New polyetherurethanes based on cellulose derivative for biomedical applications

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This study present new polyetherurethanes (PEU) based on cellulose derivative, allowing for their application for medical devices. The polyurethane samples were synthesized from polytetramethyleneetherglycol (PTMEG), as macrodiol, 1,6-hexamethylene diisocyanate (HDI), 4,4'-methylene bis(cyclohexyl isocyanate) (HMDI), isophorone diisocyanate (IPDI), as diisocyanate components and hydroxypropyl cellulose (HPC) as chain extender, by the one-shot process without catalyst. The properties of these materials, such as water vapours sorption capacity, contact angles, thermal, mechanical and dielectrical behaviour have been evaluated with respect to their structure. By careful selection of polyurethane composition it is possible to design a range of polymers, which may have great potential in tissue engineering applications.

1. Introduction

The use of polymeric scaffolds in tissue regeneration occurred in the early 1980s, and it continues to play an important role in tissue engineering [1–3]. The function of a degradable scaffold is to act as a temporary support matrix for transplanted or host cells so as to restore, maintain, or improve tissue. Synthetic polyurethane elastomers are extensively utilized as engineering materials in various domains and are well known for their outstanding properties. Recent investigations have developed polyurethane polymers as scaffold materials. They are generally formed by polyaddition reaction of diisocyanates with hydroxyl-terminated polyether or polyester and extended with alcohols and/or amines [4-6]. Segmented polyurethane elastomers have been incorporated in a number of biomedical devices [7] due to their excellent mechanical properties and adequate biocompatibility [8]. Polymeric scaffolds may be used to support a variety of cells for numerous tissues within the body. Most polymeric scaffolds are designed to provide temporary support and, therefore to be biodegradable. Biodegradable materials are of great interest both for environmental reasons and in biomedical applications. The biodegradable properties of polymers can be improved by increasing their hydrophilicity. One way of increasing the hydrophilicity of polyurethanes is the introduction of hydrophilic segments, such as polyethers and/or renewable resources, into the backbone of the polyurethane chains [9-11]. However, the degraded products of the scaffold must have a safe route for removal from the host. Therefore, due to the toxicity of common diisocyanates such as 4,4'-diisocyanate (MDI) and toluene diisocyanate (TDI), other biocompatible aliphatic diisocyanates have been investigated for the development of biodegradable polyurethanes. Hexamethylene diisocyanate (HDI), hydrogenate diphenylmethane diisocyanate (HMDI) and isophorone diisocyanate (IPDI) are the diisocyanates, which are used in this study. Therefore, several important properties must be considered: fabrication, structure, biocompatibility, biodegradability, and mechanical strength. The main advantage for using natural polymers is that they contain bio-functional molecules that aid the attachment, proliferation, and differentiation of cells. However, disadvantages of natural polymers do exist. Polyurethanes that are chemically synthesized offer several notable advantages over natural-origin polymers. A major advantage of synthetic polymers is that they can be tailored to suit specific functions and thus exhibit controllable properties.

2. Experimental

2.1 Materials

The materials used in this research were Terathane 1400 (polytetramethyleneetherglycol - PTMEG - generous gift from INVISTA BV, Nederland), Mw 1374 g/mol, mp 35-40 $^{\circ}$C, water 115 ppm, hydroxyl number 81.7 mgKOH/g; 1,6 – hexamethylene diisocyanate - HDI – Fluka, M_w 168.2, bp 255 $^{\circ}$C, d_4^{20} 1.05, n_D^{20} 1.453; 4,4'-methylene bis(cyclohexyl isocyanate) - HMDI-Aldrich, M_w 262.35, Fp 113 $^{\circ}$C, mp 19-23 $^{\circ}$C, d_4^{20} 1.066; isophorone diisocyanate - IPDI-Fluka, M_w 222.29, bp 153 $^{\circ}$C (lit), d_4^{20} 1.0661; hydroxypropyl cellulose - HPC-Aldrich, average M_w ~80,000, average M_n ~10,000, powder, 20 mesh particle size (99% through). PTMEG and

chain extender were tested for the moisture content and, in some cases, dried under vacuum until content of water of less than 0.03% was reached. All diisocyanates were used as received, without further purification.

2.2 Measurements

Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/SDTA851e thermogravimetric analyzer under a flow of nitrogen (20mL/min) with a heating rate of 10 °C/min from room temperature to 700 °C and 3-5 mg of sample mass. The operational parameters were kept constant to all probes for obtainment of comparable data.

A Perkin-Elmer DSC-7 was used for thermal analysis and was operated under a nitrogen atmosphere with a heating rate of 10 °C/min and the temperature range was -100…+40 °C.

Stress–strain measurements were performed on dumbbell- shaped cut from thin films on a TIRA test 2161 apparatus, Maschinenbau GmbH Ravenstein, Germany. Measurements were run at an extension rate of 50 mm/min, at room temperature, 25 °C. All samples were measured three times and the averages were obtained.

Shore hardness was measured with calibrated Shore A Instron Durometer instruments, on a stack of compression moulded sheet at least 10mm thick on a flat surface and taking the average of three measurements. Ambient temperature was 25 °C.

Contact angles were measured by the static drop technique at room temperature, using a KSV CAM 101 goniometer, equipped with a special optical system and a CCD camera connected to a computer to capture and analyze the contact angle (five measurements for each surface). A drop of liquid (~1 μl) was placed on a specially prepared plate of substratum and the image was immediately sent via the CCD camera to the computer for analysis. The angle formed between the liquid/solid interface and the liquid/vapour interface is the contact angle. Temperature and moisture were constant during the experiment (23°C and 68 % respectively).

Water vapours sorption capacity of the samples has been measured in dynamic regime by using an IGAsorp apparatus (a fully automated gravimetric analyzer,

supplied by Hiden Analytical, Warrington - UK). This apparatus is used to study water sorption at atmospheric pressure by passing a humidified stream of gas over the sample, and can be applied to a wide range of studies from fundamental research to routine quality assurance/control. The IGAsorp is a standard sorption equipment, which has a sensitive microbalance (resolution 1μg and capacity 200 mg), which continuously registers the weight of the sample together with the temperature and relative humidity around the sample. Isothermal studies can be performed as a function of humidity (0-95%) in the temperature range 5°C to 85°C, with an accuracy of ± 1% for 0 - 90% RH and ± 2% for 90 - 95%RH. The relative humidity (RH) is controlled by wet and dry nitrogen flows around the sample. The RH is held constant until equilibrium or until a given time is exceeded, before changing the RH to the next level.

Dielectric spectroscopy was performed using the Novocontrol "Concept 40" broadband dielectric spectrometer (Hundsangen, Germany). Samples were subsequently mounted between gold platens and positioned in the Novocontrol Quatro Cryosystem. The first dielectric experiment was carried out keeping the frequency fixed but sweeping the temperature. A heating rate of 5 °C/min over the temperature range of from -120 to 50°C was utilized, and six decades of frequency from 1 up to 10^6 Hz, were scanned.

2.3 Synthesis of polyetherurethane based on derivative cellulose

The Scheme 1 illustrates the synthetic route for the preparation of polyetherurethane elastomers based on derivative cellulose. PTMEG and HPC were charged into a flamed and dry nitrogen purged 100 ml three-necked round-bottom flask and weighed. The flask was equipped with a stirrer and nitrogen inlet. The mixture of polyol and hydroxypropyl cellulose was dried under vacuum for 2 hrs at 60 °C. A predetermined and weighed amount of diisocyanate, corresponding to a diisocyanate:polyol ratio of 2:1, was added while stirring. The reaction mixture was then heated to about 80 °C and stirred for another 2 hrs.
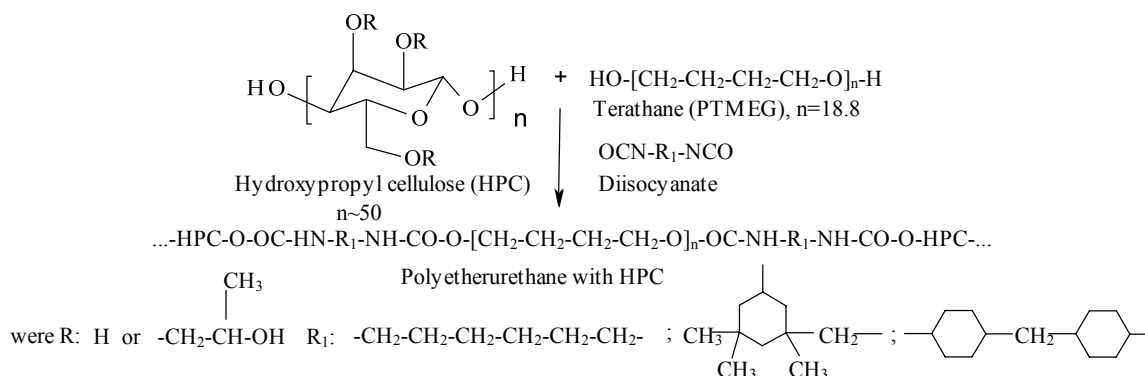
Scheme 1. Synthetic route for the preparation of polyetherurethanes based on PTMEG/Diisocyanate/HPC.

3. Results and discussion

3.1 Thermal stability study

It is largely important to study thermal stability of these polyurethanes because the scaffolds must be sterilized before implantation in the human body. The surgical implants must be freed of microorganisms by post-manufacture sterilization. This must destroy most bacteria and spores, sterilization may be achieved by the use of dry or moist heat; irradiation and chemical agents according to established practices. Heat sterilization is most common [12].

3.1.1 Thermogravimetric analysis (TGA)

The information about of degradation temperatures have been detailed in Table 1. The TGA was used to study some polyetherurethanes attempting to outline the increase in the thermal stability brought by diisocyanate components from their structures. To achieve this, the same testing conditions were used for all samples being analyzed. The onset degradation temperature was defined as the initial temperature of degradation, corresponding to the intersection of the tangent drawn at the inflection point of the decomposition step with the horizontal zero-line of the TG curve [13, 14].

Table 1. Results of thermogravimetric analysis of polyetherurethane based on PTMEG/Diisocyanate/HPC.

Sample	Reaction Order*		Energy activation, KJ/mol		Weight loss, %			Residue, %
	Step II	Step III	Step II	Step III	Step I <100 ^{o}C	Step II 100-400 ^{o}C	Step III >400 ^{o}C	
HDI	0.1	0.6	81.5	107.5	2.0	30.0	67.0	1.0
HMDI	1.2	0.9	127.7	140.4	1.5	30.4	67.3	0.8
IPDI	-	0.5	-	69.6	3.4	-	96.4	0.2

* Calculated by Reich – Levi method.

Generally, polyurethanes analyzed decomposed in three steps and the temperature to which the weight losses were maximum is >400 ^{o}C (Fig. 1). The first stage decomposition was associated with loss of physical water (<100 ^{o}C), the second stage with the hard segment degradation (100-400 ^{o}C), and the last one, with the soft segment degradation (>400 ^{o}C). The reaction orders, calculated through Reich-Levi method [15], are between 0 and 1, this suggests that some diffusion processes accompany decomposition in various conditions.
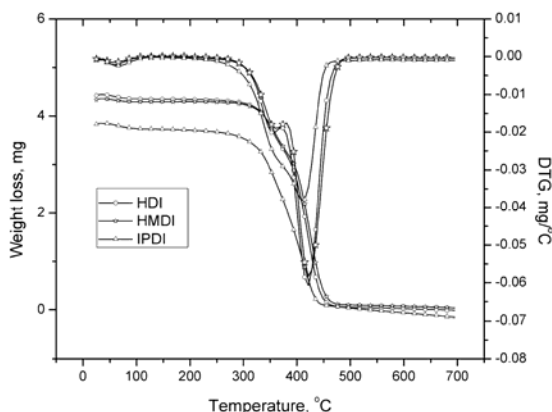
conversion can be observed at the beginning of degradation for each sample. This behaviour was also characteristic to an autocatalytic reaction. In connection with this, one should note that the oxygen traces from the polymer were acted as a catalyst for the decomposition process [16].
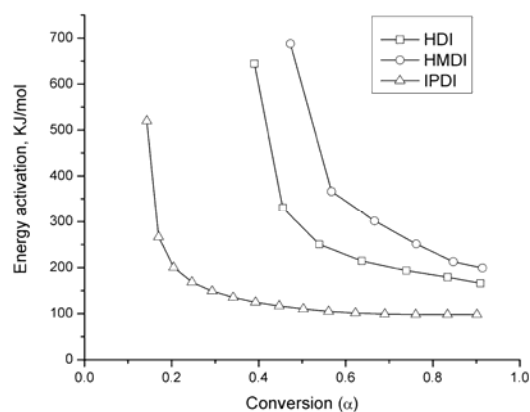

Fig. 2. Energy of activation vs. conversion of polyetherurethanes based on PTMEG/Diisocyanate/HPC.

Fig. 1. TG and DTG curves of polyetherurethanes based on PTMEG/Diisocyanate/HPC.

The dependence of the energy of activation versus conversion degree is presented in Fig. 2, and illustrate that the energy of activation decreased with conversion. An important depression in activation of energy values versus

3.1.2 Thermal stability- DSC study

The thermal properties of the samples were studied too, by means of Differential Scanning Calorimetry (Fig. 3). DSC is a thermal analytical technique which measures the amount of energy absorbed or released by a material as it is heated, cooled or held at constant temperature. This

method was appropriate for the evaluation of the glass transition temperature. So, the aliphatic diisocyanate structure influence (linear or cyclic) on the transition behaviour of polyetherurethane samples may be considered by DSC analysis.
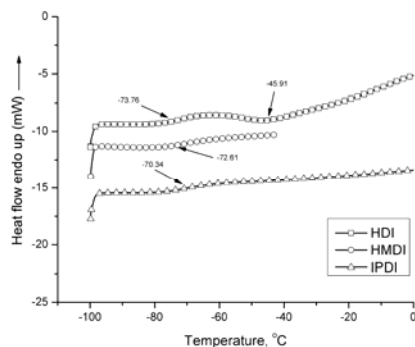

Fig. 3. DSC behaviour of polyetherurethane based on PTMEG/Diisocyanate/HPC.

The polyurethane based on linear aliphatic diisocyanate (HDI) exhibit two T_g at -73.76 and respectively -45.91 °C, while the polyurethanes based on cyclic aliphatic diisocyanate (HMDI and IPDI) exhibit only a T_g at -72.61 respectively at -70.34 °C. The second T_g (-45.91 °C) of the polyetherurethane based on HDI corresponding to a crystallinity most prominent of this polymer. Crystallinity influence of this sample it is observed more pregnant and by high Young's modulus (Table 2).

The semicrystalline structure provided by diisocyanate component (HDI>HMDI) provoke, to these samples, a decrease glass transition (T_g) in opposition with polyetherurethane samples based on IPDI, which don't have crystalline structures.

3.2 Mechanical strength

Since many tissues undergo mechanical stresses and strains, the mechanical properties of a scaffold should be considered. This is especially true for the engineering of weight-bearing orthopaedic tissues. In these instances, the scaffold must be able to provide support to the forces applied to both it and the surrounding tissues. Furthermore, the mechanical properties of the polymeric scaffold should be retained until the regenerated tissue can assume its structural role [17].

In this instance, the tensile test was used for study the influence of diisocyanate structures on the mechanical properties of polyetherurethane samples based on PTMEG and HPC (Table 2). The stress-strain traces of samples used in this study were presented in Fig. 4.
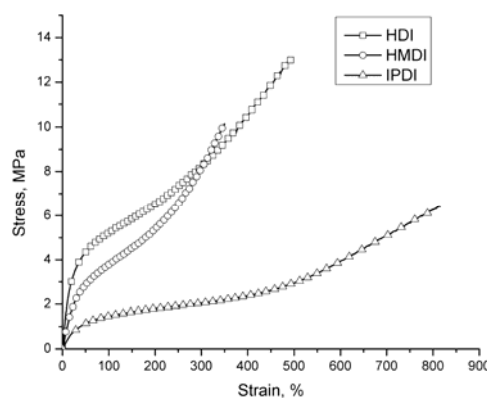

Fig. 4. Stress-strain curves of polyetherurethane based on PTMEG/Diisocyanate/HPC.

Table 2. Mechanical strengths and glass transition of polyetherurethane samples based on PTMEG/Diisocyanate/HPC.

Sample	Young's modulus, MPa	Tensile strength, MPa	Elongation at break, %	Hardness, °ShA	Tg °C
HDI	33.9	13.0	491	85	-73.76/-45.91
HMDI	12.1	10.1	346	75	-72.61
IPDI	4.1	6.4	807	65	-70.34

Young's modulus values are in agreement with the samples crystallinity, which decrease in order: HDI>HMDI>IPDI. In general, the crystallinity causes brittleness and increasing of samples hardness. This effect is largely caused by hydrogen bonds, which are formed with greater frequency in case of HDI and HMDI in opposition with IPDI. Similar behaviour it is observed too of tensile strength, while of elongation increase with decreasing of crystallinity.

In cases where mechanical forces are thought to be required for cell growth and phenotype expression, a scaffold which displays surface eroding properties may be preferred. Alternatively, hydrophobic polymers tend to resist water absorption and thus sustain their mechanical properties longer than hydrophilic polymers. In this case hydrophilic properties decrease in order HMDI>HDI>IPDI (See Table 3).

3.3 Wettability study

3.3.1 Contact angle, work of adhesion and surface free energy

The equations (1-5) were used for calculation of the surface tension parameters and work of adhesion:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cdot \cos\theta \quad \text{Young equation} \quad (1)$$

$$W_a = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \quad \text{Dupré equation} \quad (2)$$

$$W_a = \gamma_{LV}(1 + \cos\theta) \quad \text{Young-Dupré equation} \quad (3)$$

$$\gamma_{SV} = \gamma_{SV}^d + \gamma_{SV}^p \quad \text{Fowkes equation} \quad (4)$$

$$\frac{1 + \cos\theta}{2} \cdot \frac{\gamma_{LV}}{\sqrt{\gamma_{LV}^d}} = \sqrt{\gamma_{SV}^p}\sqrt{\frac{\gamma_{LV}^p}{\gamma_{LV}^d}} + \sqrt{\gamma_{SV}^d}$$

Owens - Wendt geometric mean equation   (5)

where θ is the contact angle determine for water and ethylene glycol, subscripts 'LV' and 'SV' denote the interfacial liquid-vapour and surface-vapour tensions, respectively, while superscripts 'p' and 'd' denote the polar and dispersive components, respectively, of total surface tension, γ_{sv}. If we plot the left side of equation (5) as a function of $(\gamma_{LV}^p / \gamma_{LV}^d)^{1/2}$ we get a straight line with the slope equal to $(\gamma_{SV}^p)^{1/2}$ and intercept on the y axis equal to $(\gamma_{SV}^d)^{1/2}$. The total free surface energy is merely the sum of its two component forces.

To determine the surface free energy of polyetherurethanes based on PTMEG/Diisocyanate/HPC with its polar and dispersive portions, the contact angle is measured with a number of test liquids and evaluated according to the geometric mean equation (eq. 5). This evaluation method is integrated in the software and is fully automatically carried out by the computer. The method requires the use of at least two test liquids with known surface tension and its polar and dispersive contributions. Each additional liquid will increase the accuracy of the estimation. On the film surface, a drop is formed with the manual dosing system of the KSV CAM 101 goniometer apparatus. With the CCD camera, a digital picture of the drop on the surface is recorded and saved. The software now automatically determines the contact angle between liquid and solid. Table 3 shows the contact angles, work of adhesion and surface free energy of polyetherurethanes based on PTMEG/Diisocyanate/HPC.

Table 3. Contact angles, work of adhesion and surface free energy of polyetherurethanes based on PTMEG/Diisocyanate/HPC.

Sample	Contact Angle, deg		Work of adhesion, mN/m		Surface free energy γ_{SV}, mN/m	Polar portion γ_{SV}^p, mN/m	Dispersive portion γ_{SV}^d, mN/m
	Water	Ethylene glycol	Water	Ethylene glycol			
HDI	89.25	67.83	73.75	66.76	23.96	5.57	18.39
HMDI	88.53	65.78	74.66	67.26	24.20	5.91	18.29
IPDI	91.86	69.57	70.40	67.43	27.94	2.70	25.24

Hydrophilic polyetherurethane samples decrease in the order: HMDI>HDI>IPDI. From the table it becomes obvious that the IPDI sample leads to a significant increase of the surface free energy. It is remarkable that the surface free energy of the samples is particularly influenced by the polar portion, which is to be expected from the creation of polar functional groups. A large amount of polar portion, from surface free energy, corresponds to a pronounced hydrophilic character. The polar portions of the surface energy can be quantitatively collected by means of the contact angle measurement. In this way, wetting and adhesion properties of polyurethane samples can be predicted.

3.3.2 Humidity absorption study

Our objective is to determine the water vapour sorption behaviour and physical stability of polyetherurethane samples based on cellulose derivative using the IGAsorp system. The interaction of materials with water vapour is of interest to a broad spectrum of science and industry. Almost all materials have some interaction with moisture that is present in their surroundings. The effects of water can be both harmful and beneficial depending on the material and how it is used. The material properties can change as a function of humidity and temperature and the stability, type, magnitude and the kinetics of interaction are all important in this regard. For most materials it is this interaction with the moisture that must be understood, often the interaction of the sample with moisture leads to spoiling or changing of the sample which is very rarely desirable. Water sorption is a general term that encompasses the range of possible interactions for water molecules with surfaces and bulk matter: these include physical adsorption, chemical (hydrogen) bonding and hydroxylation. Water sorption can also induce bulk changes such as hydration and amorphous phase transitions. The measurement that is most commonly made is the percentage weight content of moisture retained in the sample at a given relative humidity (% RH) and temperature and it is the measurement of these isotherms over a given range of temperatures that can be used to characterize the sample for defined environmental conditions. Materials are broadly classed as hydrophobic or hydrophilic, but detailed measurements of the interaction are required to investigate a given specimen and this generally requires determination of the water sorption isotherm.

The sample is placed within a weighing basket and positioned on the microbalance. The chamber is then closed and the sample sealed in position.

Drying of the sample before sorption measurements is carried out at 25 ºC in flowing nitrogen (250 ml/min) until the weight of the sample is in equilibrium at RH<1%. This gives m_0 at 25 ºC. After drying, the sorption measurements can begin with the absorption curve. The vapour pressure

was increased and decreased after an established program. We used a program with 10% humidity steps between 0 and 90%RH and 10% humidity steps for all the desorption (between 90% and 0% RH), each having a pre-established equilibrium time between 40 and 50 min (minimum time and time out, respectively). The maximum time at each RH (absorption-desorption) was set to 14 hrs in these experiments. The cycle was ended by decreasing the vapour pressure in steps to obtain also the desorption isotherms. The sorption-desorption isotherms for prepared samples are presented in Fig. 5.
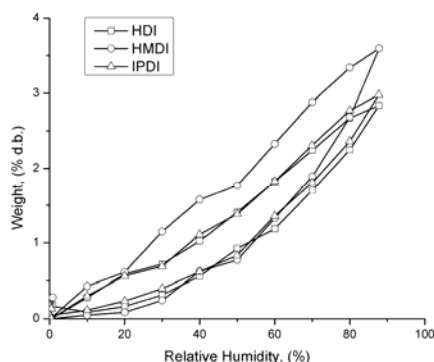

Fig. 5. Sorption/desorption isotherms of polyetherurethane based on PTMEG/Diisocyanate/HPC.

The BET (Brunauer-Emmett-Teller) model is the most widely used technique for predicting moisture sorption by solids and is used especially for evaluate the surface area of solid materials [18].

Generally, this method describes the isotherms until a relative humidity of 50%, depending on the type of sorption isotherm and on the type of material. For this, a program with 5 % humidity steps between 0 and 40 % RH and 10 % humidity steps between 40 and 90 % RH was used. The cycle was ended by decreasing the vapour pressure in steps to obtain also the desorption isotherms. For desorption, 10 % humidity steps were used for entire humidity range.

This model is limited because it cannot describe very well the water sorption in multilayer. The BET (6) equation is very often used for modelling of the sorption isotherms:

$$W = \frac{W_m \cdot C \cdot p/p_0}{(1 - p/p_0) \cdot (1 - p/p_0 + C \cdot p/p_0)} \qquad (6)$$

where: W- the weight of adsorbed water,
         W_m- the weight of water forming a monolayer,
         C – the sorption constant,
         P/P_o- the relative humidity,

The data obtained from sorption/desorption isotherms are summarized in Table 4.

Table 4. The main surface parameters evaluated by sorption isotherms.

Sample	Total water vapours sorption capacity, Weight (%db)	BET data		Average pore size (nm)
		Area (m^2/g)	Monolayer (g/g)	
HDI	2.8381	35.028	0.0099	1.62
HMDI	3.5950	43.424	0.0124	1.66
IPDI	2.9810	24.103	0.0069	2.47

The average pore size was estimated based on desorption branch assuming cylindrical pore geometry by using the following equation [19]:

$$r_{pm} = \frac{2 \cdot n}{100 \cdot \rho_a \cdot A} \qquad (7)$$

where r_{pm} is the average pore size, A is the BET surface area, n is the percentage uptake, and ρ_a is the adsorbed phase density.

By analysing the results of water vapours sorption /desorption experiments the order of the dynamic water vapour sorption capacity was HDI ≤ IPDI < HMDI, whereas the order of the BET area values was different: IPDI <HDI < HMDI. The difference between the order by water sorption capacity and area can be caused by the nature of the polar groups. The average pore size also influence the sorption capacity, the order by this criterion being HDI ≤ IPDI < HMDI. From the presented results, it is evident that because of many parameters like diisocyanate nature and NCO content, surface area and

pore size, etc, these influence, in complex mode the sorption capacity of the samples.

3.4 Dielectric behaviour

Dielectric properties of polyetherurethane samples are relevant to the potential application for electrical insulation but they are also useful for analyzing relaxation properties of these materials. Dielectric behaviour of polyetherurethane-cellulose derivative is reported in this paper as a function of frequency (1 Hz…1MHz), temperature (-140…50 °C) and the diisocyanate components, which were used inpreparing of this polymers. The polarisability of these materials depends on their structure and molecular properties. The results present some features that depend on diisocyanates, polyols and chain extenders structure. HPC based polyetherurethanes are composed from polar urethane and ester groups and nonpolar hydrocarbon chains, which is reflected in moderate permittivity. Values of ε' and ε" have a direct physical interpretation. ε' is related to the energy

stored reversible in the material whereas ε" is proportional to the energy which is dissipated per cycle.

Fig. 6 displays permittivity change of polyetherurethanes based on PTMEG/Diisocyanate/HPC as a function of frequency and temperature.

The permittivity (ε') of this polymer below Tg is constant at about 3 and shows very small dependence on frequency, but after Tg it is observed an visible increase for the whole range of frequency until to -20 ^{o}C. After that the permittivity jumps from 6 to 16, especially at lower

frequencies (ex. HDI and respectively IPDI, both at 1 Hz frequency), except HMDI, which does not present this behaviour. The loss permittivity (ε") vs. temperature curves show α transitions around -60 °C depending on frequency, and a β transition between -120 to -100 °C for frequency <10000 Hz. The origin of the β transition for this range of temperature was not well studied. It may be associated with water as in other polyurethanes types [20] or it has the same origin in the main chain motions.
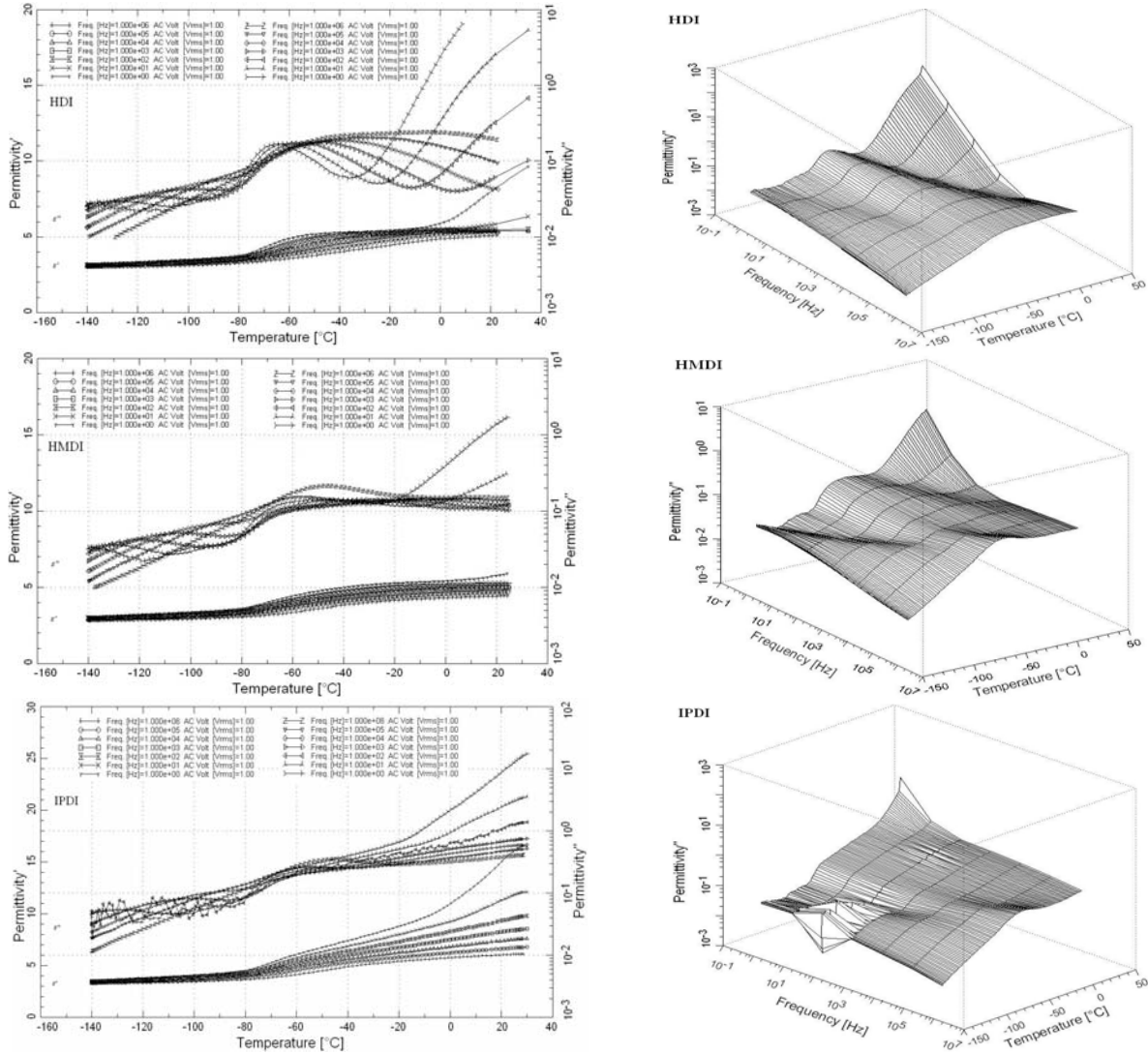

Fig. 6. Loss permittivity as a function of frequency and temperature for polyetherurethanes based on
PTMEG/Diisocyanate/HPC (2D and 3D representation).

4. Conclusions

This study present some polyetherurethanes (PEU) based on cellulose derivative, which may have great potential in tissue engineering applications. Wettability study classified these polymers, which have cellulose derivative in its composition, as amphiphile materials.

Based on the sorption/desorption isotherms registered in certain condition, BET surface area as well as average pore size were estimated, and placed these polymers, set by IUPAC, between microporous and mesoporous materials. The effect of the chain polarity on the character of loss permittivity vs. frequency curves is more distinct in the low frequency than in the high frequency area.

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