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Synthesis and properties of vinylpyrrolidone/(trimethoxysilyl)propyl methacrylate gels containing different amounts of crosslinking agent

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Abstract: High conversion copolymers containing 90 wt % of *N*-vinylpyrrolidone (NVP) and 10 wt % of 3-(trimethoxysilyl)propyl methacrylate (TMSPM) with 0, 1, 2, 3 and 4 wt % (in conversion to mass of NVP/TMSPM) of ethylene glycol dimethacrylate (EGDMA) as crosslinker have been successfully synthesized. Proton nuclear magnetic resonance (^{1}H NMR) and Fourier transform infrared spectroscopy (FT-IR) were employed to characterize the resulting copolymers. The effect of EGDMA amount on the mechanical and thermal properties, swelling parameters, clarity, and oxygen permeability of the prepared xerogels and hydrogels were studied. 3 wt % of EGDMA is required to obtain clear xerogels and hydrogels. The water content (*EWC*), volume fraction of polymer (ϕ_2) and weight loss during swelling decrease with increasing EGDMA content. Young's and shear modulus (*E* and *G*) increase as EGDMA content increases, the values of *E* and *G* are 0.570–3.531 MPa and 0.217–1.359 MPa, respectively. The hydrogels were characterized in terms of modulus crosslinking density (v_e and v_t) and polymer-solvent interaction parameters (χ). The results are 0.220–0.613 mol/dm^3 for v_e, 0.105–0.441 mol/dm^3 for v_t, and 0.595–0.822 for χ. Thermal properties enhance by adding EGDMA whereas the oxygen permeability (*P*) of hydrogels decreases from 48.6 to 44.3 as water content decrease from 70.3 to 55.1.

Keywords: high conversion copolymers, swelling parameters, mechanical properties, oxygen permeability, crosslinking density.

Synteza i właściwości żelu *N*-winylopirolidon/metakrylan 3-(trimetoksysililo)propylu z różną zawartością czynnika sieciującego

Streszczenie: Kopolimery zawierające 90 % mas. *N*-winylopirolidonu (NVP) i 10 % mas metakrylanu 3-(trimetoksysililo)propylu (TMSPM) z udziałem 0, 1, 2, 3 i 4 % mas. (w przeliczeniu na masę NVP/TMSPM) dimetakrylanu glikolu etylenowego (EGDMA) jako środka sieciującego zsyntetyzowano z wysokim stopniem konwersji. Otrzymane kopolimery charakteryzowano metodami protonowego rezonansu jądrowego (H^1 NMR) i spektroskopii w podczerwieni (FT-IR). Badano wpływ udziału środka sieciującego na właściwości mechaniczne i termiczne, parametry pęcznienia, klarowność i przepuszczalność tlenu wytworzonych hydro- i kserożeli. Stwierdzono, że dodatek już 3 % mas. EGDMA wystar-

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cza do uzyskania klarownego żelu, a w miarę zwiększania zawartości EGDMA zmniejsza się zawartość wody (*EWC*), ułamek objętości polimeru (ϕ_2) oraz strata masy w procesie pęcznienia żelu NVP/TMSPM. Wartość modułu zarówno Younga (*E*), jak i ścinania (*G*) zwiększa się (E = 0,570–3,531 MPa, G = 0,217–1,359 MPa) wraz ze wzrostem udziału EGDMA w kompozycji. Wytworzone hydrożele charakteryzowano za pomocą modułów gęstości sieciowania (v_e = 0,220–0,613 mol/dm^3, v_t = 0,105–0,441 mol/dm^3) i parametru oddziaływania polimer-rozpuszczalnik (χ = 0,595–0,822). Właściwości termiczne otrzymanych hydrożeli zawierających EGDMA poprawiły się wraz ze zmniejszeniem zawartości wody (70,3–55,1), natomiast przepuszczalność tlenu się pogorszyła (P = 48,6–44,3).

Słowa kluczowe: kopolimery o wysokim stopniu konwersji, parametry pęcznienia, właściwości mechaniczne, przepuszczalność tlenu, gęstość sieciowania.

In the last two decades, the field of synthetic and natural hydrogel study has extended drastically, primarily on the grounds that hydrogels perform well for different applications [1]. Hydrogels refer to the hydrophilic polymers that absorb water and are insoluble in water at physiologic temperature, pH and ionic strength because of the presence of a three-dimensional network [2]. The hydrophilicity of hydrogel is because of the hydrophilic groups, like amide $CONH_2$, CONHR, amine NH_2, carboxyl COOH, and hydroxyl OH group, in the polymer backbone or substituent groups. The network consists of homopolymer, copolymer or terpolymer and is insoluble because of the presence of physical or chemical crosslink [3]. The crosslinks provide the network structure and physical integrity. Their thermodynamic compatibility with water allows the network to swell in aqueous media from 10 % to hundreds times their dry weight [4]. The more hydrophilic the polymer and/or monomers used to prepare the hydrogel, the higher the degree of hydration. This hydration can also, to some extent, be controlled through crosslink density. The higher degree of crosslinking for a given polymer system will result in a corresponding decrease in water content.

The high water content gives these materials excellent biocompatibility to be used in immobilization of proteins, peptides and other biological compounds. Some other biomedical applications of hydrogels include controlled drug delivery [5], blood-compatible membranes [6], bone ingrown sponges [7], burn dressings [8], and contact lenses [9].

Hydrophilicity, softness and oxygen permeability are the requirements that polymeric materials must fulfill to permit their use in certain medical application fields. The usefulness of a range of polymeric materials in applications related to medical fields (*e.g.*, contact lenses) has already been demonstrated. However, despite their properties that make them suitable for different medical applications, polymeric materials also have features that constrict their use. For example, the poly(methyl methacrylate) (PMMA) material employed in contact lenses lacks sufficient oxygen permeability and hydrophilicity, despite possessing the demands of rigidity and durability [10]. On the other hand, the poly(hydroxyethyl methacrylate) (PHEMA) material used in hydrogel contact lenses does possess hydrophilicity and softness, but it is not durable or dimensionally stable and lacks sufficient oxygen permeability [11]. Similarly, another polymeric material popular in medical applications is silicone rubber, which displays softness, durability, and high oxygen permeability, although it lacks hydrophilicity.

Hence, polymeric materials must meet all three requirements of being hydrophilic, soft and oxygen permeable in order to expand the medical applications and fields in which they can be employed. The ideal contact lens material would incorporate the favorable properties of each of these materials, whilst not exhibiting their drawback, *i.e.*, a copolymer of MMA, HEMA and silicon rubber may give the optimum properties for a contact lens [12]. For other prosthetic devices, features such as increased hydrophobicity, softness after hydration and gas permeability are also very useful and desirable.

It is clear that the combination of a hydrophilic group with a siloxane group in the polymer may give a suitable biomedical material, and it may have the following properties: soft when hydrated with a good degree of swelling, a moderate elastic modulus, oxygen permeable, chemical stable and transparent.

Based on what has been reported before, two types of monomers have been chosen to prepare hydrogels for biomedical applications:

– 3-(Trimethoxysilyl)propyl methacrylate (TMSPM) was chosen as the hydrophobic component containing a siloxane group. PTMSPM has transparency, low wettability, a moderate elastic modulus and oxygen permeability.

– *N*-vinylpyrrolidone (NVP) was chosen as the hydrophilic component. The very high glass transition temperature (T_g) of its polymer makes it difficult for processing. Its high water content causes mechanical instability, but it is transparent and oxygen permeable.

A copolymer of NVP and TMSPM, however, shows a range of incompatibility. This is interphase with a third component, *viz.* ethylene glycol dimethacrylate (EGDMA) in addition to its basic function as a crosslinking agent.

EXPERIMENTAL PART

Materials

Commercial samples of monomers (NVP) and 3-(trimethoxysilyl)propyl methacrylate (TMSPM) from Aldrich

Chemical Co. were purified by passing them through an aluminum oxide (Al_2O_3) column (2.5 × 15 cm) until colorless products were obtained. The initiator benzoyl peroxide (BPO) was recrystallized from chloroform and dried in a vacuum. Ethylene glycol dimethacrylate (EGDMA), dichlorodimethylsilane (DMDCS), methanol and deionized water were used as received.

Preparation of xerogels

Sample ampoules which have enough surface area and 13 mm diameter, were used to be suitable for the isothermal condition during the polymerization. The ampoules were siliconized with a 2 % solution of DMDCS in chloroform and kept in an air oven for one day at 75 °C to allow the removal of polymer rods. Monomers' mixture of 1 g TMSPM/9 g NVP containing 0.5 wt % BPO as initiator and different amounts of EGDMA as crosslinker (0, 1, 2, 3 and 4 wt %) was made up in a small stopper flask. The mixture was stirred for 15 minutes, and then transferred to the glass ampoules which have been siliconized previously. The contents of tubes were purged with nitrogen for (15 minutes) prior to the reaction in order to remove all oxygen. The glass ampoules were placed in a water bath at 50 °C, and allowed to polymerization for a specified time (2 days). The temperature is then raised and the tubes are placed in an oven at 70 °C for another one day. At the end of this time, polymerization is normally completed, after which the polymerized rods were removed from the tubes. The rods were then post cured for one day at 70 °C to complete the polymerization process and relieve any mechanical stresses present. The resulting xerogels were cut into a disk and put in methanol to remove the residual unreacted monomers. All discs were dried exhaustively in an oven at 35 °C to constant weight. The structure of NVP-co-TMSPM crosslinked *via* EGDMA is shown in the following Scheme A.

Methods of testing

Characterization of the structure

– FT-IR spectra of the copolymers were recorded using Perkin Elmer-1650 spectrometer on KBr pellets in the range 280–4000 cm^{-1}.

– The ^{1}H-NMR of the copolymers was recorded with a JOEL JMTC-500/54/SS (500 MHz) spectrometer using dimethylsulfoxide (DMSO) as the solvent and tetramethylsilane (TMS) as the internal standard.

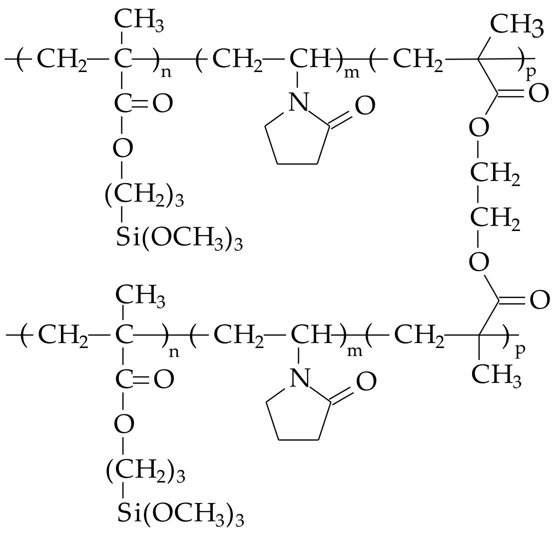
Swelling studies

The swelling of the discs was carried out at room temperature 25 °C. The known weight and diameters of dried discs were put in sample vials (50 cm^3). The swelling time was counted from the moment when the deionized water was added into the vial. At regular time intervals, the swollen discs were taken out using tweezers, and the excess water on the surface of the discs was removed by wiping with the edge of Whitman No. 1 qualitative filter paper. They were weighted and returned to the vials immediately. The water content (*EWC*), reduction in the weight of the xerogels, extension ratio (*ER*) and volume fraction of polymer (ϕ_2) were calculated as [13]:

$$EWC = \frac{(W_s - W_d)}{W_s} \cdot 100\ \% \tag{1}$$

$$\text{Weight loss} = \frac{(W_0 - W_d)}{W_0} \cdot 100\ \% \tag{2}$$

where: W_0, W_s, W_d – the weights of the xerogel, swollen sample after 30 days fully hydrated, and after drying in an oven at 40 °C for 48 h, respectively.



Scheme A. Schematic illustration of the structure of NVP-*co*-TMSPM crosslinked *via* EGDMA

$$ER = \frac{d}{d_0} \quad (3)$$

$$\phi_2 = \left(\frac{d}{d_0}\right)^3 \quad (4)$$

where: d_0, d – the diameters of dry and fully hydrated discs, respectively. Thus, the volume fraction of water ϕ_1 in the hydrogel at equilibrium is equal to $1 - \phi_2$.

Compression measurements

An Instron 3366 machine analyzer was used for compression strain-stress testing. The crosshead speed was set at a fixed rate of 2 mm/min, and the load was run until the sample was broken. For testing, the hydrogels were cut into strips with dimensions of 25 mm in length, 5 mm in width and 2 mm in thickness.

Young's modulus (E) for the hydrogels was obtained as the slopes in plots of the stress (τ) *versus* strain ($\lambda - 1$), as follows:

$$\tau = E\,(\lambda - 1) \quad (5)$$

where: τ – the applied force per unit area of hydrogel, λ – the ratio of deformed length (l) of hydrogel to its undeformed length (l_0).

The effective crosslinking density (v_e) of hydrogels can be obtained from the compression-strain measurements *via* the kinetic theory of rubbery elasticity [14]:

$$\tau = G\,(\lambda - \lambda^{-2}) \quad (6)$$

$$G = RT\, v_e \phi_2^{1/3} \quad (7)$$

where: G – can be obtained from the slope of the stress τ *versus* $\lambda - \lambda^{-2}$, ϕ_2 – the volume polymer fraction, R – the gas constant (8.314 J · K^{-1} · mol^{-1}), T – the absolute temperature.

The polymer/solvent interaction parameter, χ, which represents the specific interaction between water and polymers, can be calculated from the Flory-Rehner Equation [15]:

$$\ln(1-\phi_2) + \phi_2 + \chi\phi_2^2 + v_e V_1(\phi_2^{1/3} - 2\phi_2 f^{-1}) = 0 \quad (8)$$

where: V_1 – the molar volume of water (18.05 · 10^{-3} dm^3/mol at 298 K) [16], f – the functionality of the crosslinking agent.

The molecular mass between crosslinks, M_c, can be calculated *via* Eq. (9), in which ϱ is the density of the xerogel:

$$M_c = \varrho / v_e \quad (9)$$

The theoretical crosslinking density v_t was calculated from the following relationship:

$$v_t = C\frac{f}{2} \quad (10)$$

where: C – the concentration of crosslinking agent with functionality f. Because $f = 4$ for EGDMA [16], Eq. (10) is reduced to:

$$v_t = 2C \quad (11)$$

The values of C were calculated from the weight concentration of EGDMA by using 198.22 g/mol as the molar mass of EGDMA and by taking the densities of the xerogels.

Oxygen permeation evaluation

Stainless steel filter holder (Merck, Frankfurter, Darmstadt, Germany) was used for oxygen permeation experiments. Glass soap bubble flowmeter was employed for measuring rate of permeate stream. Glass soap bubble flowmeter is useful for measuring any gas flow rate and it gives accurate measurement [17, 18]. The gases below the surface of a soap bubble solution and the bubble moves up the flowmeter. We measured the time needed to move the edge of the bubble from one line to another. To ensure accuracy in our experiments, the gas permeation test was repeated two times in the steady state. Permeability across polymer matrix can be described as follows [19]:

$$(P / L) = Q / (A \cdot \Delta p) \quad (12)$$

where: P – permeability, L – hydrogel thickness, Q – gas flow (at standard pressure and temperature), A – the hydrogel effective area, and Δp – the differential partial pressure through the sample. The common unit of permeance is GPU and 1 GPU is equal to 1 · 10^4 Barrer.

Thermal properties

Thermal degradability of the polymer was studied by TGA using Perkin Elmer in a nitrogen atmosphere at a heating rate of 10 °C/min from 0 to 800 °C and glass transition temperature (T_g) was determined using a DSC-Mettler calorimetric system.

RESULTS AND DISCUSSION

Characterization of copolymer

The structure of NVP/TMSPM copolymer is confirmed by FT-IR as shown in Fig. 1.

The absorption bands which appear in the FT-IR spectra of the copolymer (Fig. 1c) belong to the stretching vibration in different functional groups of corresponding homopolymers (Figs. 1a, 1b). The absorption bands of NVP/TMSPM copolymer are as follows: 2925 cm^{-1} (alkane

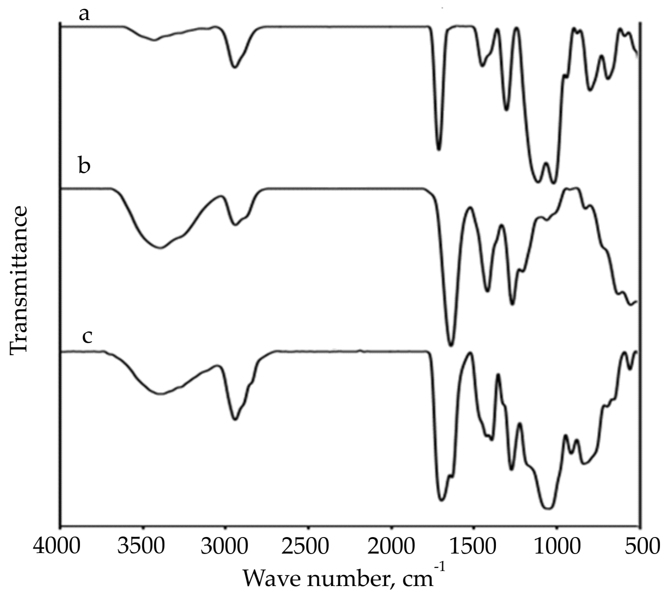


Fig. 1. FT-IR spectra of: a – PTMSPM, b – PNVP, c – NVP-*co*-TMSPM

C-H), the carbonyl absorption of TMSPM observed at 1710 cm^{-1} (ester C=O), 1650 cm^{-1} (tertiary amide C=O), 1270 cm^{-1} (amide C-N), 1075 cm^{-1} (Si-O), 850 cm^{-1} (Si-C) and alkane C-H bending vibration at about 1400 cm^{-1}.

Figure 2 shows ^{1}H-NMR spectrum of the copolymer. Methylene protons in NVP ring resonate in 2.5, 3.2 and 4.4 ppm, while CH$_2$ protons for main chain backbone of monomers resonate at 1.8–2.4 ppm. CH proton for main chain backbone of NVP resonates at 4.6 ppm. The signal corresponding to the protons of the methoxy groups linked to the silicon atom in TMSPM at about 3.5 ppm can be clearly observed. The ester and methyl groups in TMSPM resonate at 3.8 and 1.2 ppm, respectively. The stronger peak appearing at about 6.9 ppm could be attributed to the proton of =C-H.

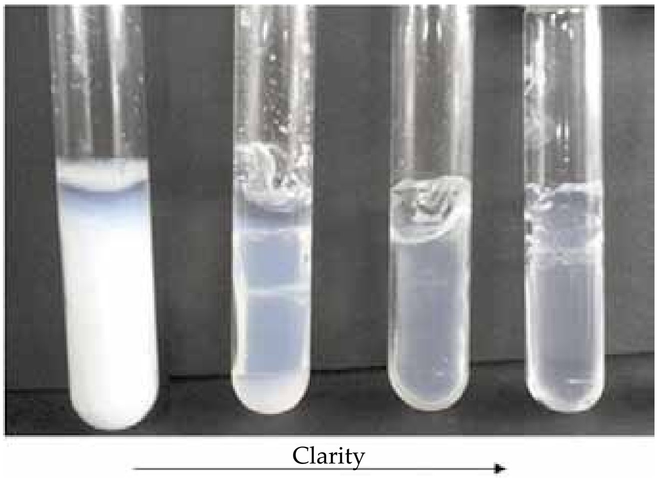


Fig. 3. Picture of some prepared xerogels with different optical clarity

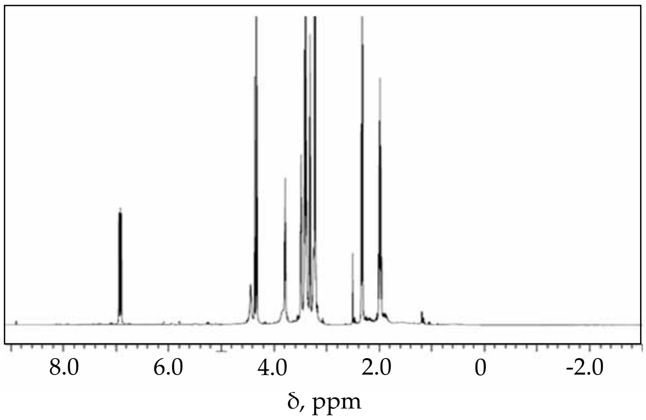


Fig. 2. ^{1}H-NMR spectrum of NVP-*co*-TMSPM copolymer

Optical homogeneity

When the preparation process of xerogels and hydrogels was completed, a visual assessment of homogeneity and optical clarity was made. Figure 3 shows picture of some prepared xerogels with different degree of optical clarity. The hydrogel and xerogel without EGDMA are opaque to translucent, respectively. The results clearly reveal that: the increased in compatibility with concentration of EGDMA enhanced transparency for xerogels and hydrogels; this may be explained by the fact that EGDMA increases compatibility in addition to functioning as a crosslinking agent, yielding enhanced transparency for xerogels. In addition, the improvement of optical homogeneity may be expected from the fact that, the introduction of EGDMA as a crosslinking agent increases the crosslink density, and hence restricts the mobility of the polymer chain. Figure 4 indicates that translucent xerogel requires only 2 wt % EGDMA for transparency, and the opaque hydrogel requires 3 wt % of EGDMA. Light transmission of UV visible spectra confirms these results; an increase in the transmission is expected as the

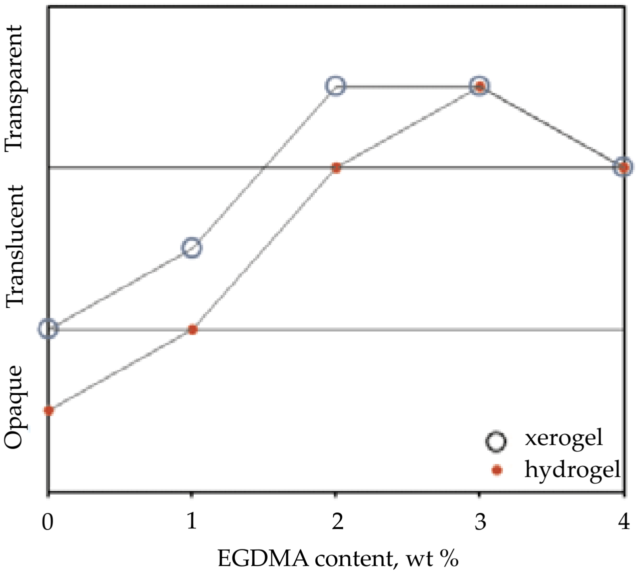


Fig. 4. Optical homogeneity of NVP90/TMSPM10 xerogels and hydrogels with various amount of EGDMA

Table 1. Swelling parameters of NVP90/TMSPM10 hydrogels with different amount of EGDMA

EGDMA wt %	*EWC* %	*ER*	ϕ_2	ϕ_1	Weight loss %
0.0	72.05	1.53	0.277	0.723	20.23
1.0	68.16	1.32	0.429	0.571	16.35
2.0	64.02	1.28	0.471	0.529	13.84
3.0	61.16	1.24	0.516	0.484	11.92
4.0	58.19	1.20	0.567	0.433	10.56

EGDMA content increased. A maximum transmission of more than 88 % has been achieved through xerogel discs (1 mm thickness).

Swelling behavior

Table 1 summarizes the swelling properties of five NVP90/TMSPM10 copolymers with different amounts of EGDMA within the range 0–4 wt %. All swelling parameters decrease with increasing amount of EGDMA present in the gel formation system. The *EWC* values are in the range 58.19–72.05 %. The results clearly reveal that with increasing crosslinker content in the hydrogel, the swelling capacity significantly decreases. The observed results are quite common and may be explained by the fact that the greater number of crosslinks in the hydrogel results in a restrained mobility of the macromolecular chains that does not permit water penetration and brings about a depression in the swelling ratio [20]. Another explanation for the observed finding may be that the increasing number of crosslinks in the hydrogel lowers the molecular weights between the crosslinks [21] and thereby reduces the free volumes between the macromolecular chains, which then become accessible to penetrant water molecules. It was found from Table 1 that the weight loss in the hydrogels (20.23 %) decreases to its half value (10.56 %) by the increasing of crosslinker to 4 wt %. The decreasing in *ER* with increasing EGDMA amount is attributed to the increase of the crosslinking density.

Tensile testing

The initial crosslinking concentration also plays an important role in determining mechanical properties of hydrogels. A higher EGDMA concentration generally leads to a stronger and harder gel with lower water content. Results derived from stress-strain measurements as depicted in Table 2 show that an increase in the concentration of EGDMA results in increasing Young's and shear modulus. Young's moduli are significantly smaller for hydrogels, which exhibit more swelling. Thus, when EGDMA content decreases, the final material is very soft with poor mechanical properties (lower modulus). This indicates that the degree of crosslinking in the network played a major role in the mechanical properties of the hydrogel. As it is well known from Fig. 5, the extent of crosslinking in the network is inversely proportional to the amount of water found on swelling and directly proportional to the Young's modulus. For an elastic hydrogel, the ratio of *E* to *G* should be equal to 3.0 for a small strain. From the set of data in Table 2, the values of *E*/*G* do not deviate significantly from the average value of 2.8.

Table 2. Tensile properties of NVP90/TMSPM10 hydrogels system containing different concentration of EGDMA

EGDMA content wt %	Young's moduli (*E*) MPa	Shear moduli (*G*) MPa	*E*/*G*
0.0	0.570	0.217	2.626
1.0	1.158	0.413	2.803
2.0	1.652	0.588	2.856
3.0	2.831	1.059	2.787
4.0	3.531	1.359	2.803

Network structures

Determination of share modulus (*G*) allowed the effective crosslinking density (v_e) to be evaluated; thereby yielding the molar mass between crosslinks (M_c). Table 3 contains the effective crosslinking density in the swollen state. Increase in crosslinking agent content enhanced hydrophobic bonding and, consequently, the effective crosslink density increased. Table 3 shows also the values of densities, concentration and theoretical crosslinking densities.

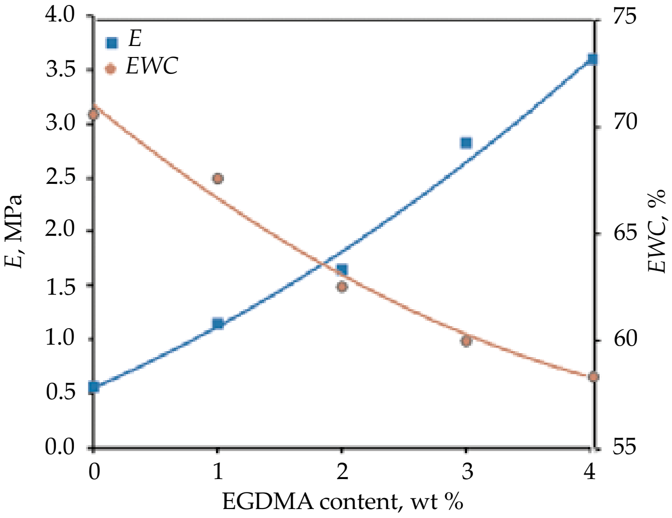


Fig. 5. The dependence of *EWC* and Young's modulus (*E*) for NVP90/TMSPM10 hydrogels system on the concentration of EGDMA

Table 3. Theoretical network parameters of xerogels containing different concentrations of EGDMA with effective network densities of the swollen gel

EGDMA wt %	P_x kg/dm^3	Moles	V (molar volume of xerogel) dm^3	$C \cdot 10^{-2}$ mol/dm^3	v_t mol/dm^3	v_e mol/dm^3
0.0	1.019	–	0.0981	–	–	0.143
1.0	1.037	0.0050	0.0964	5.253	0.105	0.220
2.0	1.059	0.0100	0.0944	10.592	0.211	0.304
3.0	1.085	0.0151	0.0925	16.411	0.328	0.533
4.0	1.096	0.0201	0.0917	22.080	0.441	0.613

P_x – here means the density of xerogel not permeability, so its unit is kg/dm^3; Moles – number of EGDMA moles.

In general v_e varies with v_t according to the following equation [22]:

$$v_e = \alpha + \beta v_t \tag{13}$$

where: α – the value of effective crosslinking induced even in the absence of any included chemical crosslinker. It may arise from physical crosslinking, chain transfer, defects in the network and presence of dimethacrylates as an impurity in methacrylates [23].

The parameter β is a measure of crosslinking efficiency ($\beta = v_e / v_t$ when $\alpha = 0$). The linear dependence of v_e on v_t according to equation (13) is indicated in Fig. 6, and by applying a linear least-square fit of the data, the following interrelationship was found:

$$v_e = 0.065 + 1.25 v_t \tag{14}$$

For the present system obtained by thermal polymerization, the values of v_t are smaller than v_e. The system *n*-butyl acrylate/*N*-vinyl-2-pyrrolidone copolymer which has been prepared by irradiation has shown the same trend, but with a large discrepancy between v_e and v_t ($v_e \gg v_t$) where irradiation contributed to additional chemical crosslinks [24], because poly(acrylates) are known to have a high tendency to crosslink under irradiation. The average molecular weight between consecutive crosslinks (M_c) is another structural parameter characterizing the three-dimensional network structure. It is directly related to the crosslink density. The M_c values determined for every gel system are given in Table 4. The results obtained show that the average molecular weight between the crosslinks is affected by the concentration of EGDMA and significantly decreased with increasing the crosslinking concentration.

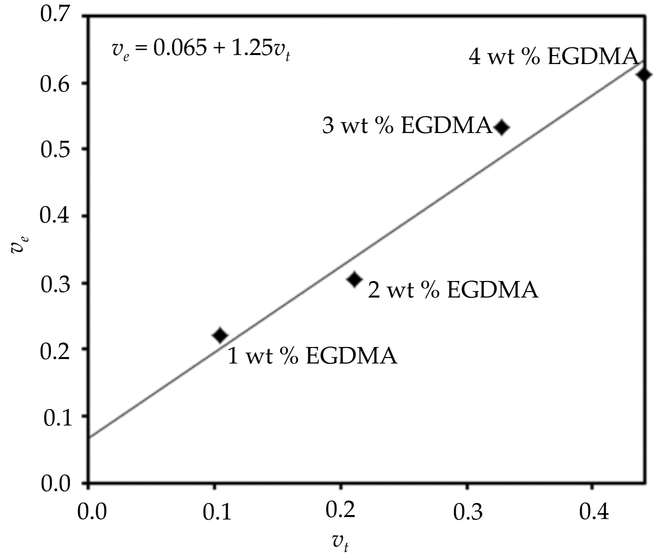


Fig. 6. Dependence of measured effective crosslink density (v_e) on theoretical crosslink density (v_t) for the gels at different amounts of EGDMA

The polymer-solvent interaction parameter χ at swelling equilibrium represents the specific interaction between water and polymers. Values of $\chi > 0.50$ suggest that the solvent employed is thermodynamically poor. Table 4 reports the values of the polymer-solvent interaction parameter; an increase in EGDMA content led to an increase in χ. This behavior can be explained by the relative hydrophobicity of the EGDMA. All calculated χ values exceeded 0.50, thus an increase in the EGDMA content leads to a reduction in the polymer/water interaction.

Thermal analysis

In addition to characterization the polymeric sample, the thermal analysis processes provide important information regarding the effect of temperature on sample's physical properties. Thermal analysis can be used to characterize a polymer before, during, or after crosslinking. The glass transition temperatures (T_g) were measured for constant composition of NVP90/TMSPM10 xerogels with different concentration of EGDMA (0, 1, 2, 3 and 4 wt %). The T_g values of xerogels were 97.48, 110.50, 121.50, 130.05 and 138.02 °C, respectively. These values are lower than T_g of PNVP (172 °C) and higher than T_g of PTMSPM (45 °C). As expected, the data revealed that with an increase in EGDMA content, the value of T_g increased. The thermal stabilities of the xerogels were determined by TGA and are presented in Fig. 7.

It is observed that the percentage weight loss decreased against the temperature by increasing amount of EGDMA in xerogels. The larger amount of a crosslinking agent restricts the segmental mobility of the macromolecular chains, thereby the T_g increased and weight

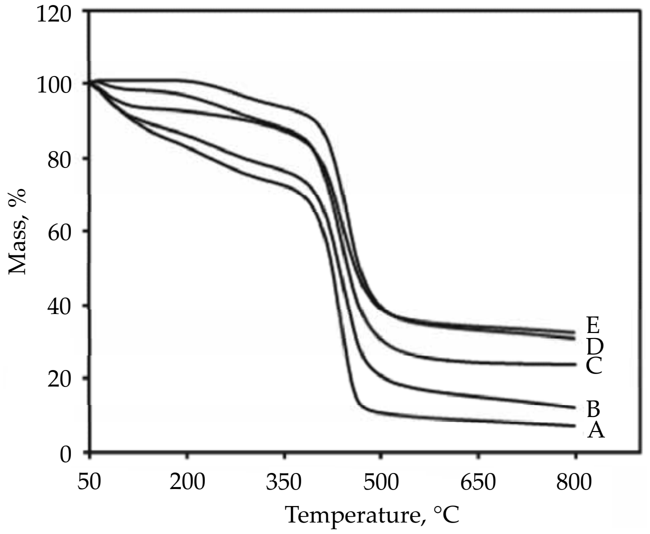


Fig. 7. TGA thermograms for NVP90/TMSPM10 xerogels containing: A – 0.0, B – 1.0, C – 2.0, D – 3.0, E – 4.0 wt % EGDMA

loss decreased, this is a common effect of crosslinker on thermal properties of a polymer [25].

Oxygen permeability

The permeability of silicone compounds for such gases as oxygen, makes them useful for medical applications in which increased aeration is desired. The enhancement of oxygen permeability in siloxane compounds is associated with high relative proportions of silicon-oxygen and silicon-carbon bonds. These long bonds lead to a free volume element which is greater than in other organic compounds [10]. Table 5 shows the relationship between water content and oxygen permeability. From this table two points can be clearly observed, the values of oxygen permeability of the prepared hydrogels (> 50 Barrer) are higher than oxygen permeability of other nonsiliconehydrogels [26, 27] such as polyvinylpyrrolidone (35.1 Barrer), poly(hydroxyethyl methacrylate) (10.5 Barrer) and their copolymer (28 Barrer). In addition, the oxygen permeability enhanced as TMSPM composition increased in the feed mixture. For conventional hydrogels, oxygen transport is provided by water contained within the polymer network with an exponential relationship between permeability and *EWC*. An increase of EGDMA decreases the water content of hydrogels and this leads to a reduction in the amount of oxygen permeable. This occurs since oxygen is able to pass through the water rather than through the material itself [28].

CONCLUSIONS

High conversion copolymers were successfully prepared by polymerization mixture of NVP/TMSPM and EGDMA *via* free radical polymerization using benzoyl peroxide as initiator. Optical clarity of products enhances with increasing EGDMA content. Swelling properties have been determined in deionized water and it was found out that they decrease with addition of EGDMA. Stress-strain measurements yielded the Young's module, the effective crosslinking density and the copolymer-water interaction parameters. The restriction of chain mobility has been shown by the increase of the Young's modulus of hydrogels and glass transition temperature of xerogels. The oxygen permeability of hydrogels decreases with the water content decrease.

Table 4. Network parameters of NVP90/TMSPM10 hydrogels containing different concentrations of EGDMA

EGDMA wt %	ϕ_2	$M_c \cdot 10^{-3}$ g/mol	χ
0.0	0.277	7.604	0.595
1.0	0.429	4.713	0.702
2.0	0.471	3.483	0.732
3.0	0.516	2.035	0.767
4.0	0.567	1.787	0.822

Table 5. Effect of water content on oxygen permeability of NVP90/TMSPM10 hydrogels containing different concentrations of EGDMA

EGDMA wt %	Water content %	Oxygen permeability Barrer
0.0	70.3	48.6
1.0	66.7	47.5
2.0	62.4	46.4
3.0	57.1	45.8
4.0	55.1	44.3

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