showed a distinct melting peak at 50°C, which can be attributed to crystalline PEG. When the sample was cooled and reheated directly no melting point was observed; but after a few days at room temperature the melting peak reappeared as the entrapped PEG crystallized. After removal of the entrapped PEG by leaching in toluene, the DSC trace was similar to that for the original PUR and no PEG melting peak could be detected.

Leaching of toluene-extracted grafted films in physiological NaCl solution induced large changes in the surface properties, that is, in contact angles and XPS spectra, but negligible amounts of hydrophilic material were extracted after 2000 h. This was

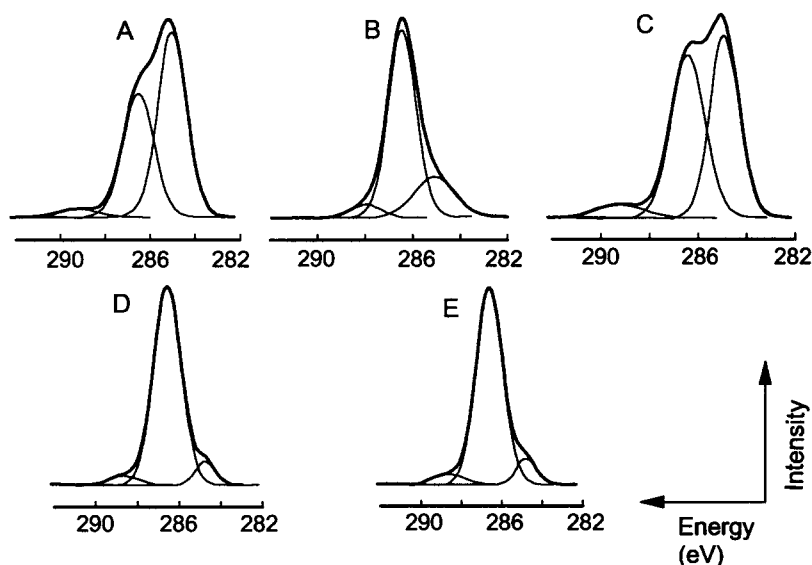
also an indication that the grafted PEG chains were hydrolytically stable under the conditions used.

### Surface Properties

In Figure 5, C1s XPS spectra of unmodified [Fig. 5(a)] and grafted PUR surfaces [Fig. 5(b–e)] are shown. As expected, the ether carbon peak at 286.5 was substantially increased in the grafted samples, as compared to the original PUR, indicating the presence of large amounts of PEG at the surface [Fig. 5(b)]. After toluene extraction of the films the dominant ether carbon signal decreased significantly [Fig. 5(c)], but increased again to nearly its original value after treatment with saline [Fig. 5(d)]. The reason for the latter behaviour is presumably a rearrangement of the polymer chains in the surface regions of the film, which allows grafted PEG chains to be exposed to the hydrophilic environment, thereby decreasing the free energy of the polymer/water interface.

For the PEG grafted films that were extracted only in an aqueous NaCl solution, the C1s XPS spectrum showed a large amount of ether carbons [Fig. 5(e)], and the spectra were quite similar to the spectrum of an unextracted film [Fig. 5(b)].

From the XPS spectra the elemental compositions of the surfaces were calculated, and these results together with the shape of the C1s peaks in-



**Figure 5** XPS spectra of surface modified PUR: (a) untreated PUR; (b) PEG grafted PUR; (c) PEG grafted PUR, leached in toluene for 140 h; (d) PEG grafted PUR, leached in toluene for 140 h followed by leaching with 0.9% aqueous NaCl for 1000 h; and (e) PEG grafted PUR, leached in aqueous 0.9% NaCl in water for 4000 h.

**Table I Elemental Ratios from XPS Analyses**

Sample	C/O	C/N
PUR	5.1	29
PUR-HDI-PEG, unleached	2.0	—
PUR-HDI-PEG, toluene leached	3.8	26
PUR-HDI-PEG, leached in toluene and 0.9% aqueous NaCl solution	2.2	194
PUR-HDI-PEG, leached in 0.9% aqueous NaCl solution	2.3	212

Ratios between areas of C1s, O1s, and N1s peaks in XPS spectra, recalculated to elemental ratios using Scofield cross-sections.

dicates that a large amount of PEG is present at the surface after the grafting procedure. The C/O and C/N ratios for Pellethane and the grafted films are given in Table I. Directly after the grafting procedure, when the films still contained entrapped PEG, the C/O ratio was found to be 2.0, which is the value also obtained for pure PEG. The corresponding C/O ratio for the original Pellethane surface was 5.1. Also, no N1s signal was possible to detect due to the large amount of PEG present at the surface. When the entrapped PEG was removed by toluene leaching, the C/O ratio increased to a value between the values for PEG and Pellethane, and the N1s signal increased to the same level as in the ungrafted material. Subsequent extraction with saline decreased the C/O ratio again to 2.2 due to restructuring of the surface in the hydrophilic environment, as noted above. The N1s signal again decreased considerably, presumably due to shielding by the PEG grafts. It can be concluded from the XPS spectra of leached samples that there is a high coverage of the surfaces by PEG grafts.

When PUR surfaces were grafted with PEG they became strongly hydrophilic, and the water contact

angles decreased considerably as compared to the angles for an ungrafted surface, as shown in Table II. As mentioned previously, the grafted surfaces were rough and opaque due to the presence of crystallized PEG, and measurements of contact angles were difficult to carry out because of this fact. Removal of the entrapped PEG by leaching in toluene gave the surfaces a smooth appearance similar to the ungrafted reference surfaces, and they were still quite hydrophilic, as evidenced by their low water contact angles.

After leaching of toluene extracted films in saline their contact angles with water decreased, that is, the surfaces become more hydrophilic after extraction with saline, and the contact angle hysteresis increased considerably. This is in accordance with the view that grafted PEG chains in the surface regions of the material can rearrange and accumulate at the surface. The increase in the number of PEG chains at the surface was also observed in the XPS spectra, as noted above. The large hysteresis is an indication of a high mobility of the surface bound hydrophilic and hydrophobic groups. A similar change of surface properties after hydration has also been observed for a poly(ether urethane urea) containing small amounts of an amphiphilic block copolymer.<sup>14</sup>

### Mechanical Properties

The grafting procedure affected the mechanical properties of the polyurethane material, for example the stress-strain properties, as shown in Table III. The entrapped PEG present in the films after the grafting apparently acted as a plasticizer, and decreased the stiffness of the polyurethane. On extraction of entrapped PEG with toluene the stiffness of the material increased, and the difference between grafted and the ungrafted material became smaller.

**Table II Contact Angles with Water**

Sample	Contact Angles		Hysteresis Degrees
	$\theta_{ADV}$	$\theta_{REC}$	
PUR	75 ± 3	51 ± 3	25 ± 3
PUR-HDI-PEG, unleached	24 ± 8	9 ± 6	15 ± 9
PUR-HDI-PEG, toluene leached	64 ± 7	37 ± 8	27 ± 8
PUR-HDI-PEG, leached in toluene and 0.9% aqueous NaCl solution	59 ± 2	14 ± 8	45 ± 8
PUR-HDI-PEG, leached in 0.9% aqueous NaCl solution	36 ± 4	9 ± 1	27 ± 5

**Table III Stress-Strain Properties of PUR and Grafted PUR**

Sample	Stress at 300% Elongation (N/m <sup>2</sup> )	
	Unleached Film	Film Leached in Toluene
Pellethane 2363-80AE	6.3 ± 0.4	6.6 ± 0.6
HDI reaction time (min)		
30	4.6 ± 0.4	5.8 ± 0.4
60	5.2 ± 0.4	6.2 ± 0.3
120	5.3 ± 0.4	7.3 ± 0.4

It was also found that at long reaction times with HDI in the grafting procedure the material became stiff, and the entrapped PEG did not have the softening influence described above. Presumably the difunctional HDI acts as a crosslinker for the material at long reaction times.

Dynamic mechanical properties of different film samples were determined by torsional pendulum analysis, and the results from these measurements are shown in Figure 6. For the grafted samples containing free PEG, a glass transition was registered at -41°C, which should be compared to -30°C for unmodified Pellethane. Furthermore, a new diffuse damping peak appeared as a shoulder on the tan  $\delta$  curve at +30°C, indicating a phase separated structure. When the entrapped PEG was removed by tol-

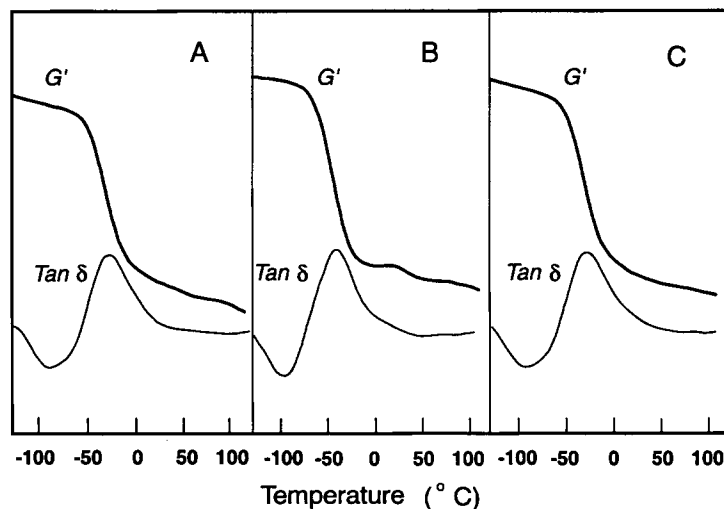
**Table IV Glass-Transition Temperatures for PUR and Grafted PUR**

Sample	$T_g$ (°C)	
	DSC	Torsional Pendulum
PUR	-31	-30
PUR-HDI-PEG, unleached	-38	-41
PUR-HDI-PEG, toluene leached	-30	-29

uene extraction,  $T_g$  increased to its original value, and the shoulder at +30°C disappeared. Data obtained by DSC measurements are in agreement with the torsional pendulum results, as shown in Table IV. The diffuse damping peak observed by torsional pendulum corresponds to a crystalline melting peak in the DSC trace, and both measurements point to the presence of a dispersed PEG phase melting in the range of 30–50°C. It may also be noted that the plasticising effect of PEG is observed in the DSC trace as a decrease of the glass transition by 11°C.

## CONCLUSIONS

On grafting of polyurethane surfaces with PEG in toluene, one fraction of PEG is covalently bonded to the surface, and one is entrapped in the material. The entrapped PEG, which has a large effect on the



**Figure 6** Storage modulus ( $G'$ ) and loss tangent ( $\tan \delta$ ) determined at 1 Hz by torsional pendulum: (a) untreated PUR; (b) PEG grafted PUR; and (c) PEG grafted PUR leached in toluene for 250 h.

surface properties due to migration and crystallization, is easily removed by leaching the grafted films in toluene. Elimination of the entrapped PEG by leaching in aqueous NaCl solution is a slow process because the grafted polyurethane does not swell in water. Entrapped PEG acts as a plasticiser, decreasing the glass transition of the polyurethane.

After removal of entrapped PEG the polyurethane surfaces are still hydrophilic, and on contact with saline the amount of PEG grafts increases at the surface as a consequence of surface restructuring.

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