

The Influence of Pressure on Acid Polyurethane Structure

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Acid polyurethane of hard type was prepared to be further treated in hydrothermal conditions at high pressures of 20, 40, 60 and 80 atm. The influence of pressure on chemical structure and morphology of macromolecular chains have been investigated using Fourier transform Infrared Spectroscopy (FT-IR) and Differential Scanning Calorimetry (DSC). Three endothermic peaks appear in hydrothermally treated polyurethanes, being related to conformational changes due to polymer shrinking, decomposition and melting. Their corresponding enthalpies increase with pressure, probably due to a more compact polymer structure at high pressure. Under the influence of pressure, macromolecular chains modify their conformation and approach each other, leading to an increased density of the hydrogen bonds. Stretching vibrations of the –C=O group are shifted from 1746 to 1724 cm⁻¹. There is an optimum pressure (60-80 atm) range where the polyurethane presents an increased capacity of interaction through carbonyl groups ($r_1 = 1.295$ at 60 atm) which is favorable for further composite synthesis.

Keywords: acid polyurethane, high pressure, hydrothermal process, IR spectroscopy, DSC

Every year, millions of people are suffering from bone defects arising from osteoporotic fractures, osteoarthritis or other bone related diseases [1 – 3]. These defects are conventionally treated by the replacement with bone allografts or autografts and synthetic bone filling materials [4]. The search for strong artificial implants for hip or knee replacement has led to the use of organic/ inorganic composites that would combine the flexibility, toughness and bioresorbability of a polymer with the stiffness, strength and osteoconductivity of a ceramic. Perhaps the most commonly studied composites are hydroxyapatite (HAp) based materials, specially designed to have similar structure and composition with bone. Therefore, nano-hydroxyapatite (n-HAp) filled polymer composites are developed for bone repair or substitute [5].

Several studies have investigated the synthesis and characterization of hybrid HAp/polymer materials and in particular analyzed the effect of the mineral content and the processing route on the mechanical strength and toughness [6 – 12].

In recent years, composite materials with high content of HAp nanoparticles intended for biomedical applications, such as polyamides/HAp [13], poly(methyl methacrylate)/HAp [14 – 16], polylactides/HAp [9, 17, 18] and polyethylene/HAp [19 – 21] have been intensively explored. However, the incorporation of a big amount of inorganic nanoparticles into a polymer matrix would lead to aggregation of the filler particles and porosity which fails the mechanical properties of the composites seriously. Thus, for preparing a polymer composite material filled with HAp nanoparticles, the major problem faced is the dispersion and achieving strong interfacial combination between the filler nanoparticles and the matrix [22].

HAp/polylactide composites lose their strength rapidly in physiological environment and fail at the interface. Two reasons were taken into account for these interfacial failures: one is lack of effective adhesion between ceramic phase and polymer matrix and the other is self-catalytic degradation of hydroxyl groups on HAp surfaces. For solving the problem, a chemical reaction was used to produce HAp crystal on the polymer surface [23, 24]. This reaction

is similar to the biomimetic calcification which lasted for more than one week and then makes negative effect on the polymers. Biomimetic growth of calcium phosphate compounds on porous polyurethane (PU) treated with tetraethoxysilane (TEOS) and soaked in simulated body fluid (SBF) solution have been reported in 2003 [25]. The structure of HAp/(PUs) is similar to HAp/polylactide which may result in the same interface separation. But in contrast to the majority of materials made of poly(lactic acid) and poly(glycolic acid), polyurethanes can have greater elasticity. This is given by the variety of chemistry and molecular weights of the various compounds, as well as the molar ratios used in the polyurethane synthesis [26 – 28]. Moreover, PUs have proven to be biocompatible reason for that they are widely used in medical devices, e.g. heart valves, total heart diaphragms, artificial skin, bone graft and cartilage substitute [26, 29- 31]. Thus, a porous composite scaffold containing 30 wt % nanohydroxyapatite and 70 wt % polyurethane has been prepared from castor oil by a foaming method, and the biological evaluation of this material showed that the scaffold has good cytocompatibility in vitro and good biocompatibility in vivo. Also, the compressive strength degradation property is suitable for the cartilage repair [5]. Recently (2009), hydroxyapatite nanoparticles/ polyester urethane (PUR) composite scaffolds were obtained using a salt-leaching-phase-inverse process [26]. Five different ceramic filler contents of nHAp weight fractions were added (5, 10, 20, 30 and 50 wt % of the polyurethane) and the mixing times of the PUR solution with nHAp were set at 1, 3 and 7 days. Increasing the amount of nHAp particles in the composite scaffold decreased the porosity, while the Young's modulus scaffold was improved by 50% addition of 10 wt % nHA. Moreover, the process permitted the inclusion of nHAp particles not only in the PUR matrix but also at the scaffold pore surface, suggesting that the nHAp/PUR composite scaffolds could present osteoconductive properties suitable for bone tissue engineering. On the other hand, biostable PU/HAp composites with potential applications as bone replacement materials were synthesized in bulk and processed in a single screw extruder. Such composites

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with 30, 50 or 70 wt % of sintered commercial HAp powder were manufactured using polyurethanes with various content of hard segment [30]. In this case, a lubricating effect was found for composites containing 50 wt % of filler, whereas at higher filler contents, a solid like behaviour was evidenced.

To the authors knowledge, there are no reports in the literature concerning the synthesis of PU/HAp composites using hydrothermal process in high pressure conditions. We have previously investigated this route for the preparation of various nanostructured hybrids based on hydroxyapatite / collagen (HAp-COL) [32], hydroxyapatite / maleic acid copolymers [33, 34] and hydroxyapatite – purified montmorillonite – phosphorilated polysaccharide [35].

In order to obtain PU/HAp composites with ideal properties for a specific medical application, structure–morphology–biocompatibility relationships are needed. In this context, the present study is focused on the influence of pressure on the structure and morphology of the acid polyurethane after hydrothermal treatment, using Fourier transform Infrared Spectroscopy (FT-IR) and Differential Scanning Calorimetry (DSC). The evolution of the main absorption bands from hydrothermally treated PUs relative to initial polymer is studied based on peak area ratio of carbonyl group to C-H group and amide II group to C-H group. Thermal behavior of the acid polyurethane at high pressure is investigated because possible conformational changes or sterical rearrangements may appear due to hydrothermal process and will favor further chemical or physical interactions with hydroxyapatite. A pressure range where polyurethane has the most favorable conformation for hydroxyapatite bonding is selected and will be further used for the synthesis of PU/HAp composites with potential medical applications.

Experimental part

The following reactants were used: 5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethyl-cyclohexane known as isophorone diisocyanate, tartaric acid and N, N – dimethylacetamide (DMAA) 99.5% p.a, used as solvent.

Polymer synthesis

Acid polyurethane (PU) with a proportion of 100 % of hard segments was synthesized starting from isophorone diisocyanate (IPDI) and tartaric acid (TA), in equimolar amounts, according to scheme given in figure 1.

Hydrothermal treatment

Acid polyurethane prepared as described above was dissolved in DMAA ($c = 5\%$) and diluted in water

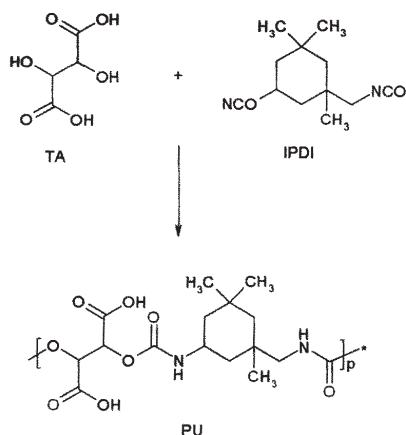


Fig.1. Reaction scheme for the synthesis of acid polyurethanes with 100% hard segments

Table 1
HYDROTHERMALLY TREATED PU SAMPLES

No. crt.	Sample	Applied pressure
1	PU20	20 atm
2	PU40	40 atm
3	PU60	60 atm
4	PU80	80 atm

(DMAA:H₂O = 1: 4). The solution was magnetically stirred and then put into autoclave vessel for 2h of hydrothermal treatment at 120°C and various high pressures (as presented in table 1). Acid polyurethane was dried by lyophilization in a freeze drier and further characterized using Fourier Transform infrared spectroscopy (FT-IR) and differential scanning calorimetry (DSC).

Characterization methods followed to reveal conformational and/or morphological changes that occur in polyurethanes after the hydrothermal treatment at high pressures.

Fourier transform infrared (FT-IR) spectroscopy

Infrared spectra of the PUs were collected with a Fourier transform infrared spectrophotometer (ABB MB 3000). Measurements were carried out using the PIKE Technologies EasiDiff diffuse reflectance accessory. Each sample was scanned 64 times at a resolution of 4 cm⁻¹ over the frequency range 4000 – 550 cm⁻¹.

Differential scanning calorimetry analysis (DSC)

DSC measurements were performed with a Netzsch DSC 200 F3 Maia thermal analyzer. The instrument was calibrated using a sapphire standard. The samples were weighed and encapsulated in aluminium pans. An empty aluminium pan served as the reference. After baseline acquisition, the samples were heated from – 20 to 500 °C at a rate of 10 °C min⁻¹ in Ar atmosphere.

Results and discussion

FT-IR spectroscopy was employed to study the influence of pressure on the chemical structure of the processed polyurethanes following the evolution of the main absorption bands compared with initial polymer (before hydrothermal treatment). IR spectra of both initial and pressure treated polymer are depicted in figure 2.

Assignments of main representative infrared peaks of the figure 2 are shown in table 2.

No significant differences are observed between the analyzed samples, except the absence of symmetric vibration of CH₂ group at 2846 cm⁻¹ in the case of sample PU60 (60 atm). All spectra exhibited characteristic PU

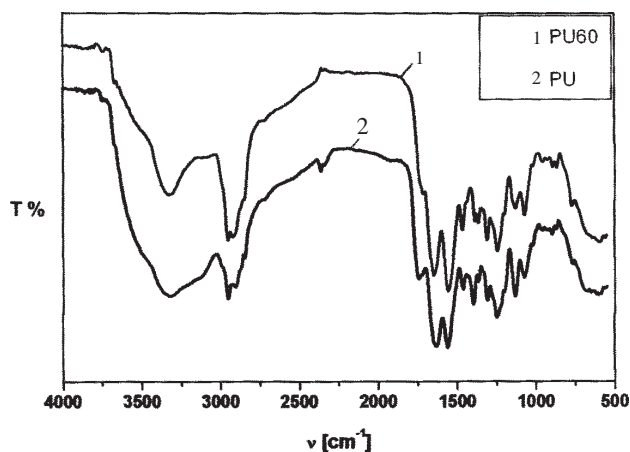


Fig. 2. Typical FT-IR spectra of polyurethane before and after hydrothermal treatment

Table 2
ASSIGNMENTS OF THE MAIN PEAKS IN THE FT-IR SPECTRA OF THE PU'S

PU	PU20	PU40	PU60	PU80	Assignments
ν [cm^{-1}]	ν [cm^{-1}]	ν [cm^{-1}]	ν [cm^{-1}]	ν [cm^{-1}]	
3326	3348	3322	3330	3334	ν N-H
2954	2952	2954	2954	2954	ν CH ₂ , CH ₃
2906	2908	2902	2922	2906	ν CH ₂ <i>as</i>
2846	2844	2846		2846	ν CH ₂ <i>sim</i>
1746	1724	1714	1714	1714	ν (C=O)
1634	1632	1638	1650	1646	ν (C=O) amide I band
1558	1560	1554	1558	1558	δ (N-H) + ν (C-N) amide II band
1462	1464	1466	1462	1462	δ CH ₂ <i>as</i>
1398	1388	1386	1386	1386	δ CH ₂ <i>sim</i>
1366	1364	1362	1366	1366	ω CH ₂ out of plane
1310	1308	1310	1310	1310	ν (C-N) in urethane + ω CH ₂
1246	1244	1242	1242	1246	ω CH ₂ out of plane
1198	1200	1198	1198		ν (C-N) in urethane + ω CH ₂
1130, 1074	1072	1070	1070	1074	ν (CO-O-CH)
1018	1020	1018		1014	ν (C-H)

bonds: N-H stretching vibration at 3320 – 3350 cm^{-1} and CH₂ or CH₃ asymmetric and symmetric stretching vibrations at 2954 – 2844 cm^{-1} . The absorption of amide I (ν (C=O)) and amide II (urethane N-H bending + C-N stretching) bands were located around 1632 – 1650 cm^{-1} and 1554 – 1560 cm^{-1} , respectively. Absorptions at 1462, 1386 and 1366 cm^{-1} evidence several vibration modes of CH₂ groups. An absorption band situated at 1746 cm^{-1} , corresponding to free C = O is present only in the initial polyurethane (fig. 2). Stretching vibrations of the carbonyl group are shifted towards lower frequencies (1724 and 1714 cm^{-1}) for all the hydrothermally treated polyurethanes, irrespective of applied pressure. This could be explained by the creation of numerous intra-molecular and extra-molecular hydrogen bonds which involve the -C=O group. These bonds are established between nitrogen of urethane groups from a macromolecular chain and oxygen of urethane groups from another chain (fig. 3), and are possible due to the urethane linkage (-NH-CO-O-) which has a strong proton donor group (N-H), and carbonyl groups (C=O) acting as proton acceptors [31].

Another possible proton acceptor is the oxy group (-O-) from the urethane group with its free electron pairs. The existence of a single N-H band at 3322-3348 cm^{-1} shows that almost all N-H groups are hydrogen bonded. Also, under the influence of pressure, macromolecular chains modify their conformation and approach each other, leading to an increased density of the hydrogen bonds between polyurethane chains.

The evolution of the main absorption bands from hydrothermally treated PUs relative to initial polymer was studied based on peak area ratio of carbonyl group to C-H group and amide II group to C-H group. The ratios of peak area corresponding to the stretching vibration of group C=O, 1714-1746 cm^{-1} (A_{1714}), and deformation vibration of N-H (A_{1558}) in urethane groups, 1554-1560 cm^{-1} , to peak area corresponding to valence vibrations of C-H in alkyl groups, 2952-2954 cm^{-1} (A_{2954}), calculated from the recorded IR spectra are as follows:

$$r_1 = \frac{A_{1714}}{A_{2954}} \quad r_2 = \frac{A_{1558}}{A_{2954}}$$

The values of the r_1 and r_2 parameters are presented in table 3.

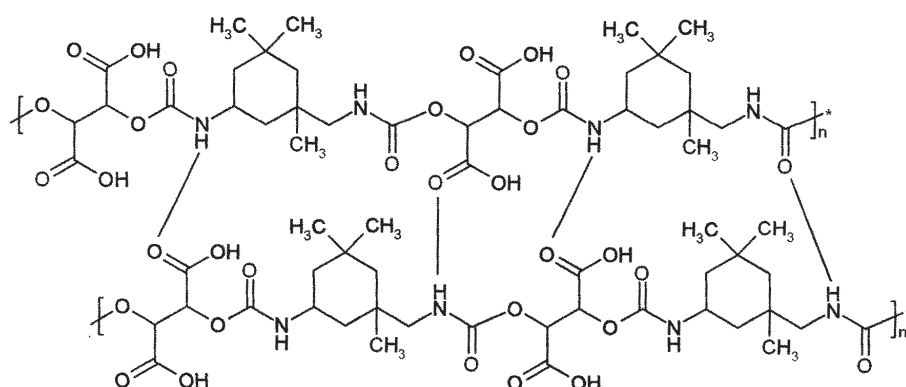


Fig. 3. Hydrogen bonding in the polyurethane chain

Table 3
ANALYSIS OF IR SPECTRA

No. crt.	Sample	A ₁₇₁₄ (relative scale)	A ₁₅₅₈ (relative scale)	A ₂₉₅₄ (relative scale)	r ₁	r ₂
1	PU	1214.18	2984.41	2268.22	0.535	1.316
2	PU20	139.59	1103.68	238.15	0.586	4.634
3	PU40	916.59	3284.65	1043.63	0.878	3.147
4	PU60	1350.71	3508.23	1042.82	1.295	3.364
5	PU80	792.51	2417.13	1711.03	0.463	1.413

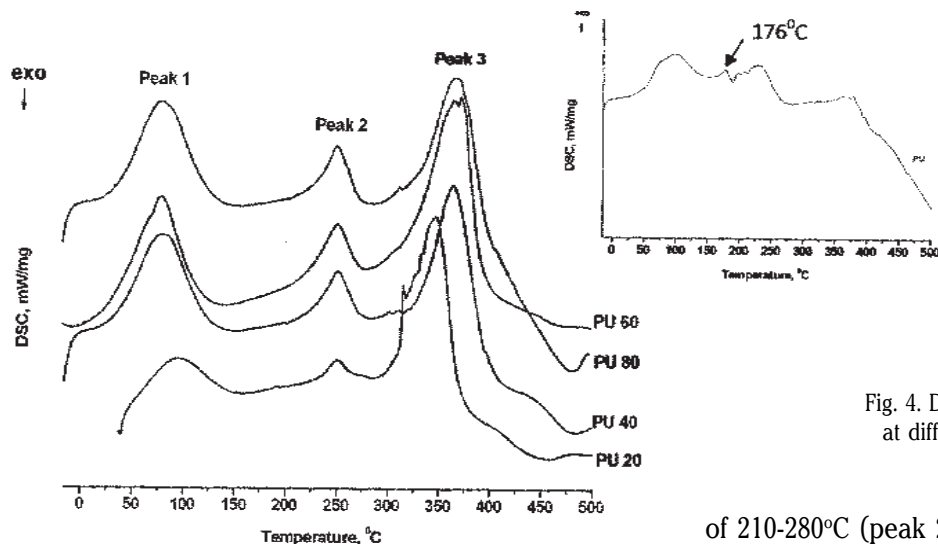


Fig. 4. DSC curves of acid polyurethanes at different high pressure conditions

The values of r_1 and r_2 give us information about the polarity of the chemical structure of the polyurethane chain after high pressure treatment. Therefore, the higher values are due to the important contributions generated of chemical interactions of the polar urethane groups and acid ones from the polyurethane backbone. In table 3 it can be observed that pressure increases the availability of acid polyurethane and implicitly their interaction capacity by the carbonyl groups (r_1 parameter) is improved. Pressure should not be raised above the critical value beyond which density of hydrogen bonds is too high and the interaction capacity is lowered. The values of parameter r_2 vary depending on the number of N-H groups involved in hydrogen bonds between macromolecular chains.

Differential scanning calorimetry analysis (DSC) was used to investigate the morphostructural differences between polyurethanes before and after hydrothermal treatment at different pressures.

DSC thermograms of PUs are shown in figure 4.

A different thermal behaviour between initial polymer (presented in right corner of the figure) and high pressure treated polyurethane could be observed from figure 4. Before hydrothermal process, acid polyurethane presented only one endothermic peak at 95°C, which could be associated with short-range order transitions (disruption of domains) or microstructural/morphological rearrangements. A very small peak at 176°C could be considered as corresponding to the dissociation of domains containing long range order, whereas above 200°C, melting process starts and lies on a wide range of temperature being accompanied by the decomposition of such polymers [36].

Thermogravimetric analysis showed that the polyurethane is relatively stable until 150°C and no mass loss of the water molecules appeared (Thermogram of the initial polymer is annexed).

Three endothermic effects can be observed for hydrothermally treated PUs, namely: one in the range of 50-140°C (peak 1 around 78-79°C); the second in the range

of 210-280°C (peak 2 around 250-251°C), and the third, situated in the range of 320-375°C (peak 3 around 360-371°C).

First endothermic peak of hydrothermally treated samples appears at a lower temperature than the initial polymer. The increase of pressure leads to conformational changes in polymer structure and thus could be a possible explanation for temperature shifting from 95 to 78-79°C. Thermal effect associated with peak 1 ($\Delta H = 1000 - 1600$ kJ/mol) is higher than that corresponding to initial polymer ($\Delta H = 760$ kJ/mol), probably due to the shrinkage of the macromolecular chains after hydrothermal treatment.

According to DSC analysis of different polyurethane structures found in the literature, endothermic peaks 2 and 3 from figure 4 could be assigned to polymer decomposition or melting, which takes place in two steps, starting at 250-251°C and lying on a wide range of temperature [36, 37]. Enthalpies of all three endothermic reactions increase with pressure, probably due to a more compact polymer structure at high pressure. The highest amounts of energies are needed for the polyurethane decomposition or melting at 360-371°C, probably because of the increasing of hydrogen bonds density in the case of PUs treated at high pressure.

Conclusions

Acid polyurethane with 100% content of hard segments was prepared and treated in hydrothermal conditions at pressures varying between 20 - 80 atm. Infrared spectroscopy and DSC analysis revealed the influence of pressure on chemical structure, conformation and morphology. The endothermic peak at 95°C in the initial polymer, which could be probably due to some microstructural/morphological rearrangements or short range order transitions, is shifted to 78-79°C after high pressure treatment, showing the pressure influence on polymer conformation. Density of hydrogen bonds between macromolecular chains increase with pressure and in the same time the hard segmented polyurethane becomes more compact and able to interact with other molecules

through carbonyl groups of the urethane structure (NH-CO-O). The interaction capacity by the carbonyl groups is improved for high pressure treated polymers and the highest value of r_1 parameter is calculated for PU60. The existence of a single N-H band at 3322-3348 cm^{-1} show that almost all N-H groups are hydrogen bonded.

Enthalpies of all three endothermic reactions increase with pressure, probably due to a more compact polymer structure at high pressure. These effects appear especially in the pressure range of 60-80 atm, and it will be considered for future synthesis of hybrid hydroxyapatite – polyurethane nanostructures in hydrothermal conditions.

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