

Structure–Property Relationships of Polyurethane-Based Materials (PUPA) for Applications in Biomedicine

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SYNOPSIS

Polyurethane poly(amido-amine) (PUPA) is a modified polyurethane whose chains are crosslinked with those of a tertiary aminic polymer [poly(amido-amine) (N₂LL)] by the bifunctional agent hexamethylenediisocyanate (HMDI). PUPA is capable of complexing heparin; a behavior that is related to the presence of poly(amido-amine). The effect of the chemical composition of the starting mixture and/or the reaction time on the morphology and physical properties was studied by using differential scanning calorimetry, dynamic mechanical experiments, x-ray, scanning electron microscopy, and Fourier transform infrared attenuated total reflection analyses. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

From the 1980s there has been an ongoing search for new sources of biomedical materials in order to satisfy the several and varied biomedical demands.

Among the polymers studied in this field, the polyurethane block copolymers have been widely used because of their good physical and mechanical properties together with a satisfactory biocompatibility factor.¹ One strategy used was to render the polymer surface capable of adsorbing heparin. This was achieved by² grafting poly(amido-amine) (N₂LL) on the surface of the polyurethane. The basic nitrogens of poly(amido-amine), once protonated, interact with the negative charges carried by the heparin molecules. This treatment had the advantage of maintaining the morphology and mechanical properties of the starting material, but the chemical procedure was difficult to perform. Therefore, a new chemical procedure³ was utilized to synthesize new materials having the heparin-complexing ability of poly(amido-amine) and the good mechanical properties of polyurethanes, by using a simpler chemical route. The new material, called PUPA, was obtained by interconnecting the poly(amido-amine) with commercial polyurethane,

Pellethane^R 2363-80AE, using hexamethylenediisocyanate (HMDI) as a crosslinking agent. This procedure allows us to obtain different series of PUPA by changing the percentage of the three components. Consequently, the properties of the materials can be adjusted and balanced by variations of the relative percentage of the components. Six different PUPA samples were synthesized in order to study the variation of the physicochemical properties with chemical composition. Results of tensile experiments indicated an increase of Young's modulus and a decrease of the elongation at failure increasing the crosslinking component (HMDI). PUPA material, once the basic nitrogens of the poly(amido-amine) chains are protonated in acid solution, can adsorb heparin in two ways. The first is a mere physical adsorption, in fact, the heparin is released when the PUPA sample is placed in a stream of plasma or saline solution; the second is a strong bond and the heparin can be removed only by 0.1 M NaOH solution. It was found that the ability of PUPA to complex heparin is closely correlated with the chemical composition of the material and in particular with the presence of N₂LL.

In this work we report the results of a study concerning the investigation of the morphology and physical properties of some samples of PUPA materials obtained by changing the ratio of the starting materials and the reaction time. The ratios of PU,

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HMDI, and N₂LL were chosen in accordance with previous experience³ for the best biomedical application.

EXPERIMENTAL

Materials

The polyurethane used is the commercial Pellethane 2363-80AE purchased from the Upjohn Polymers. The poly(amido-amine) (N₂LL) and PUPA material (see Scheme 1) were synthesized as described below.

Synthesis of the Polymer N₂LL

The amino end-capped poly(amido-amine), N₂LL, was obtained by polyaddition of *N,N'*-dimethylputrescine to 4,4'-bis-acryloylpiperazine.^{4,5} The purity of the N₂LL polymer was checked by elemental analysis: for C₁₆H₃₀N₄O₂ · 1/2H₂O. Calcd: C, 60.15%; H, 9.78%; N, 17.54%; we found: C, 60.81%; H, 9.91%; N, 17.64%. The N₂LL obtained is a semicrystalline polymer with a glass transition temperature (*T_g*) of 10 ± 2°C and melting temperature (*T_m*) of about 120°C. Its number-average molecular weight ranges from 1.0 × 10⁴ to 1.8 × 10⁴ (measured by osmometry).

Synthesis of PUPA

Synthesis involves two reaction steps: (a) Poly(amido-amine) with terminal free isocyanate groups was obtained by adding a large excess of hexamethylene diisocyanate to the dry and alcohol-free methylene chloride solution of the amino end-capped poly(amido-amine) (N₂LL) under nitrogen for 45 minutes. The quantities of the two components are reported in Table I. (b) A 10% solution of Pellethane 2363-80AE in *N,N*-dimethylformamide (DMF) was added to the methylene chloride solution of the isocyanate-terminated poly(amido-amine) with vigorous stirring. The quantities are reported in Table I. The mixture was kept at 60°C under nitrogen with vigorous stirring for a given time (see Table I). The material forms upon evaporation of the solvent under vacuum (400 mbar) at 70°C. PUPA films were extracted in Soxhlet with CH₃OH/H₂O (6/1, v/v) solution until no further weight loss was detectable, and then vacuum dried at 70°C for 1 day.

The films so obtained were used for the scanning electron microscopy (SEM), wide-angle x-ray scat-

tering (WAXS), thermal analysis (TA), dynamic mechanical thermal analysis (DMTA), and attenuated total reflection Fourier transform infrared (ATR/FTIR).

In this work four PUPA films have been synthesized (see Table I) changing the ratio of the N₂LL and HMDI and the reaction time. The PUPA A film reflects the material generally utilized for biological tests because the quantity of (tightly bound) heparin is the highest. The percentage of HMDI and N₂LL with respect to PU was changed in PUPA B and C in order to study the influence of the composition on structure and properties of the films. The sample PUPA D containing the same composition as PUPA A, was obtained by increasing the usual reaction time of the second step to investigate the influence of the reaction time.

Synthesis of Crosslinked PU

The material with PU chains interlinked via HMDI was prepared by adding 10 g of a 10% solution of PU in *N,N*-dimethylformamide to 10 mL of dry and alcohol-free methylene chloride solution containing 0.21 mL of HMDI under a nitrogen stream with vigorous stirring. The mixture was kept under vacuum (400 mbar) with vigorous stirring at 60°C for 2 h. The film of this material was then obtained by casting the mixture on a glass plate and evaporating the solvent under vacuum at 70°C. The film was extracted in Soxhlet with a CH₃OH/H₂O (6/1 v/v) solution and then vacuum dried at 70°C for 1 day.

SEM Analysis

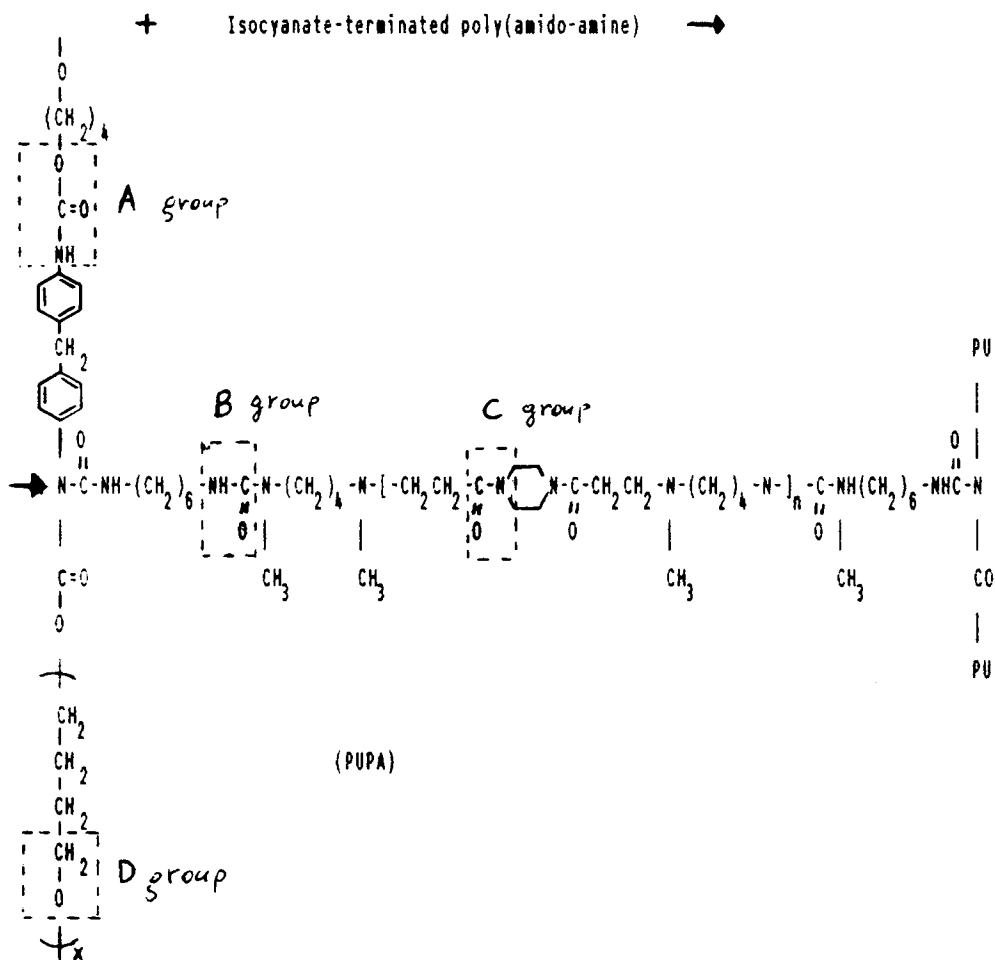
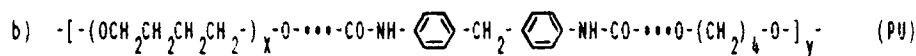
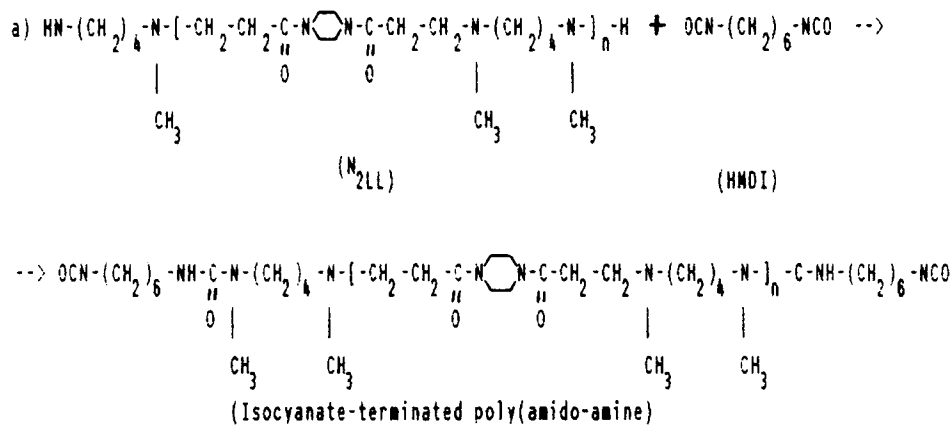
The surfaces of the PUPA samples were analyzed after coating by Au-Pd evaporation and examined by using a Philips 505 scanning electron microscope at 30 kV.

WAXS Measurements

Wide-angle x-ray scattering (WAXS) measurements were carried out with a Philips (PW 1050) model. WAXS patterns were collected by a flat camera with sample film distance = 50 mm.

Thermal Analysis

The thermal behaviors of PU and PUPA samples were investigated by a Mettler DSC-30. Two sets of experiments were performed, defined here as first run and second run. The first run experiment, carried out to characterize the thermal properties of



Scheme 1

Table I Chemical Characterization of PUPA Samples

Sample	Chemical Composition of the Starting Mixture					Reaction Time of the Second Step (h)	Titrated Nitrogens ($\mu\text{mol}/\text{cm}^2$)
	PU (g)	(ml)	HMDI ($\text{mol} \times 10^3$)	(g)	N_2LL ($\text{mol} \times 10^5$)		
PUPA A	1.0	0.210	1.3	0.4	2.9	2	2.2 ± 0.2
PUPA B	1.0	0.105	0.66	0.2	1.4	2	—
PUPA C	1.0	0.280	1.7	0.53	3.8	2	1.8 ± 0.2
PUPA D	1.0	0.210	1.3	0.4	2.9	3	2.8 ± 0.2

the cast films, consisted in heating the sample (about 15 mg) from -100 to 300°C at a heating rate (HR) of $20^\circ\text{C}/\text{min}$. The second run experiment was carried out in order to investigate the influence of the heating on the microphase separation of PUPA and consisted in heating the sample from -100 to 200°C at HR $20^\circ\text{C}/\text{min}$, then cooling to -100°C (cooling rate $50^\circ\text{C}/\text{min}$) and finally the heat involved during the scan from -100 to 200°C (at HR $20^\circ\text{C}/\text{min}$) was registered and reported here.

Dynamic Mechanical Test

Dynamic mechanical data were collected at 1 Hz at $4^\circ\text{C}/\text{min}$ heating rate from -100 up to 150°C under a N_2 purge with DMTA-Polymer Laboratories configured for automatic data acquisition. The glass transition temperature (T_g) was measured at the maximum of the loss modulus peak.

ATR/FTIR Spectra

Attenuated total reflection Fourier transform infrared (ATR/FTIR) spectra of the sample were recorded on a Perkin-Elmer FTIR spectrometer M1800 between 4000 and 750 cm^{-1} . A MCT detector was used and the apparatus was purged with nitrogen. Typically 300 scans at a resolution of 2.0 cm^{-1} were averaged and the spectra were stored on a magnetic disc. The frequency scale was internally calibrated with a reference helium-neon laser to an accuracy of 0.01 cm^{-1} . A KRS-5 crystal at an angle of 45° was used as the internal reflection element. In order to improve the observability of the overlapping bands mathematical resolution enhancement was performed by a spectral deconvolution process which is like the Fourier self-deconvolution⁶ except that the mathematical operations are performed in the spectral domain rather than in the Fourier domain.⁷

Titration of the Nitrogen Atoms

The determination of the basic nitrogens of N_2LL in PUPA was performed by dipping samples of known surface area in 10 mL of 1 M HCl for 1 h. Samples then were washed with water and dried under vacuum for 12 h. The samples were treated with 10 mL of 0.1 M NaOH for 1 h. Chloride ions in the solution were finally determined by titrating with $5 \times 10^{-3}\text{ M}$ mercury nitrate solution previously standardized against KCl.⁸

RESULTS AND DISCUSSION

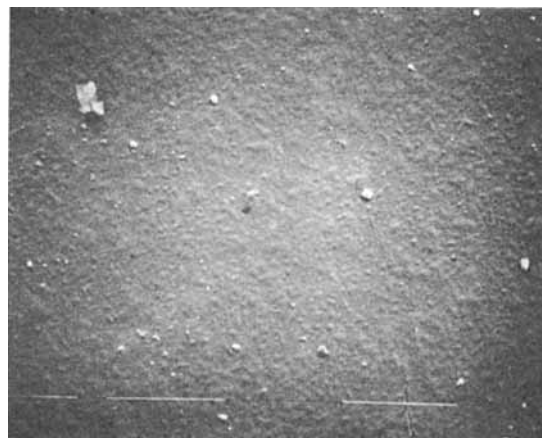
Morphology and Structure

The microscopic analysis of the film surfaces of the samples shows that the morphology depends on composition and reaction time (Fig. 1). Looking along the series from PU to PUPA C, the surfaces of the films become smoother. However, the surfaces of the samples PUPA B and C are not homogeneous. In fact for the PUPA B the surface is generally smoother than those of PU and PUPA A, but there are present also regions with higher roughness (ca. 5% of total surface). In the PUPA C sample there are also holes present (ca. 25 holes/ mm^2) probably due to the rapid evaporation of some volatile material still present in the sample. The effect of increasing the reaction time (compare PUPA A and D) results in a smoother surface for PUPA D but characterized by a wave-like type morphology.

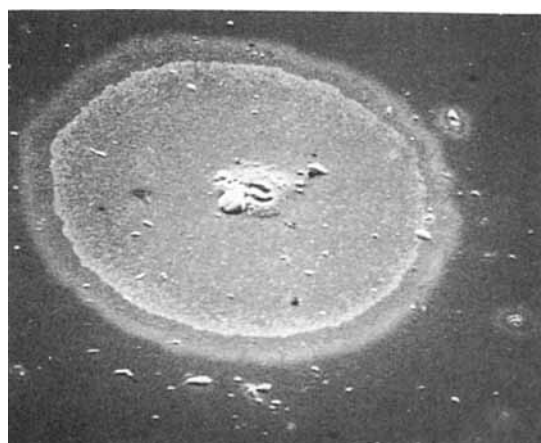
The wide angle x-ray patterns of PU, N_2LL , and PUPA films are shown in Figure 2. The patterns indicate that PU and all the PUPA films are amorphous whereas the N_2LL is semicrystalline. These results indicate that the N_2LL is not able to crystallize during the synthesis process of PUPA.



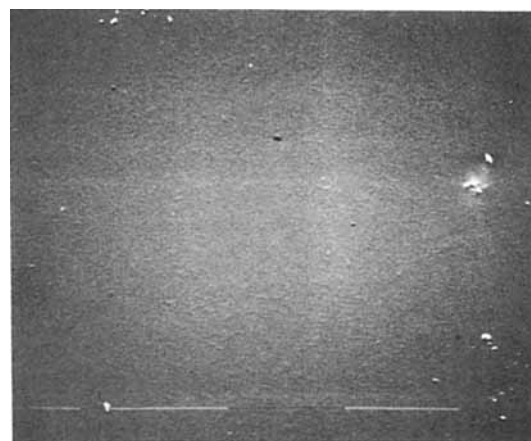
PU



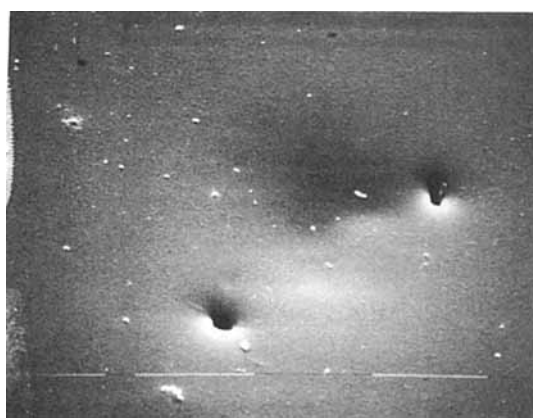
PUPA A



PUPA B



PUPA B



PUPA C



PUPA D

10 μ m
|-----|

Figure 1 SEM micrographs of PUPA film's surfaces.

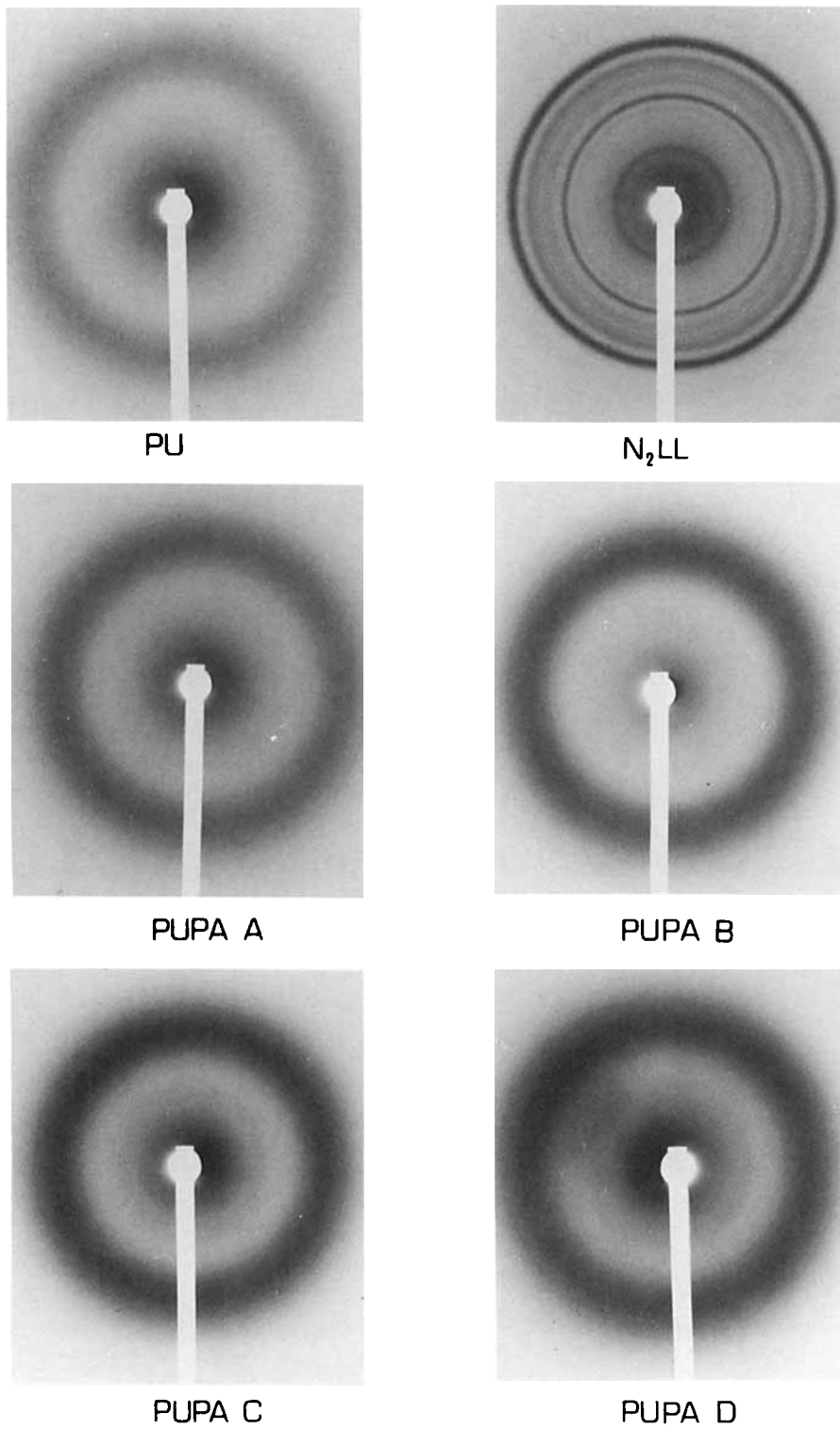


Figure 2 X-ray patterns of PUPA films.

Thermal Properties

Differential scanning calorimetry (DSC) thermograms relative to the first run scanning of PU and PUPA samples are shown in Figure 3. The thermograms present the same value of T_g , $-42 \pm 2^\circ\text{C}$, for the PU and PUPA films, independent of composition. Also present on the thermograms in the temperature range $80\text{--}150^\circ\text{C}$, are endotherm peaks that can be ascribed to the dissolution of short-range order of hard segments as proposed by Seymour and Cooper.⁹ The presence and the positions of these endotherm peaks seem to be a function of the composition.

For the PU and PUPA samples the endotherm peak relative to the well-ordered microcrystalline phase of hard segments⁹ is not observed in agreement with the x-ray patterns.

The second run thermogram (Fig. 4) of the PU sample presents a value of T_g at about $-20 \pm 2^\circ\text{C}$ (20 degrees higher than that of the first run) and a small endotherm peak centered at about 150°C . The increase of T_g and the decrease of the short-range order content, could be explained by assuming that the thermal treatment undergone by the PU during the previous heating, and cooling processes, could have produced an increase of the percent of hard segments dissolved in the soft segments phase.¹⁰ This phenomenon, likely for molecules having a discrete mobility in the melt phase and short length of the hard segments, does not seem possible for PUPA A, C, and D samples because of their content

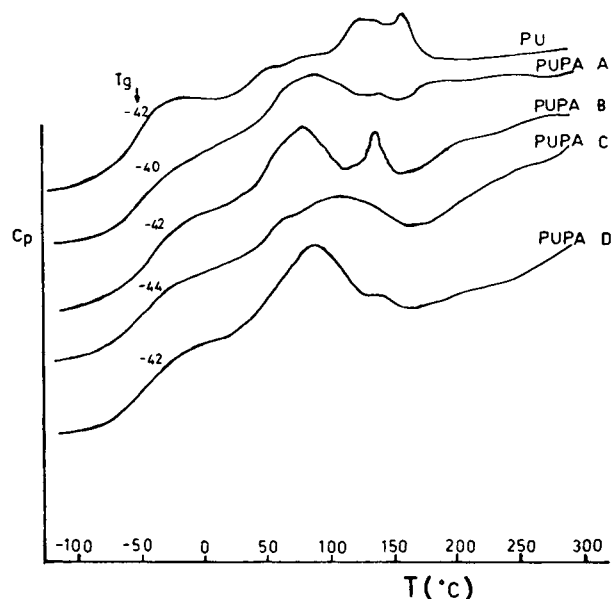


Figure 3 First run DSC thermograms of PUPA films.

of cross-linking agent. In fact, the T_g values of the second run of these PUPA samples are very similar ($-40 \pm 2^\circ\text{C}$) to those observed on the first run thermograms; moreover, no presence of any endotherm peak is detectable. The sample PUPA B, having a content of cross-linking agent lower than the other PUPA samples, presents a T_g value at about -30°C and a small endotherm peak centered at about 150°C . These results indicate that it is still possible for this material to have a certain dissolution of the hard segments in the soft segments phase and some formation of short-range order of hard segments.

Mechanical Dynamic Properties

The storage modulus (E') and loss modulus (E'') of PU and PUPA films are plotted as a function of temperature in Figures 5 and 6 respectively. The PU film presents the lowest value of E' with a glassy plateau of up to -50°C , followed by the drop of E' at the T_g region. Not dissimilar to that of PU is the behavior of E' relative to PUPA B. The curves relative to the films of PUPA A and D display almost identical behavior with values of the E' higher than those of PU and PUPA B. This increase is accounted for by the HMDI and N_2LL content of the PUPA A and D in the two films. The identical behavior of PUPA A and D indicates that the two different reaction times do not induce any difference in their mechanical dynamic properties even if the surface analysis reveals differences in the morphology. Finally, the curve of PUPA C shows that this film has the highest value of the storage modulus at low temperature. This behavior is related to fact that this film has the highest content of HMDI and N_2LL and also the highest degree of crosslinking. Figure 6 shows the presence of only one peak in the E'' curve in the range of temperature investigated. The position of the peak, approximately at -35°C , for all the samples, indicates that the cast PUPA films have the same T_g , in agreement with the DSC results of the first run experiments.

CHEMICAL CHARACTERIZATION OF PUPA SAMPLES

Table I summarizes the chemical composition of the starting mixture, reaction time of the second step, and the quantity of the basic nitrogens titratable on the surfaces. The titration results are affected by the swelling behavior of the material. In fact, the

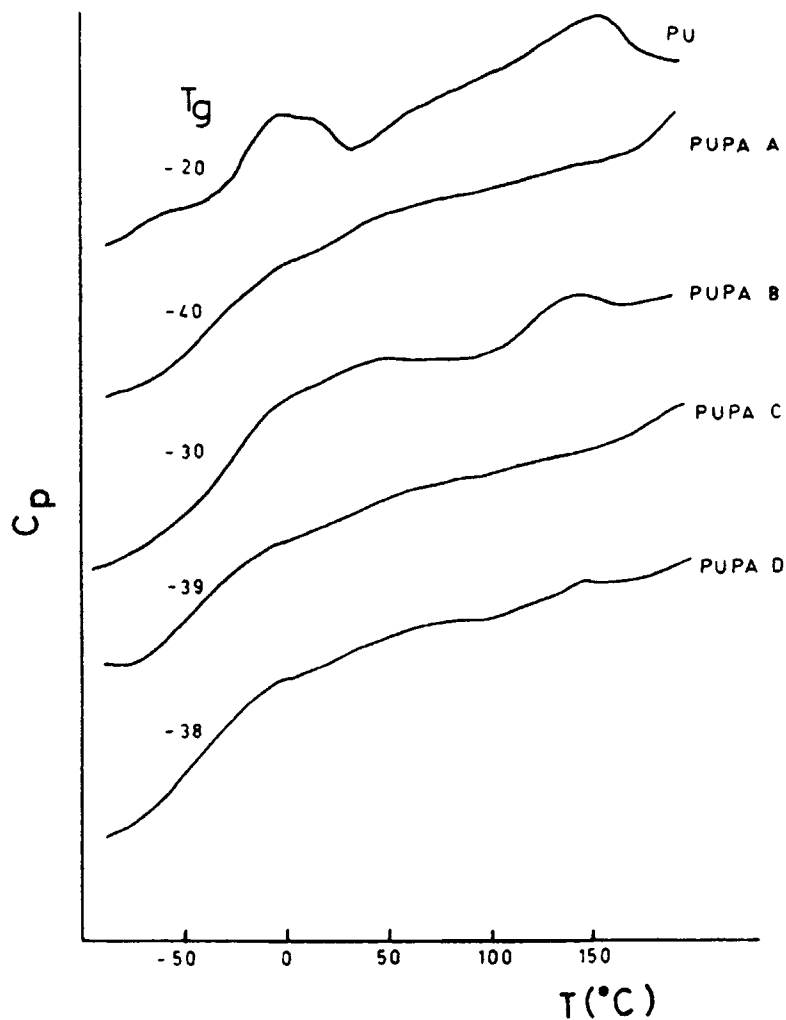


Figure 4 Second run DSC thermograms of PUPA films.

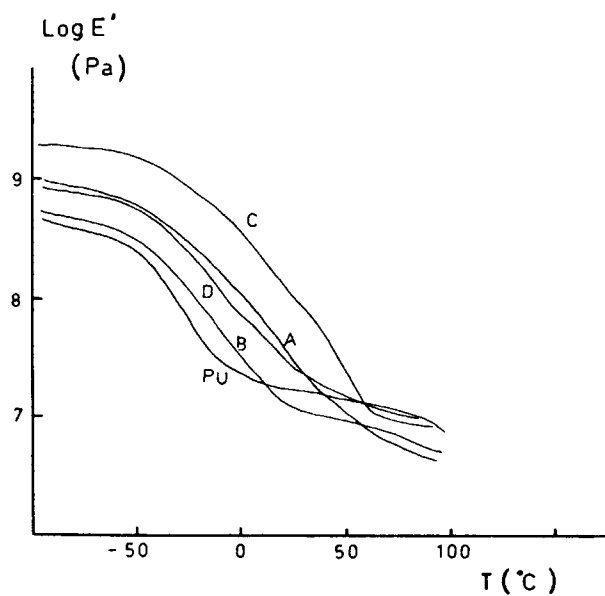


Figure 5 Storage modulus E' of PUPA films.

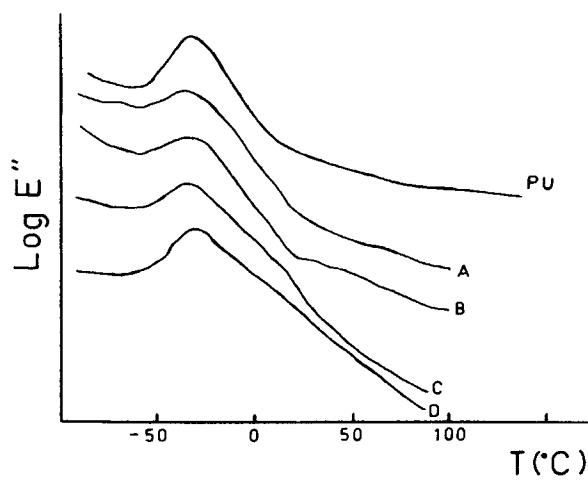


Figure 6 Loss modulus of PUPA films.

films swell in water and even more in acidic solution¹¹ and the degree of swelling is directly correlated to the amount of N₂LL in the sample. Thus, the fact that the sample PUPA B did not reveal any titratable nitrogens does not mean that they are not present in the material. Since the HMDI is present in all the samples in large excess with respect to the N₂LL, with which it has to react in the first step, we can suppose that in PUPA material the PU chains are linked not only via the isocyanate-terminated poly(amido-amine), but also by the HMDI bridges. In fact, spectroscopic analysis of a sample of PU containing only HMDI (PU-HMDI) shows that the latter component is crosslinked to the PU chains.

ATR/FTIR MEASUREMENTS

Attenuated total reflection Fourier transform infrared (ATR/FTIR) spectra of the four PUPA samples are shown in Figure 7. Listed in Table II are the main observed frequencies together with their tentative assignments. The major differences

are shown in the 1750–1550 cm⁻¹ wave number range.

In the forthcoming discussion we analyze separately the spectral regions associated with the different groups involved in hydrogen-bonding interaction labelled in Scheme 1.

N—H Stretching [A]

Figure 8(a) shows the 3800–3000 cm⁻¹ region of PUPA samples together with that of PU-HMDI.

A single more or less symmetric band is observed near 3320 cm⁻¹ corresponding to the hydrogen-bonded N—H stretching vibration.¹² A free (not hydrogen-bonded) N—H stretching band absorbing near 3500 cm⁻¹ is present only as a shoulder in all PUPA samples. This means that in PUPA material all the N—H are largely involved in hydrogen bonds as occurs in polyurethane.¹³

Urethane C=O Stretching [A]

The urethane C=O wavenumber range of PUPA samples is shown in Figure 8(b) together with those

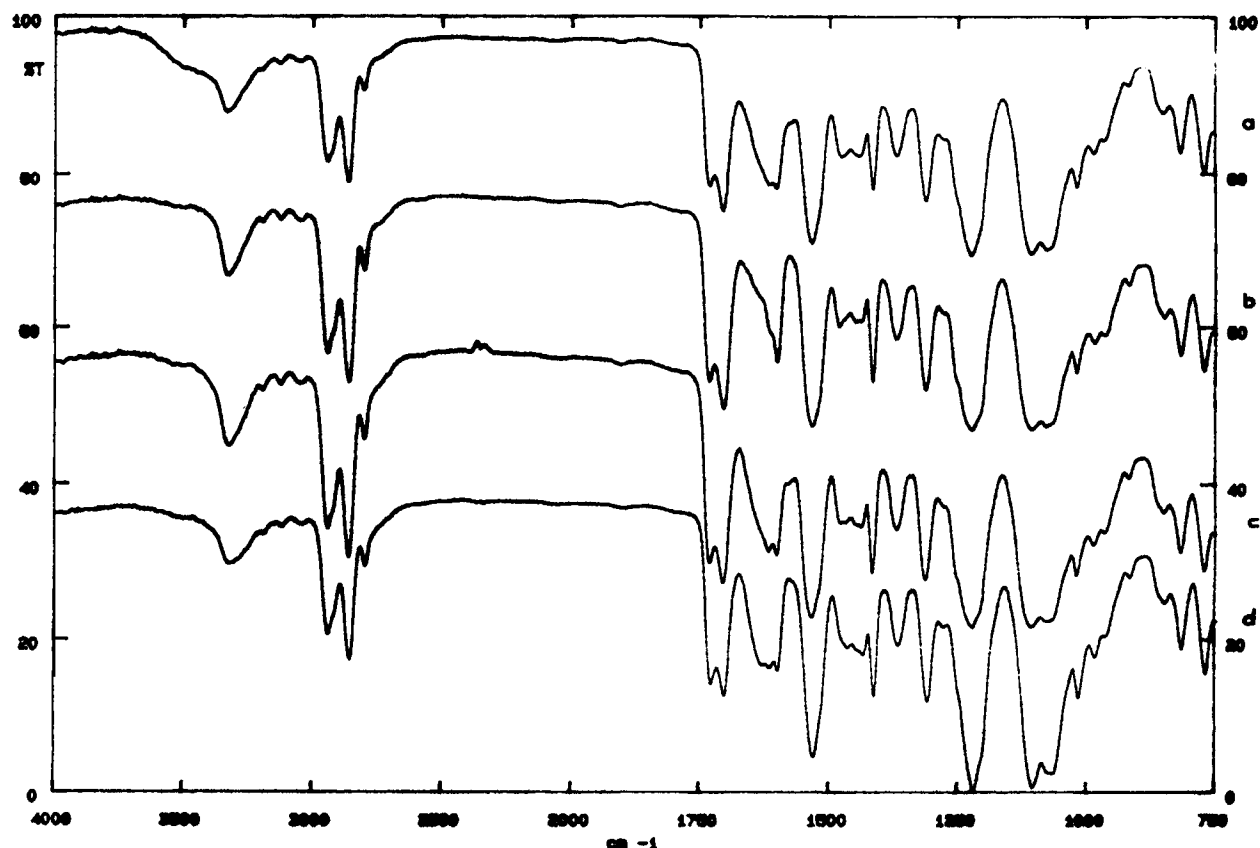


Figure 7 ATR/FTIR spectra of: (a) PUPA A; (b) PUPA B; (c) PUPA C; (d) PUPA D samples.

Table II Main Frequencies Observed in the Spectra of PUPA and Tentative of Assignment

Frequency (cm^{-1})	Tentative Assignment
3485 sh	N—H stretching (free)
3326 m	N—H stretching (H-bonded)
2941 s	CH_2 stretching (asym.)
2857 s	CH_2 stretching (sym.)
1730 s	Urethane C=O stretching (free)
1703 s	Urethane C=O stretching (H bonded)
1647 sh	Amide C=O stretching (free)
1631 m	Amide C=O stretching (H bonded)
1615 m	Urea C=O + benzene C=C stretching
1597 m	Benzene C=C stretching
1450 m	CH_2 bending
1413 m	Benzene C=C stretching
1107 vs	C—O—C stretching
1076, 1062 s, m	C—O—C + O=C—O stretching

of PU and PU-HMDI. The peak height of H-bonded urethane C=O stretching at 1703 cm^{-1} normalized to that of C=C stretching of benzene at 1412 cm^{-1} decreases as follows:¹⁴

$$\text{PU} = \text{PUPA B} > (\text{PU-HMDI}) > \text{PUPA A} \\ = \text{PUPA C} > \text{PUPA D}$$

suggesting the hypothesis that the formation of some hydrogen bonds between the urethane N—H and C=O groups is hindered by the presence of poly(amido-amine) and hexamethylenediisocyanate components in the polymer matrix (see also Urea and Amide Carbonyl Stretching Region). This is because the urea [B] and amide [C] C=O groups compete with the urethane [A] C=O group to form a primary interaction with the N—H group. The trend observed can be well correlated to the chemical composition of the sample starting mixture (see Table I) except for PUPA C, which contains the highest amounts of N_2LL and HMDI.

Ether Oxygen Stretching [D]

Investigation of the ether region ($1300\text{--}1000\text{ cm}^{-1}$) [Fig. 8(c)] gave no useful information on the hydrogen-bonding interaction involving the ether group because of the complexities introduced by the presence of the amide III bands.¹⁴

Upon introduction of N_2LL and HMDI we can observe a decrease of the band intensity only at 1076

and 1062 cm^{-1} (which are composite bands containing also the contribute of urethane and urea moieties) with respect to that at 1107 cm^{-1} due to the C—O—C stretching.

Urea [B] and Amide [C] Carbonyl Stretching

Figure 8(d) shows the $1700\text{--}1550\text{ cm}^{-1}$ wavenumber range for the four PUPA samples together with those of PU, PU-HMDI.

In the spectrum of polyurethane the two bands at 1615 and 1597 cm^{-1} are due to the C—C stretching of benzene.

Poly(amido-amine) by itself shows a strong band at about 1650 cm^{-1} due to the stretching of amide C=O group.²

In the spectrum of polyurethane as well as in those of PUPA, the increase in band intensity at

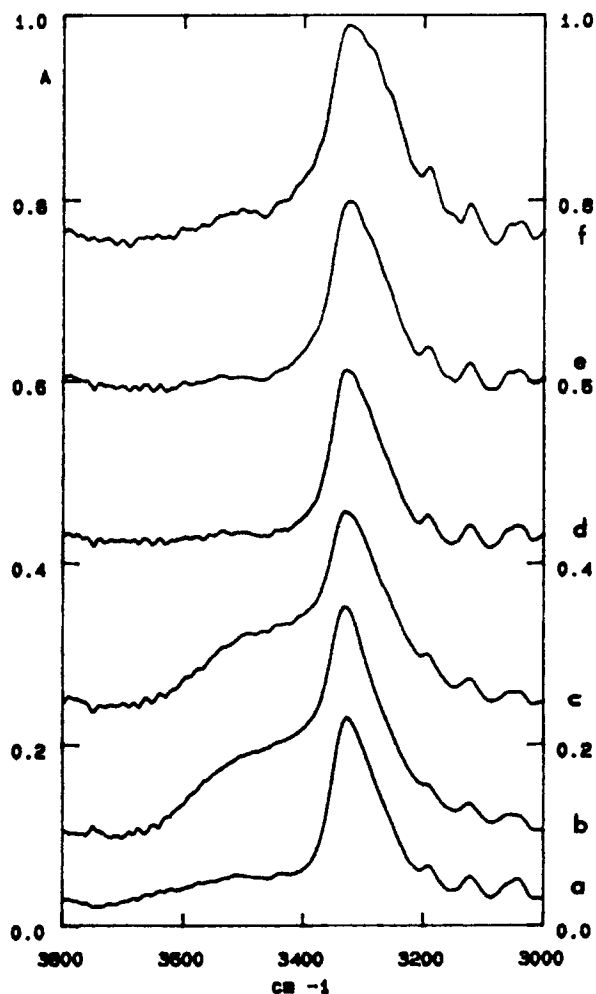


Figure 8(a) N—H stretching region of (a) PU; (b) PU-HMDI; (c) PUPA A; (d) PUPA B; (e) PUPA C; (f) PUPA D samples.

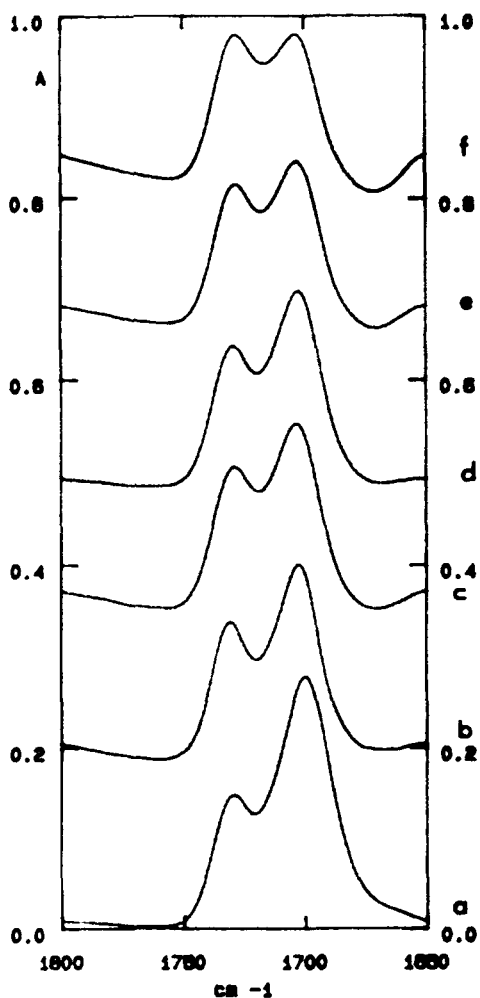


Figure 8(b) Urethane C=O stretching region [A] of (a) PU; (b) PU-HMDI; (c) PUPA A; (d) PUPA B; (e) PUPA C; (f) PUPA D samples.

1615 cm^{-1} can be ascribed to the presence of urea groups, since the urea [B] C=O stretching absorption falls at the same frequency of benzene C=C stretching. Spectra of PUPA samples show two shoulders at about 1647 and 1631 cm^{-1} ; the latter can be attributed to the amide C=O group hydrogen bonded to the N—H group.

Both band heights at 1647 and 1631 cm^{-1} normalized to that of C—C stretching of benzene at 1597 cm^{-1} (see Table III) decrease passing from PUPA D to PUPA B as follows:

$$\text{PUPA D} > \text{PUPA A} = \text{PUPA C} > \text{PUPA B}$$

This is in accordance with the amount of titrated aminic nitrogens found on the different PUPA samples (see Table I) and the trend observed for the normalized peak heights of the H-bonded urethane C=O stretching bands in the different PUPAs.

CONCLUSION

We have studied the effects of the chemical composition and reaction time on the morphology and physical properties of a new biomedical polymer capable of complexing heparin.

Experiments using DSC indicate that the PU and PUPA samples are amorphous and exhibit the same values of T_g at ca. $-42 \pm 2^\circ\text{C}$ independent of composition. Thermal treatment reveals that the PUPA films have very low mobility in the melt phase compared with the pure PU, this is because the cross-linked structure of the PUPA hinders the dissolution of hard segments in the soft segments phase. However, the phenomenon of the dissolution of hard segments in the soft segments phase occur in the plain PU.

Infrared data show that HMDI molecules cross-link with PU chains hindering some hydrogen bonds that normally occur in polyurethanes.

Due to the large excess of HMDI with respect to N_2LL in PUPA materials (see Table I) we can as-

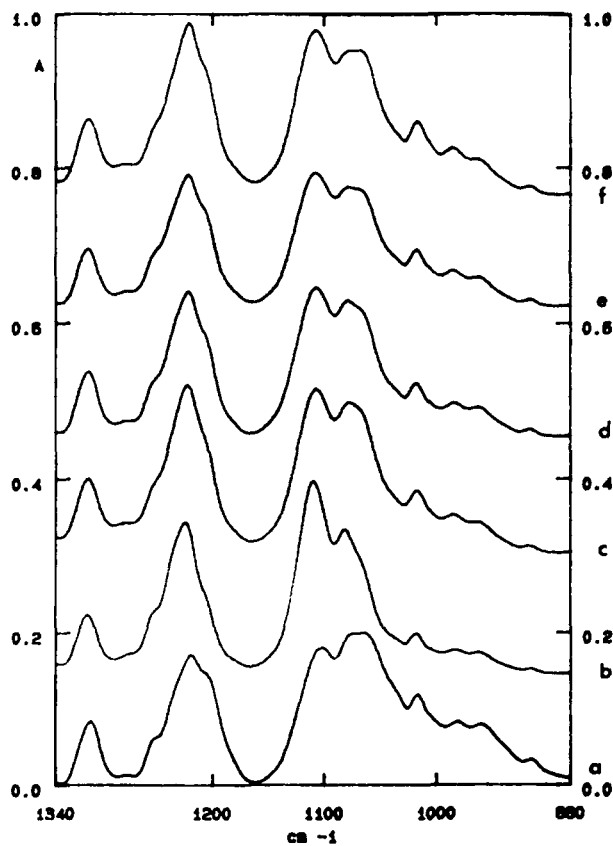


Figure 8(c) Ether oxygen stretching region [D] of: (a) PU; (b) PU-HMDI; (c) PUPA A; (d) PUPA B; (e) PUPA C; (f) PUPA D samples.

Table III Normalized Peak Height^a for Urethane [A] and Amide [C] C=O Stretching

Sample	Urethane C=O (free) 1730 ± 0.002 cm ⁻¹	Urethane C=O (H-bonded) 1703 ± 0.002 cm ⁻¹	Amide C=O (free) 1647 ± 0.002 cm ⁻¹	Amide C=O (H-bonded) 1631 ± 0.002 cm ⁻¹	Amide C=O (H-bonded)/ Amide C=O (free)
PU	1.00	1.55	—	—	—
PUPA A	1.00	1.20	0.40	0.50	1.25
PUPA B	1.00	1.50	0.20	0.25	1.25
PUPA C	1.00	1.20	0.40	0.50	1.25
PUPA D	1.00	1.10	0.45	0.70	1.60
PU-HMDI	1.00	1.42	—	—	—

^a The normalization is performed by rationing the peak of urethane [A] and amide [C] C=O stretching to those of benzene C—C stretching at 1412 and 1597 cm⁻¹, respectively, then the absorbance of free urethane C=O is normalized to 1.00.

sume that several HMDI bridges are formed among PU chains and the N₂LL chains accommodate in an already crosslinked structure.

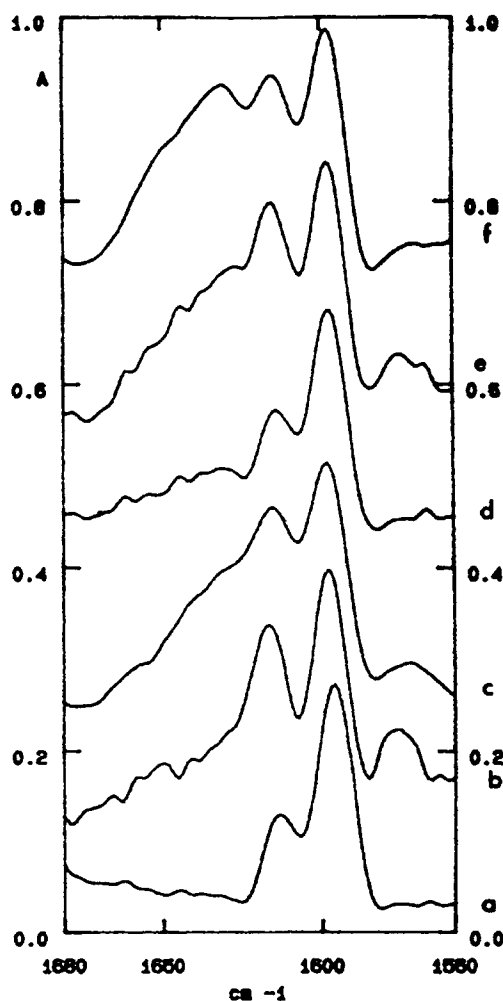


Figure 8(d) Urea [B] and Amide [C] C=O stretching region of (a) PU; (b) PU-HMDI; (c) PUPA A; (d) PUPA B; (e) PUPA C; (f) PUPA D samples.

The disposition of these chains within the cross-linked matrix is such that other hydrogen bonds are formed between the basic polymer and polyurethane. The increase of the amount of N₂LL in the sample is reflected by an increase of both H-bonded and free amide C=O bands intensity of N₂LL, whereas the ratio between them remains unchanged (Samples A, B, C,). This means that the number of H bonds that the N₂LL forms with PU chains is independent of composition. In other words, all N₂LL chains seem to assume the same orientation with respect to those of PU in the network.

The increase in the reaction time between polyurethane and the prepolymer (Sample D) may lead to a different network which allows the N₂LL chains to form a greater number of hydrogen bonds with polyurethane. This is reflected in an increased ratio between the “H-bonded” and “free” amide C=O bands intensity of N₂LL.

Finally, the morphology analysis found that the surfaces become smoother with increasing content of HMDI and N₂LL.

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