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Influence of diisocyanate structure on the properties of some polyetherurethanes based on renewable resources

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This study present two series of polyetherurethanes (PEUs) based on cellulose derivatives. First series was synthesized from polytetramethylene ether glycol (PTMEG-2000), as macrodiol, 1,6-hexamethylene diisocyanate (HDI), 4,4'-methylene bis(cyclohexyl isocyanate) (HMDI), isophorone diisocyanate (IPDI), as aliphatic diisocyanate components and hydroxypropyl cellulose (HPC) as chain extender, by one-shot technique without catalyst. The second series differs from the first through diisocyanate components; these are 4,4'-diphenylmethane diisocyanate (MDI) and 2,4-toluene diisocyanate (TDI). The properties of these materials have been evaluated with respect to aliphatic or aromatic structure influence.

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1. Introduction

Polyurethanes represents a very large class of materials, including segmented polyurethane elastomers, rigid thermoset networks, adhesives, and flexible elastomeric foams [1]. Many studies have developed polyurethane materials as candidate for biomedical applications [2,3]. The polyurethanes are generally formed by polyaddition reaction of diisocyanates with hydroxyl-terminated polyether or polyester and extended with glycols and/or diamines [4-6]. Segmented polyurethane elastomers have been included in many biomedical devices due to their excellent mechanical properties and satisfactory biocompatibility [7,8].

The biodegradable properties of these polymers can be improved by adjustment of their hydrophilicity, which depends on the structure of polyurethanes. One way of increasing the hydrophilicity of polyurethanes it is the introduction of hydrophilic segments, such as polyethers and/or renewable resources, into the backbone of the polyurethane chains [9-11]. A positive aspect associated with polyurethane system is the ease with which the end properties can be modified with good control by simple modification in the formulation. So, the ultimate polyurethane properties can be varied and through the wide range of isocyanate utilized.

In the present work were synthesized some polyurethane based on renewable resources and the influence of two categories of diisocyanates - aliphatic and aromatic - on the properties of this polyurethanes are reported.

2. Experimental

2.1. Materials

The materials used in this research were Terathane 2000 (polytetramethylene ether glycol - PTMEG - generous gift from INVISTA BV, Nederland), M_w 2026 g/mol, mp 35-40 ^oC, water 53 ppm, hydroxyl number 55.4 mgKOH/g; 1,6 – hexamethylene diisocyanate - HDI – Fluka; 4,4'-methylene bis(cyclohexyl isocyanate) - HMDI-Aldrich; isophorone diisocyanate - IPDI-Fluka; 4,4'-diphenyl methane diisocyanate - MDI – Fluka; toluene 2,4-diisocyanate - TDI – Fluka; hydroxypropyl cellulose - HPC- Aldrich, average M_w ~80,000, average M_n ~10,000, powder, 20 mesh particle size (99% through). PTEMEG and HPC extender were checked for moisture and if it was necessary, it was lowered at 0.3%. All diisocyanates were used as received, without further purification.

2.2. Measurements

The FTIR spectra were measured on a Bruker Vertex 70 instrument, equipped with a Golden Gate single reflection ATR accessory, spectrum range 600-4000 cm^{-1}, at ambient temperature.

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 heating rate of 10 ^{o}C/min and the temperature range was -100…+40 ^{o}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 ^{o}C. All samples were measured three times and the averages were obtained.

Shore hardness was measured with Digital Shore Durometer HT-6510A of the company Huatec Group Corporation, China, on a stack of compression moulded sheet at least 10 mm thick on a flat surface and taking the average of three measurements. Ambient temperature was 25 ºC.

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. 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.

2.3. Synthesis of PEUs

The Scheme 1 illustrates the synthetic route for the preparation of polyetherurethane elastomers based on derivative cellulose. PTMEG and HPC (stoichiometric quantities) 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 ^{o}C. A predetermined and weighed amount of diisocyanate, corresponding to a diisocyanate: polyether ratio of 2:1, was added while stirring. The reaction mixture was then heated at 80 ^{o}C and stirred for another 2 hrs. Finally, the polymer was moulded into plate and treated at 80 ^{o}C for 24 hrs.

3. Results and discussion

3.1. FTIR analysis

Figs. 1and 2 show PEUs spectra based on aromatic and respectively aliphatic diisocyanates. The spectra confirm, in principal, the formation of polyetherurethane structures. This is shown by the disappearance of the signal corresponding NCO (isocyanate) group at 2260 cm^{-1}.

The spectra of PEU samples are characterized by amide I bands (C=O stretch) between 1730-1718 cm^{-1}, an amide II band (the joint vibration resulting from combination of NCO and NH) at 1534-1559 cm^{-1}, C-O stretches at 1220-1259 cm^{-1}, a C=C stretch (aromatic ring) at 1597-1600 cm^{-1}, and NH stretch at 3337 – 3286 cm^{-1}.

The peaks for CH_2 stretch appears at 2938 cm^{-1}, 2853 cm^{-1} and 2796 cm^{-1}, respectively at 1483 cm^{-1}, 1413 cm^{-1} and 1367 cm^{-1}. At 1309 cm^{-1} appear signal for C-N vibration aromatic secondary amine. The peak of benzene ring is present at 816 cm^{-1}.

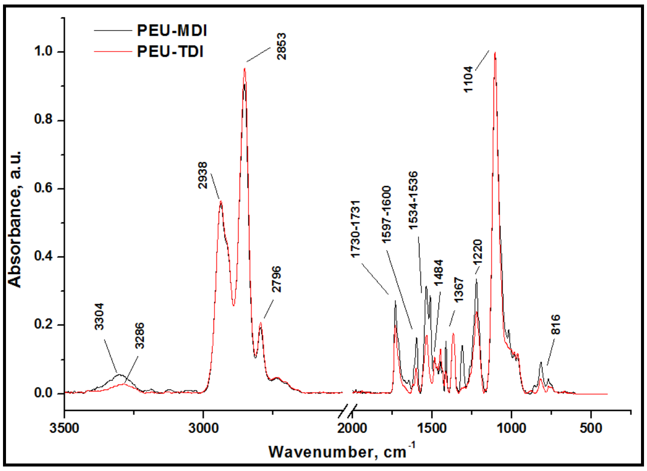
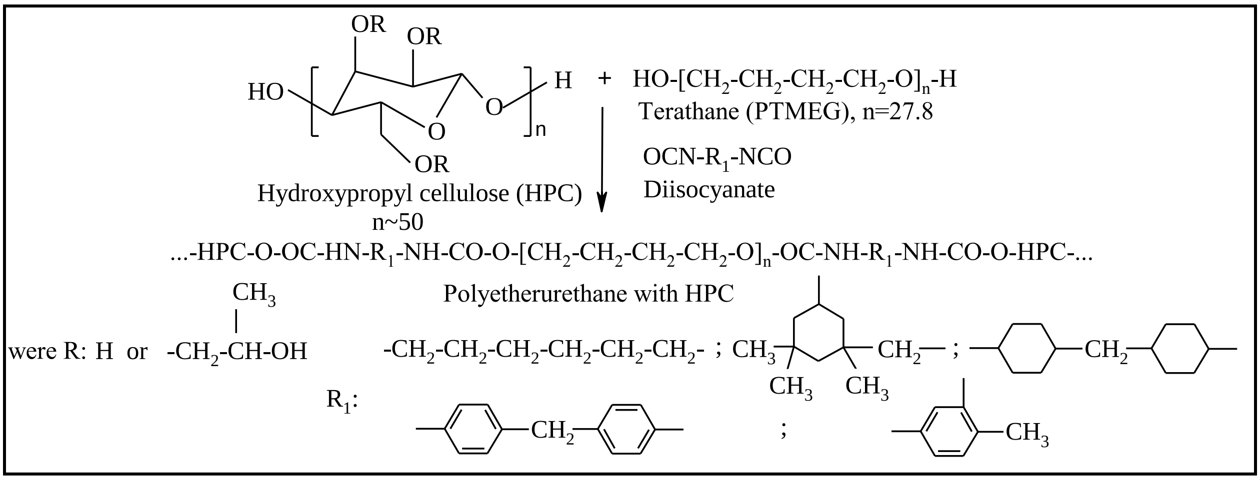


Fig. 1. FTIR spectra of samples based on aromatic diisocyanates



Scheme 1. Synthetic route for preparation of polyetherurethanes based on PTMEG/Diisocyanate/HPC

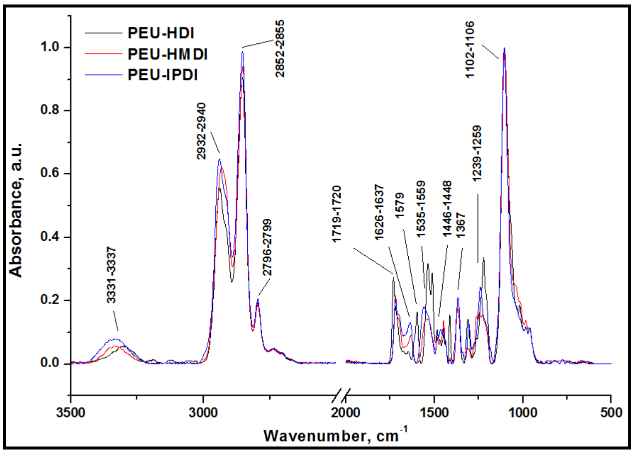


Fig. 2. FTIR spectra of samples based on aliphatic diisocyanates

3.2. Thermal stability study

Thermal stability study of these materials is particularly important because they must be sterilized before implantation. 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].

3.2.1. Thermogravimetric analysis (TGA)

In Table 1 are presented information about of degradation temperatures of the samples analyzed in this study. The TGA was used to characterize these polyetherurethanes, attempting to outline the increase in the thermal stability, brought by diisocyanate components from their structures. To achieve this, same testing conditions were used for all samples 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].

Generally, polyurethanes analyzed present three steps of decomposition and the temperature maximum of weight loss was >400 ^{o}C (Figure 3). The first stage decomposition correspond of the loss of the physical water (<100 ^{o}C), the second stage was associated with the hard segment degradation [15] (100-400 ^{o}C), and the last one, was associated with the soft segment degradation (>400 ^{o}C).

The reaction orders, calculated through Reich-Levi method [16], are between 0 and 1 suggesting that, in various conditions, some diffusion processes accompany the decomposition.

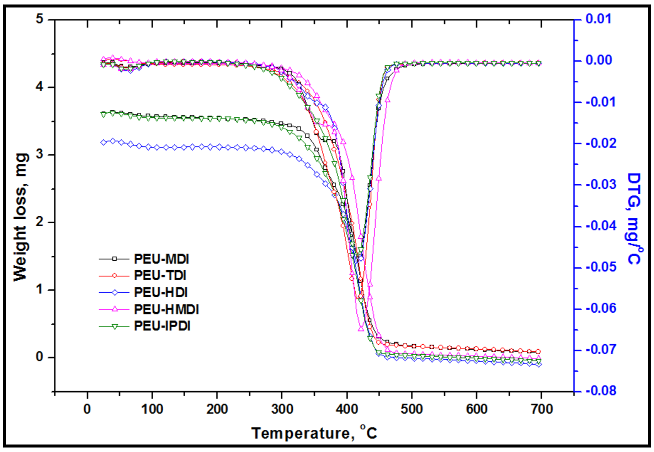


Fig. 3. TG and DTG curves of polyetherurethanes based on PTMEG/Diisocyanate/HPC

The dependence of the energy of activation versus conversion degree is presented in Figure 4, and illustrate that the energy of activation decreased with conversion.

At low levels of conversion is observed a significant decrease of activation energy for each of the samples studied. This behaviour can be attributed of some autocatalytic reaction. It should be noted that the oxygen traces from the polymer composition, act as a catalyst for the decomposition process [17,18].

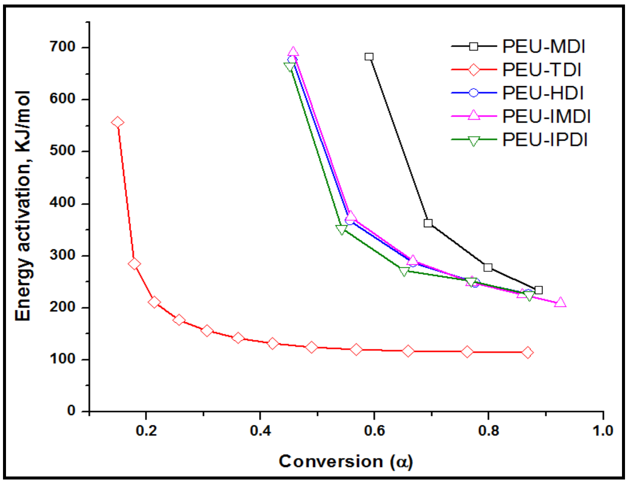


Fig.4. Energy activation vs. conversion of PEU based on PTMEG/Diisocyanate/HPC.

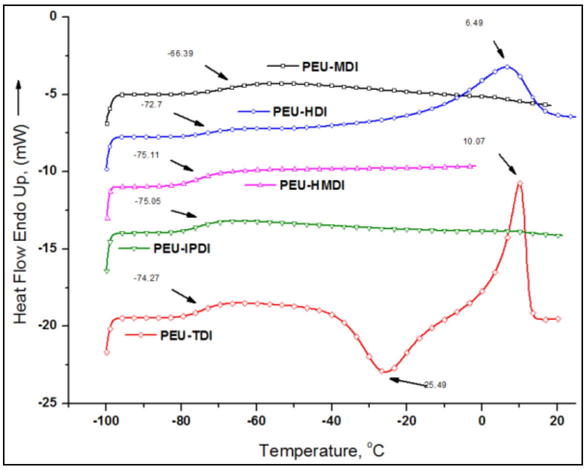


Fig. 5. DSC behaviour of PEU based on PTMEG/Diisocyanate/HPC

Table 1. The main 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 °C	Step II 100-400 °C	Step III >400 °C	
PEU-HDI	0.3	0.9	66.6	154.8	2.8	20.2	73.0	4.0
PEU-HMDI	0.2	0.9	69.8	150.8	1.8	27.1	70.6	0.3
PEU-IPDI	-	0.0	-	63.6	2.2	-	97.6	0.2
PEU-MDI	0.4	0.7	98.0	124.3	2.6	35.8	59.8	1.8
PEU-TDI	-	0.2	-	78.7	1.9	-	96.5	1.6

** Calculated by Reich – Levi method.*

3.2.2. DSC study

The thermal properties of the samples were studied too, by means of Differential Scanning Calorimetry (Figure 5) and was evaluated the glass transition temperature. The diisocyanate structure influence aliphatic and aromatic on the transition behaviour of polyetherurethane samples may be considered by DSC analysis. The polyurethanes based on aliphatic diisocyanate (HDI, HMDI and IPDI) exhibit T_g at -72.70; -75.11 and respectively -75.05 ^{o}C, while the polyurethanes based on aromatic diisocyanates (MDI, TDI) exhibit T_g at -66.39 respectively at -74.27 ^{o}C. The sample based on HDI exhibit melting temperature-T_m at +6.49 ^{o}C, and the samples based on TDI exhibit crystallization temperature-T_c at -25.09 ^{o}C and T_m at +10.07 ^{o}C (Table 2).

The glass transition temperature (T_g) decrease in order: MDI>TDI and HDI>HMDI≥IPDI. This order it is in concordance with increase of crystalline structure of polyetherurethane samples (see Young's modulus). In addition, the PEU-TDI sample, which has the highest modulus, presents crystallization temperature-T_c at -25.09 ^{o}C.

3.3. Mechanical strength

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 Figure 6.

Young's modulus values are in agreement with the samples crystallinity, which decrease in order: TDI>MDI for aromatic diisocyanate and respectively HDI>HMDI>IPDI, for aliphatic structures. 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 MDI>IPDI>TDI>HDI>HMDI (see Table 3).

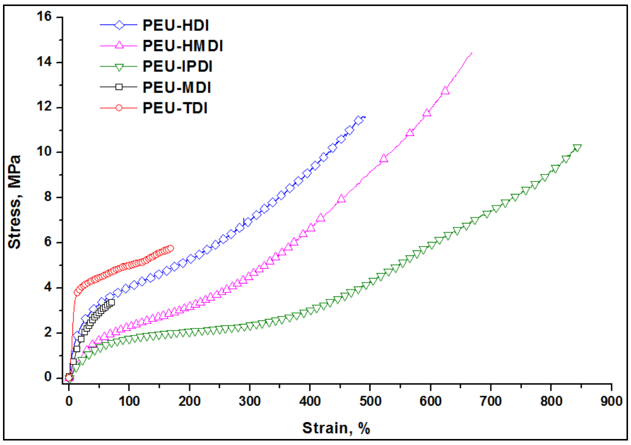


Fig. 6. Stress-strain curves of polyetherurethane based on PTMEG/Diisocyanate/HPC.

3.4. Wettability study

3.4.1. Contact angle, work of adhesion and surface free energy

Following equations were used for calculation of the surface tension parameters and work of adhesion:

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

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

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

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

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

Owens - Wendt geometric mean equation (5)

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, ^{o}ShA	*Tg/Tc/Tm* ^{o}C
PEU-HDI	26.54	10.88	490	85	-72.70/-/+6.49
PEU-HMDI	6.18	14.43	660	75	-75.11/-/-
PEU-IPDI	4.50	10.36	840	70	-75.05/-/-
PEU-MDI	10.73	3.00	140	80	-66.39/-/-
PEU-TDI	59.68	5.77	170	90	-74.27/-25.09/+10.07

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	Surface free energy γ_{SL}, mN/m
PEU-HDI	88.71	74.43	24.42	5.66	18.76	22.78
PEU-HMDI	84.79	79.41	26.49	7.25	19.24	19.87
PEU-IPDI	89.66	73.23	28.79	3.35	25.44	28.35
PEU-MDI	98.79	61.66	19.33	2.74	16.59	30.46
PEU-TDI	89.32	73.65	26.61	4.27	22.34	25.75

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)	
PEU-HDI	2.2691	20.869	0.00594	2.17
PEU-HMDI	2.5051	35.597	0.01010	1.41
PEU-IPDI	2.3366	26.749	0.00762	1.75
PEU-MDI	2.0271	22.026	0.00627	1.84
PEU-TDI	1.7906	24.480	0.00669	1.46

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, while superscripts ‘p’ and ‘d’ denote the polar and dispersive components of total surface tension, γ_{SV}.

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). 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. Table 3 shows the contact angles, work of adhesion and surface free energy of polyetherurethanes based on PTMEG/ Diisocyanate/ HPC.

Hydrophilic polyetherurethane samples based on aliphatic diisocyanates decrease in the order: HMDI>HDI>IPDI, while those based on aromatic diisocyanates decrease in the order TDI>MDI.

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.

3.4.2. Humidity absorption study

One aim of this paper 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 data obtained from sorption/desorption isotherms are summarized in Table 4.

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.

The sorption-desorption isotherms for prepared samples are presented in Figure 7.

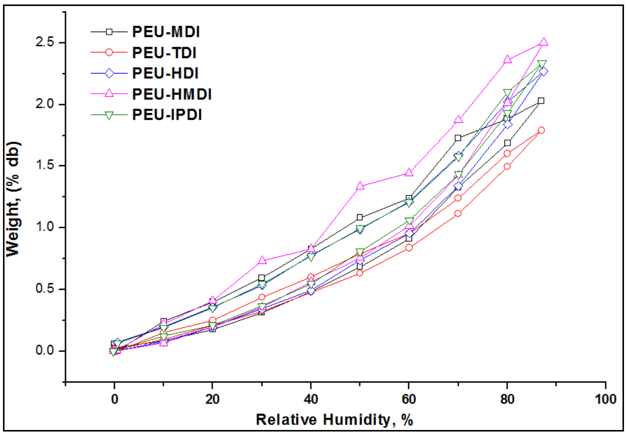


Fig. 7. Sorption/desorption isotherms of PEU based on PTMEG/Diisocyanate/HPC

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 [19].

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

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 average pore size was estimated based on desorption branch assuming cylindrical pore geometry by using the following equation [20]:

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

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.

The order of the dynamic water vapour sorption capacity was TDI<MDI<HDI<IPDI< HMDI, whereas the order of the BET area values was different: HDI<IPDI<HMDI for samples based on aliphatic diisocyanates and MDI<TDI for aromatic diisocyanates. 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 HMDI<IPDI<HDI, respectively TDI<MDI. 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.

4. Conclusions

In this paper has been studied the influence of diisocyanate structure on the thermal, mechanical and wetting properties of some polyurethanes. Thermal stability and glass transition depend on the structure of diisocyanates. Polyurethanes based on aliphatic diisocyanates shows slightly lower *Tg* than those based on aromatic diisocyanates. Young's modulus values are in agreement with the samples crystallinity, which decrease in order: TDI>MDI for aromatic diisocyanate and respectively HDI>HMDI>IPDI for aliphatic structures. Wettability study classified these polymers, which have cellulose derivative in its composition as low hydrophilic materials (contact angles values are between 84-89 deg, except sample with MDI which has 98 deg), hydrophilic properties decreasing in order MDI>TDI, respectively IPDI>HDI>HMDI. 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.

Acknowledgements

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