

# The novel semi-biodegradable interpenetrating polymer networks based on urethane-dimethacrylate and epoxy-polyester components as alternative biomaterials

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**Purpose:** This paper presents the pilot study aimed at the development of new full interpenetrating polymer networks based on urethane-dimethacrylate and biodegradable epoxy-polyester as the proposition of new biomaterials with gradually emerging porosity. **Methods:** The urethane-dimethacrylate monomer was obtained from 4,4'-methylenebis(phenyl isocyanate) and tetraethylene glycol monomethacrylate. The redox-initiating system was employed for its radical polymerization. The epoxy-polyester was produced by oxidation of the polyester, synthesized from succinic anhydride and allyl glycidyl ether. It was cured in a step-growth process with biogenic, aliphatic amine – spermidine. The mixtures of both monomers with adequate curing agents were room temperature polymerized. The hardened materials were characterized for damping behavior and dynamic modulus, hardness, water sorption, the course of hydrolytic degradation as well as the morphology – before and during the degradation process. **Results:** The cured materials revealed the non-porous, dense morphology. In the hydrolytic environment, the epoxy-polyester network degraded and the porous urethane-dimethacrylate scaffold remained. The epoxy-polyester appeared to prevent the urethane-dimethacrylate from attaining a high degree of conversion, even if the polymerization rate and the molecular mobility of the latter one are higher than those of the epoxy-polyester. The most homogeneous material with the best physico-mechanical properties was obtained when the urethane-dimethacrylate content was smaller than the epoxy-polyester content, respectively 25 and 50 wt%. **Conclusions:** The system presented in this work could be useful in tissue engineering, where at the beginning of the tissue regeneration process it would meet the implant mechanical properties and then would deliver its porosity, facilitating the tissue regeneration process.

*Key words:* interpenetrating polymer networks, urethane-dimethacrylates, epoxy-polyesters, dynamic-mechanical analysis, porous biomaterials, biodegradation

## 1. Introduction

Di(meth)acrylates and epoxy resins are commonly combined in the manufacturing of full interpenetrating polymer networks (Full-IPN). Monomers of these types simultaneously harden via non-interfering mechanisms resulting in IPN materials, in which both polymers are in a network form, there are no covalent bonds between them and phase separation is limited

[18], [21]. IPNs can have numerous advantages as biomaterials. They can be used as drug delivery systems [17], dental materials [24] as well as in tissue engineering, as bone substitutes, scaffolds and tissue adhesives [11], [17]. Although biomaterials are usually nonporous [22], [23], their porosity is sometimes very useful for maintaining the desired mechanical functions and mass transport properties [16], [19]. Designing porous materials for such applications necessitates a compromise between porosity and ade-

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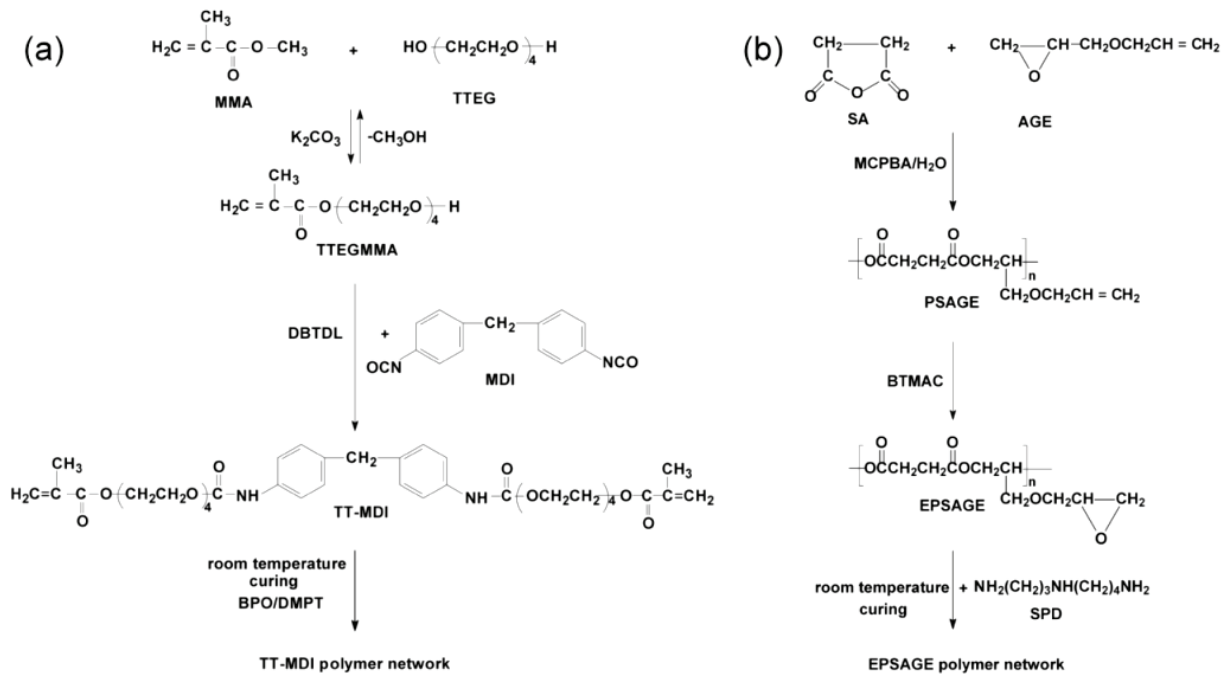
quate mechanical characteristics. An increasing degree of porosity provides a favorable environment for biofactor delivery and tissue regrowth, however, it usually makes the material mechanically weaker [16].

In the present paper, the IPN composed of urethane-dimethacrylate (UDMA) and epoxy-polyester (EPSAGE) is presented, as the prospective biomaterial with gradually emerging porosity. After the completion of the hardening process, the non-porous, dense form is created, fulfilling the tissue mechanical requirements. Along with its regeneration process, the EPSAGE network is successively degraded and thus, a porous scaffold is remained.

The most common UDMA monomer, used in tissue engineering is 1,6-bis-(methacryloyloxy-2-ethoxycarbonylamino)-2,4,4-trimethylhexane [5]. In fact, UDMA

corresponds to a broad family of non-biodegradable monomers [1]. They undergo extensive radical cross-linking polymerization due to the presence of two double bonds in one molecule [2]. Their properties can be easily tailored through an appropriate choice of the wing and core segments [1]. For the purpose of this study, the monomer obtained from 4,4'-methylenebis(phenyl isocyanate) and tetraethylene glycol mono-methacrylate (TT-MDI) was chosen (Scheme 1 a) [4].

Aliphatic polyesters are known from their biocompatibility, good mechanical properties and resorbability [20]. Epoxy resins also offer polymer networks with a wide range of physical properties and can be found in demanding structural applications, also as biomaterials [7], [10]. Used in this work, the biodegradable epoxy-polyester (EPSAGE) was obtained by the epoxidation of biocompatible polyester PSAGE



Scheme 1. The synthesis route and curing of: (a) the TT-MDI monomer and (b) the EPSAGE oligomer

Table 1. Sample names, their composition and selected properties of the IPNs: the storage shear modulus above the glass transition ( $G'_{rubbery}$ ), the degree of conversion of the methacrylate double bonds ( $DC_{C=C}$ ), the unreacted monomer content ( $UMC$ ), the Brinell hardness ( $HB$ ) and the water sorption ( $WS$ ).

Sample name	IPN composition		IPN properties				
	TT-MDI (wt%)	EPSAGE (wt%)	$G'_{rubbery}$ (MPa)	$DC_{C=C}$ (%)	$UMC$ (%)	$HB$ (N/mm <sup>2</sup> )	$WS$ (%)
TT-MDI/EPSAGE 100/0	100	–	6	76	1.4	81	4.87
TT-MDI/EPSAGE 75/25	75	25	3	35	29.2	41	38.5
TT-MDI/EPSAGE 50/50	50	50	6	43	12.6	79	27.1
TT-MDI/EPSAGE 25/75	25	75	9	54	5.8	115	31.6
TT-MDI/EPSAGE 0/100	–	100	14	100 <sup>a)</sup>	0.8	159	26.3

<sup>a)</sup> The value refers to the degree of conversion of epoxy groups in the EPSAGE phase.

(Scheme 1 b) [13]–[15]. The EPSAGE curing was performed with the non-toxic aliphatic amine hardener – spermidine (SPD), which is found in ribosomes and living tissues, having various metabolic functions [12]. An additional advantage of EPSAGE is the possibility of intentionally leaving a certain amount of pendant allyl functionalities during PSAGE epoxidation, which gives the perspective for chemical coupling of drug carriers.

This work focused on the development and characteristic of Full-IPN with different TT-MDI/EPSAGE ratios (Table 1). The effects of the IPN composition on the degree of conversion, thermal and dynamic-mechanical properties, hardness, water sorption, the course of the hydrolytic degradation and morphology (before and during the degradation process) were investigated.

## 2. Materials and methods

### 2.1. Materials

The chemicals used in this study, their acronyms and manufacturers are listed in Table 2. All of these substances, except BPO, were used as received. BPO was purified by dissolving in chloroform and precipitated by adding methanol.

TT-MDI was synthesized from MDI and tetraethylene glycol monomethacrylate (TTEGMMA) in the presence of DBTDL (the catalyst), in  $\text{CH}_2\text{Cl}_2$  solution, according to the procedure previously reported [4].

TTEGMMA was obtained from MMA and TTEG in the presence of  $\text{K}_2\text{CO}_3$  (the catalyst), in toluene solution, as previously reported [4].

EPSAGE was obtained through the complete oxidation of the polyester bearing allyl pendant groups (PSAGE), carried out in  $\text{CH}_2\text{Cl}_2$  solution, with 30% excess of MCPBA, at room temperature, as described earlier [14]. PSAGE was produced by the copolymerization of SA and AGE, carried out in a melt, at 120 °C, under nitrogen, in the presence of BTMAC and some water (the catalyst system), as described elsewhere [13], [15].

### 2.2. Curing procedure

TT-MDI monomer was cured with BPO (radical polymerization initiator) 1 wt. % and DMPT (redox activator for BPO) 0.075 wt. %, both with respect to the dimethacrylate weight. EPSAGE was cured with stoichiometric amount of SPD (1H amine/1 epoxy group). All curing processes were conducted at room temperature.

To obtain UDMA single network, two equimass TT-MDI components (one with the proper amount of BPO and the second with the proper amount of DMPT) were thoroughly mixed for 60 s. After stirring, the mixture was poured into the glass mould and left for 24 h. The EPSAGE single network was obtained by accurate mixing of EPSAGE with calculated amount of SPD for 60 s. The mixture was then poured into the glass mould and left for 24 h.

IPNs with varied TT-MDI/EPSAGE ratios, shown in Table 1, were obtained as follows. First, 40% of the

Table 2. Reagents and chemicals used in the study

Sample name	Acronym	Manufacturer
Allyl glycidyl ether	AGE	Acros
Benzoyl peroxide	BPO	POCh
Benzyltrimethylammonium chloride	BTMAC	Acros
m-Chloroperbenzoic acid	MCPBA	Acros
Chloroform	–	POCh
Dibutyltin dilaurate	DBTDL	Acros
N,N-Dimethyl-p-toluidine	DMPT	Acros
Methanol	–	POCh
Methyl methacrylate	MMA	Acros
Methylene chloride	$\text{CH}_2\text{Cl}_2$	POCh
4,4'-Methylenebis(phenyl isocyanate)	MDI	Sigma-Aldrich
Phenothiazine	PTZ	Sigma-Aldrich
Potassium carbonate	$\text{K}_2\text{CO}_3$	POCh
Succinic anhydride	SA	Sigma-Aldrich
Spermidine	SPD	Acros
Tetraethylene glycol	TTEG	Acros
Toluene	–	POCh

TT-MDI total amount, the total amount of EPSAGE and the total amount of BPO were mixed together for about 10 minutes to dissolve BPO crystals. Next, the calculated amounts of SPD and DMPT were introduced into the remaining 60% of the TT-MDI total amount and stirred for 5 minutes. After that, both components were combined and thoroughly mixed for about 60 s, poured into glass moulds and left for 24 h.

### 2.3. Experimental techniques

Viscosity of the resins ( $\eta$ , Pa·s) was measured by means of a rotating spindle viscometer (Brookfield FUNGILAB, VISCO STAR PLUS L) at 25 °C, using an appropriate spindle, at various spindle speeds, which allowed for recording viscosity values at around 50% torque.

The gelation time was determined by stirring the polymerizing system with a glass rod in a test tube maintained at a constant temperature of 25 °C. Gelation time was taken up until the point, when stirring showed that the composition had become stringy [6].

The dynamic-mechanical behavior of the cured samples was measured on disc-like specimens 4 mm in diameter and 1 mm thick by utilizing DMA 361° (Mettler Toledo). A shear mode was used with a frequency of 1 Hz, over the temperature range of –60 °C to 120 °C, at a heating rate of 3 K/min.

The FTIR measurements were carried out on the Bio-Rad FTS 175C spectrophotometer. The spectra of the monomers and their polymers were recorded with 128 scans at a resolution of 1 cm<sup>-1</sup>. The monomer compositions were analyzed as films formed onto potassium bromide pellets. The cured samples were pulverized into fine powder with a planetary ball mill (Pulverisette, Fritsch GmbH), sifted to a particle diameter of less than 24 µm, then admixed with potassium bromide and examined as pellets.

The degree of conversion ( $DC_{C=C}$ ) in the TT-MDI crosslinked phase of the IPNs was calculated by measuring the decrease of the absorption intensity of the peak at 1636 cm<sup>-1</sup> assigned to double bond stretching vibrations ( $A_{C=C}$ ). The peak at 1601 cm<sup>-1</sup> assigned to aromatic stretching vibrations ( $A_{Ar}$ ) was used as the internal standard. The absorption intensity of these peaks was measured in the 1800–1500 cm<sup>-1</sup> range as a baseline [2].

$$DC_{C=C}(\%) = 100 \times \left( 1 - \frac{(A_{C=C} / A_{Ar})_{pol}}{(A_{C=C} / A_{Ar})_{mon}} \right). \quad (1)$$

The utilization of the epoxy group for curing was confirmed by detecting the peak at 910 cm<sup>-1</sup>, assigned to the C-O deformation vibrations in the oxirane ring, before and after the hardening process [9].

In order to estimate the amount of unreacted monomer content ( $UMC$ ) in the final polymer network, its known weight ( $m_0$ ) was extracted in a Soxhlet with chloroform for 24 hours. After extraction the sample was dried in a vacuum oven for 8 hours at 50 °C and reweighed ( $m_1$ ). The Mettler Toledo XP Balance with 0.01 mg accuracy was used for weighing. The  $UMC$  was calculated according to the following equation

$$UMC(\%) = \frac{m_0 - m_1}{m_0} \times 100. \quad (2)$$

The Soxhlet leachates, after the solvent removal with a rotary evaporator, were analyzed for composition by means of 1H NMR technique.

The ball indentation hardness ( $HB$ ) was determined in accordance with ISO 2039 (Plastics – Determination of hardness – Part 1: Ball indentation method), on disc-like test specimens (60 mm in diameter and 4 mm thick), using VEB Werkstoffprüfmaschinen apparatus.  $HB$  was calculated according to

$$HB(N/mm^2) = \frac{F_m \left( \frac{0.21}{h - h_r + 0.21} \right)}{\pi d h_r} \quad (3)$$

where  $F_m$  – the test load on the indenter ( $F_m = 490$  N),  $h_r$  – the reduced depth of impression ( $h_r = 0.25$  mm),  $d$  – the diameter of the ball indenter ( $d = 5$  mm),  $h$  – the depth of impression.

Hydrolytic degradation was performed in phosphate buffer solution of pH = 7.41 (PBS) at 37 °C. Samples of 1 mm in thickness and 0.2 g in weight ( $m_0$ ) were placed in vials containing 20 ml of phosphate buffer solution. The vials were incubated at 37 °C for various time (from 7 to 56 days). After incubation, the samples were separated, washed with water, dried in vacuum at 50 °C and weighed ( $m_1$ ) to estimate the weight loss ( $WL$ ).

$$WL(\%) = \frac{m_0 - m_1}{m_0} \times 100. \quad (4)$$

Water sorption was measured according to ISO 62 (Plastics – Determination of water absorption). Rectangular specimens (5 mm in width and 1 mm thick) of each polymer network were dried in a pre-conditioning oven at 37 °C until their weight was constant. This result was recorded as  $m_0$ , (Mettler

Toledo XP Balance with 0.01 mg accuracy). The specimens were then immersed in distilled water and kept at 37 °C for 24 h. Afterwards, the samples were removed, blotted dry and weighed ( $m_1$ ). Water sorption ( $WS$ ) was calculated using the following formula

$$WS (\%) = \frac{m_1 - m_0}{m_0} \times 100. \quad (5)$$

Morphology investigations were performed on fractured surfaces of the cured materials with the Hitachi TM-3000 Scanning Electron Microscope (SEM). The sample surfaces, before the observations, were sputter coated with gold. Microphotographs were made in magnification 500 $\times$  and 2500 $\times$ .

### 3. Results

For the purpose of this study the dimethacrylate TT-MDI monomer was synthesized (Scheme 1a), having a molecular weight of 775 g/mol and the concentration of double bonds of 0.26 mol/100g. It was characterized by a viscosity of 8.21 Pa·s, which is lower than both, the viscosity of its shorter UDMA homologous [1] as well as EPSAGE (56.25 Pa·s) – the second resinous IPN component applied in this work. Such a difference in viscosity was beneficial during homogenizing operations at the stage of IPN composition preparation. The BPO/DMPT redox-initiating

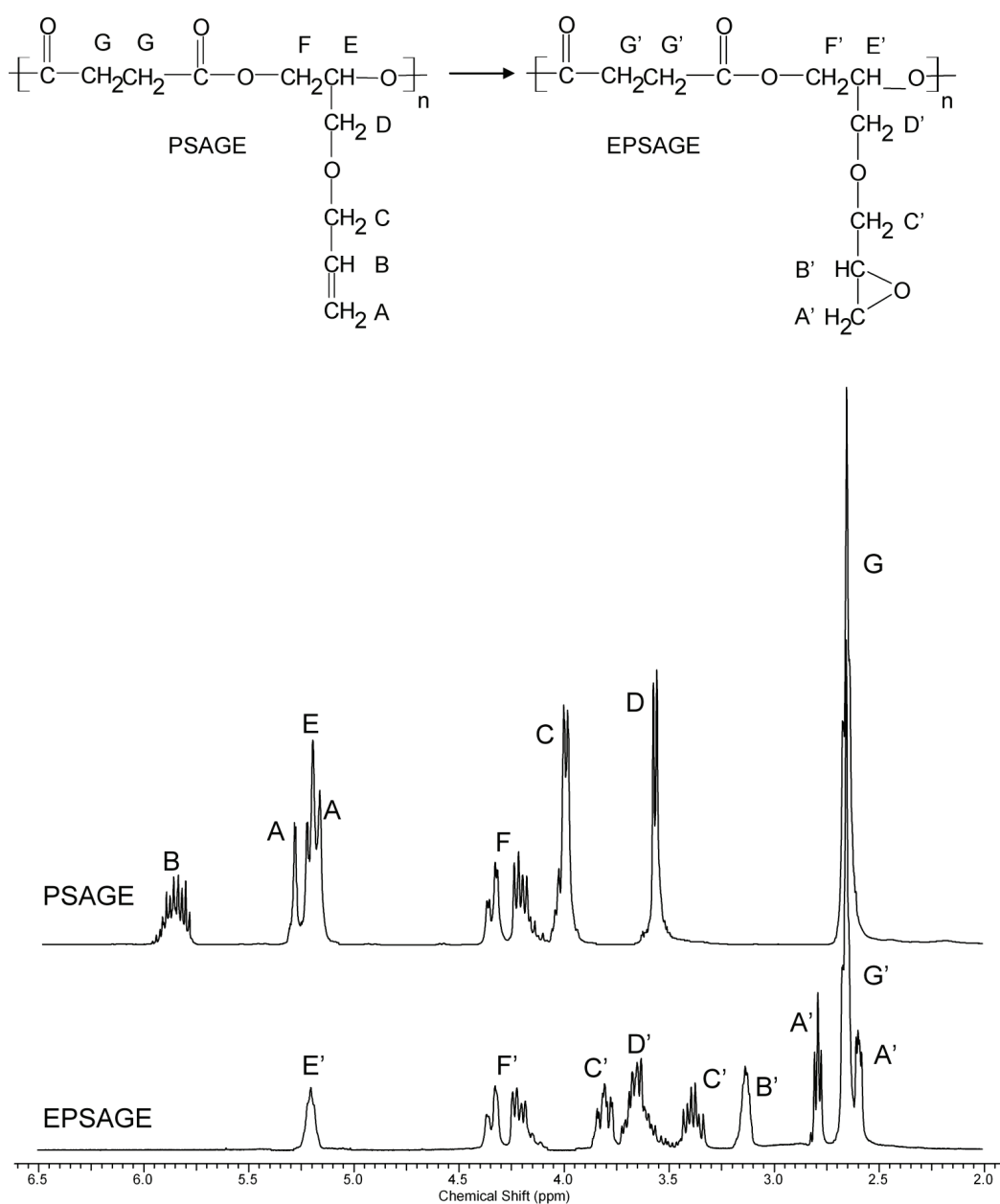


Fig. 1. The confirmation of the EPSAGE formation, resulting from the PSAGE complete epoxidation by means of <sup>1</sup>H NMR

system was employed for the radical polymerization of the UDMA double bonds as the common one for biomedical applications [5].

The EPSAGE, with epoxy value of 0.47 mol/100g,  $M_n = 3700$  as well as  $M_w/M_n = 1.61$  [14], was obtained by the complete epoxidation of PSAGE (Fig. 1). The latter one was synthesized from SA and AGE (Scheme 1b) [13]. It was cured in a step-growth process with an aliphatic amine hardener. The biogenic amine – spermidine (SPD) was used for this purpose.

In this study, the simultaneous polymerization of both resins was performed at room temperature for TT-MDI/EPSAGE weight ratios of 75/25, 50/50 and 25/75 (Table 1). The TT-MDI and the EPSAGE single networks were also obtained for comparison purposes. Cured samples were solid and macroscopically homogeneous.

The DMA analysis delivered information of their viscoelastic behavior and structural heterogeneity by the determination of damping factor ( $\tan\delta$ ) and storage shear modulus ( $G'$ ) as a function of temperature. Fig. 2a shows the DMA plots of  $\tan\delta = f(T)$ , whereas in Fig. 2b  $G' = f(T)$  plots are presented. The UDMA as well as EPSAGE single networks delivered single peak on the  $\tan\delta = f(T)$  curve, of which the maximum corresponded to the glass temperature ( $T_g$ ). Its value of 31.5 °C was the same for both single polymers. The  $\tan\delta$  curve of each IPN displayed double peak characteristics. The main peak was found in the range between 19 and 25 °C, whereas at its left side, in the range from -32 to -25 °C, a shoulder was located. Temperatures of both  $\tan\delta$  peaks decreased as the TT-MDI content increased.

The curves of the storage modulus versus temperature are shown in Fig. 2b. The EPSAGE single network had modulus in the glassy state ( $G'_{glassy}$ ) higher than the TT-MDI one, respectively 1940 and 1640 MPa. The combination of both networks resulted

in the decrease of the  $G'_{glassy}$  value with the increase of the TT-MDI content. The TT-MDI/EPSAGE 25/75 IPN was characterized by the highest modulus amongst studied IPNs and its value was close to the TT-MDI single network (1666 MPa). The analysis of the rubbery plateau region revealed that the shear modulus ( $G'_{rubbery}$ ) was also influenced by the TT-MDI/EPSAGE ratio and dropped with the increase of the TT-MDI content (Table 1).

The results of FT-IR analysis of monomer samples and their cured forms are presented in Table 1, whereas Fig. 3 shows the exemplary FT-IR spectra of the decreasing peak intensity assigned to double bonds as well as epoxy groups in the TT-MDI/EPSAGE 25/75 system. The TT-MDI did not reach as high  $DC_{C=C}$  in IPNs as it did during individual polymerization ( $DC_{C=C} = 76\%$ ). The increasing TT-MDI content resulted in decreasing  $DC_{C=C}$  in the IPN. The highest  $DC_{C=C}$  of 54% was determined in the TT-MDI/EPSAGE 25/75 IPN. On the other hand, the epoxy group reacted completely (Fig. 3b).

The TT-MDI, when individually polymerized, reached the gel point in 3 minutes and the EPSAGE in 30 minutes. In order to estimate the amount of unreacted resins in the final IPNs and thus the efficiency of curing, a Soxhlet extraction was carried out. As indicated in Table 1, for both single networks, the unreacted monomer content ( $UMC$ ) was close to 1wt%. Each IPN was characterized by higher amounts of soluble fraction and their increase was accompanied by an increase in the TT-MDI weight percentage. The significantly high  $UMC$  values of 29 and 13 wt. % were measured for the networks containing, respectively the 75 and 50 wt. % of TT-MDI. Only the TT-MDI/EPSAGE 25/75 IPN revealed a satisfactory  $UMC$  value of 6 wt. %.

As shown in Table 1, the EPSAGE single network was characterized by higher hardness than TT-MDI single network, 159 and 81 N/mm<sup>2</sup>, respectively.

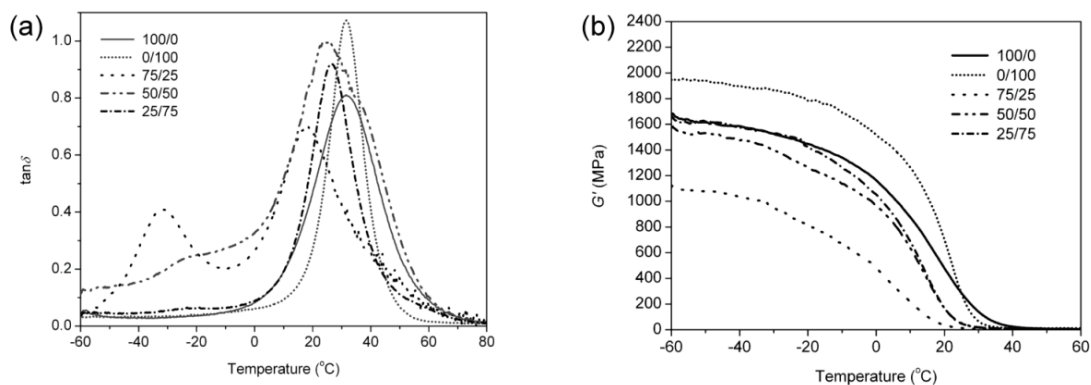


Fig. 2. The results from the DMA analysis of TT-MDI/EPSAGE IPNs under study: (a) the  $\tan\delta$  curves, (b) the  $G'$  curves

Their combination into the IPN caused the reduction in hardness. The TT-MDI/EPsAGE 25/75 IPN, in which the dimethacrylate content was significantly lower than the EPsAGE one, revealed the highest hardness among studied IPNs ( $115 \text{ N/mm}^2$ ).

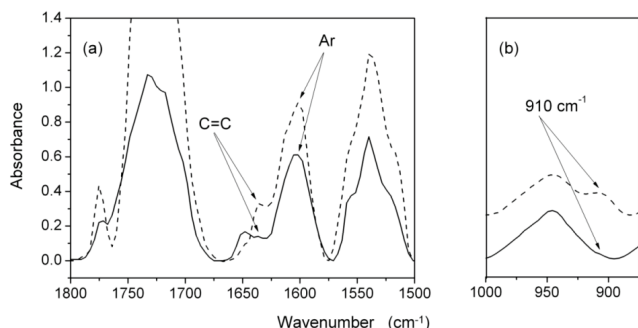


Fig. 3. The decrease of characteristic absorption peaks resulting from the polymerization of TT-MDI/EPsAGE 25/75 IPN. (a) the TT-MDI double bonds at  $1636 \text{ cm}^{-1}$ , (b) the EPsAGE epoxy groups at  $910 \text{ cm}^{-1}$

The hydrolytic degradation of all polymer networks was conducted in PBS at  $37^\circ \text{C}$  and was monitored mainly by the determination of the sample weight loss as a function of time. Figure 4 displays the weight loss of studied IPNs having various TT-MDI to EPsAGE ratios as well as both single polymer networks, for comparison purposes. The EPsAGE single network achieved full degradation after 56 days, while the UDMA single network showed a negligible weight loss of 1%, due to the monomer leaching. The TT-MDI/EPsAGE 75/25 IPN was characterized by the highest

weight losses, 12%, 35% and 74%, after 7, 21 and 56 days, respectively. The increase in the EPsAGE content caused, first – the decrease, and thereafter the increase in the degradation rate. When the EPsAGE weight fraction was raised from 50 to 75 wt. %, respectively, the following weight losses were observed: 7 and 9% after 7 days of the degradation, 22 and 29% after 21 days of the degradation, 49 and 72% after 56 days of the degradation.

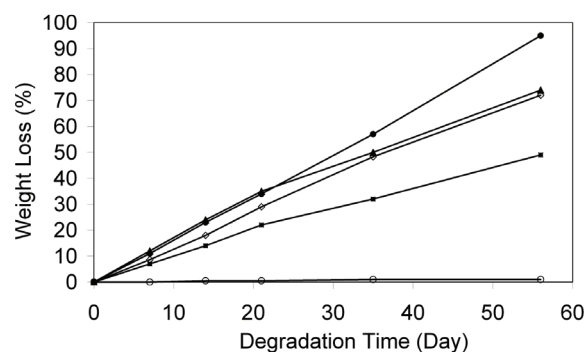


Fig. 4. The effect of the TT-MDI/EPsAGE IPN composition: 100/0 (○), 0/100 (●), 75/25 (▲), 50/50 (■), 25/75 (◇) on the hydrolytic degradation course

The water sorption of IPNs was also studied (Table 1). As can be seen, the EPsAGE single polymer network exhibited significantly higher water uptake (26 wt. %) than that of TT-MDI (5 wt. %). It is caused by the formation of the hydroxyl group during the reaction between epoxy resin and amine hardener. Studied IPNs revealed *WS* values higher than EPsAGE

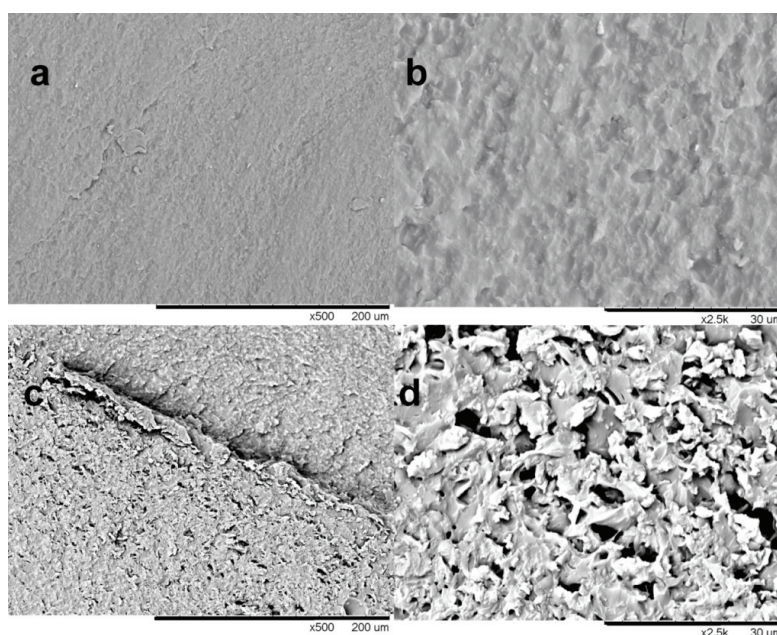


Fig. 5. SEM images of the TT-MDI/EPsAGE 25/75 IPN fracture surface morphology: (a), (b) before and (c), (d) after 14 days of the hydrolytic degradation. (a) and (c) scale bars represent  $200 \mu\text{m}$ , (b) and (d) scale bars represent  $30 \mu\text{m}$

single network. The maximum water absorption, was obtained for the IPN with the smallest EPSAGE content, i.e., 38.5 wt. %.

The morphology of the fractured IPN sample surfaces before and during hydrolytic degradation process was examined by SEM. The exemplary image of the TT-MDI/EPSAGE 25/75 IPN, taken before the degradation, illustrates smooth and dense fractured surface (Fig. 5a and b). In contrast, after 14 days of the degradation process, the surface of the inner layer had visibly eroded and the IPN presented porous morphology (Fig. 5c and d).

## 4. Discussion

The main objective of this work was the preparation and characterization of partially degradable Full-IPNs achieved by simultaneous polymerization of urethane-dimethacrylate (UDMA) (Scheme 1 a) and epoxy-polyester (EPSAGE) (Scheme 1 b) resins.

The curves of the damping factor ( $\tan\delta$ ) (Fig. 2a) and the storage shear modulus ( $G'$ ) (Fig. 2b) versus temperature showed varied viscoelastic behavior and high structural heterogeneity of obtained polymers. The existence of the shoulder as well as its varying location and intensity in the  $\tan\delta = f(T)$  curve suggest

the biphasic character of studied IPNs. The presence of a well resolved shoulder peak in the  $\tan\delta$  curve of the TT-MDI/EPSAGE 75/25 IPN revealed the most heterogeneous structure of this system among those studied. With the increasing EPSAGE content a shoulder in the  $\tan\delta$  curve changed into the inflection, was less evident and raised to higher temperatures, suggesting a more homogeneous system. On the other hand, the decrease of the  $G'_{\text{glassy}}$  value with the increase of the TT-MDI content informs about the increasing flexibility of the partially cross linked networks. The analysis of the rubbery plateau region also revealed that cross link densities in studied IPNs were lower compared to single networks and decreased with the increased TT-MDI content.

The FT-IR analysis of monomer samples and their cured forms confirmed this conclusion. Only, the TT-MDI/EPSAGE 25/75 IPN reached the  $DC_{C=C}$  higher than 50% (Table 1), which could indicate that nearly all the UDMA molecules were incorporated into the polymer network with at least one reactive group [3]. On the other hand, the full conversion of epoxy group (Fig. 3b), suggests that the cross linking of EPSAGE oligomer is favored. As the epoxy group is present in each EPSAGE repeating unit, the close proximity to each other favors the formation of highly cross linked EPSAGE domains, effectively increasing the EPSAGE network cross link density and providing a steric bar-

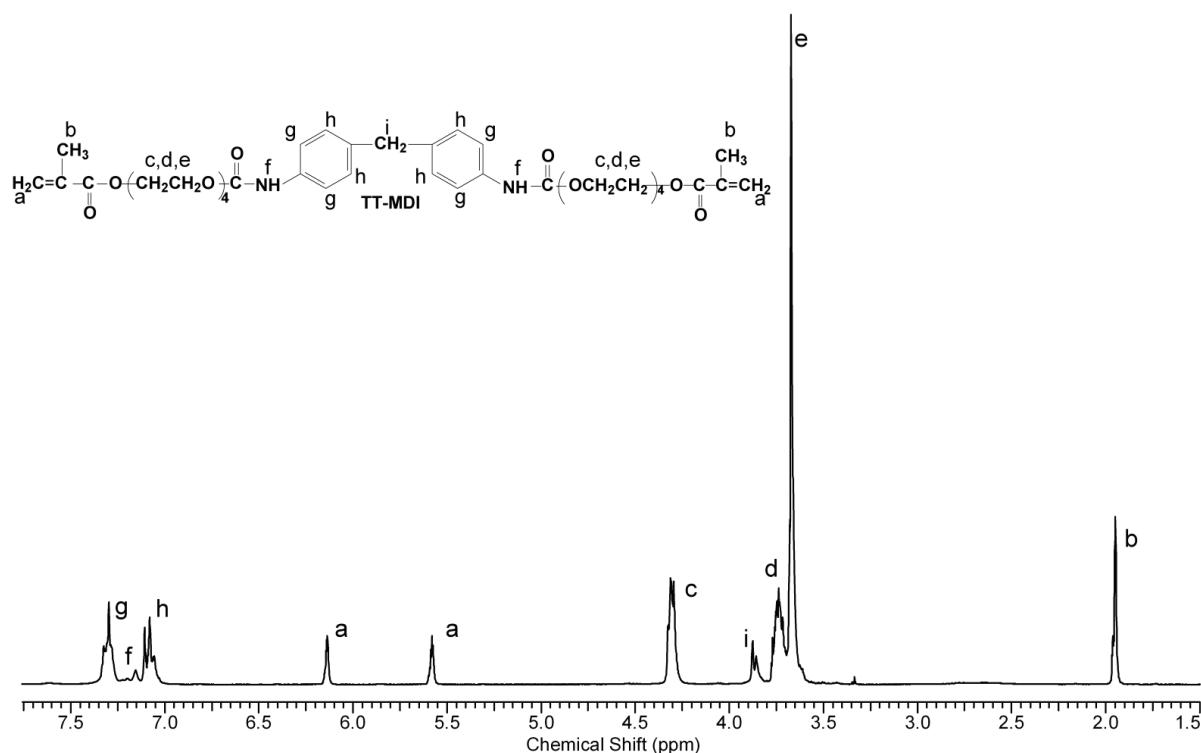


Fig. 6. The  $^1\text{H}$  NMR spectrum of the TT-MDI/EPSAGE 25/75 IPN leachates after the Soxhlet extraction carried out in chloroform for 24 h



rier to the TT-MDI polymerization. Due to a steric isolation, two double bonds located at each end of the dimethacrylate molecule can not readily react. Usually, in methacrylate/epoxy IPN systems, the methacrylate monomer polymerizes faster, reduces the molecular mobility of the epoxy groups and causes the primary vitrification as the whole IPN vitrifies [21]. The gelation time TT-MDI as well as EPSAGE resins was also determined and the results confirmed that the TT-MDI, when individually polymerized, reaches the gel point much sooner than the EPSAGE. It suggests that in studied IPNs the network formation is mainly affected by the steric effects than by the polymerization kinetics.

The results of hardness, water sorption and hydrolytic degradation revealed the incomplete conversion in IPNs (Table 1). The increasing TT-MDI content in the IPNs caused the reduction in hardness and the increase in degradation rate, whereas the increase in hardness and the decrease in the degradation rate were expected. The lowest hardness, the maximum water absorption and the highest degradation rate were obtained unexpectedly for the IPN with the smallest EPSAGE content, i.e., 25 wt. %. This result can be explained by the distinctly low cross link density of TT-MDI network in the TT-MDI/EPSAGE 75/25 system and unreacted TT-MDI monomer release, due to its insufficient curing (Fig. 6). The results obtained for the remaining two IPNs, showed to be a function of the IPN content, rather than the TT-MDI phase cross link density. However, if compared to the TT-MDI single network, the values of hardness, water sorption and rate of hydrolytic degradation suggest lower cross link density [8].

The morphology of the degrading fractured IPN samples confirmed the degradation of the EPSAGE phase and the remaining of the TT-MDI scaffold (Fig. 5). Hence, the concept of gradually emerging porosity was confirmed, which potentially is to be used in biomaterials and to work as scaffolds, benefiting new tissue regrowth.

## 5. Conclusions

In this study, a strategy to produce urethane-dimethacrylate/epoxy-polyester IPN by a simultaneous, room temperature polymerization was developed. The novel IPN, after curing, presents dense and solid material. When it is subjected to hydrolysis, EPSAGE component degrades and the porous UDMA scaffold remains. This material property is expected to be use-

ful in tissue engineering, where at the beginning of the tissue regeneration process it would meet the implant mechanical properties and then would deliver its porosity, facilitating the tissue regeneration process. The IPN systems, presented in this work, are exemplary. In fact, they can display a broad range of properties from elastomers to tough plastics, depending on the substrates used and their ratios.

Studied IPNs are characterized by high structural heterogeneity. The high level of EPSAGE crosslinking imposes topological restrictions on the neighboring TT-MDI monomer and prevents it from attaining a high degree conversion, even if the polymerization rate as well as the molecular mobility of TT-MDI are higher than those of EPSAGE. In order to obtain the IPN material with adequate mechanical properties, the EPSAGE content should be higher than the TT-MDI content. In this study, the TT-MDI/EPSAGE 25/75 IPN was the most structurally homogeneous and was characterized by the best physico-mechanical parameters.

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