DMA analysis of the structure
of crosslinked poly(methyl methacrylate)s

Izabela M. Barszczewska-Rybarek[1]*, Anna Korytkowska-Wałach[2],
Małgorzata Kurcok[3], Grzegorz Chladek[4], Jacek Kasperski[5]

[1] Department of Physical Chemistry and Technology of Polymers, Silesian University of Technology, Gliwice, Poland.
[2] Department of Organic Chemistry, Bioorganic Chemistry and Biotechnology, Silesian University of Technology, Gliwice, Poland.
[3] Institute for Engineering of Polymer Materials and Dyes, Paint and Plastics Department, Gliwice, Poland.
[4] Institute of Engineering Materials and Biomaterials, Silesian University of Technology, Gliwice, Poland.
[5] Chair of Prosthetics and Dental Materials, Department of Dental Prosthetics, Medical University of Silesia in Katowice,
School of Medicine with the Division of Dentistry in Zabrze, Zabrze, Poland.

Purpose: This paper presents the study aimed at the development of crosslinked poly(methyl methacrylate)s (X-PMMA) of varied crosslink density and the investigation of the relationships between the polymer network structure and dynamic mechanical properties. *Methods*: A series of model X-PMMA networks were crosslinked by the introduction of: 1, 2, 5, 10 and 20% of triethylene glycol dimethacrylate (TEGDMA). The copolymerizations led to various glass-rubber relaxation properties of the polymer networks, as revealed by dynamic-mechanical analysis (DMA). Glass temperature (T_g) and storage modulus above the T_g ($E'_{rubbery}$) were a sensitive function of network architecture. DMA data were used for calculating the network parameter (M_c), crosslink density (q) and its alternative measure – the degree of crosslinking (DX). *Results*: The viscoelastic properties as well as structural parameters calculated from those showed correlation with the amount of the crosslinker. The increase in TEGDMA content resulted in the T_g, q and DX increases, whereas M_c decrease. The possible incomplete conversion of double bonds was detected in the DMA analysis, which was confirmed by the degree of conversion (DC), measured by FTIR spectroscopy. Additionally, some amount of sol fraction was found by 1H NMR experiments. *Conclusions*: The structure-property relationships developed for the system presented in this work could be useful in tissue engineering, where X-PMMA is applied. The direct measure of storage modulus values before and above glass transition may serve as a simple and fast indicator of the X-PMMA crosslink density.

Key words: PMMA, corosslink density, network parameter, DMA, storage modulus, glass temperature

1. Introduction

The importance of poly(methyl-methacrylate) in biomedical applications is evident [2], [3], [6], [14], [20]. Many of them employ a crosslinked form of poly(methyl methacrylate) (X-PMMA). X-PMMA is used as bone cements [3], [8], [20], carrier systems in medical technologies [11] and teeth dentures [15], [18]. Structurally, crosslinked poly(methyl methacrylate)s are polymer networks consisting of poly(methyl methacrylate) primary chains, pendant side groups or chains, derived from the crosslinking monomer mole-

cules with one double bond reacted, and crosslinks formed by those crosslinker molecules with both the double bonds reacted [10]. The system may also contain some entanglements, working as physical crosslinks as well as some amounts of a soluble fraction, consisting of unreacted monomer or short, linear oligomers (Fig. 1) [21]. The network molecular structure, equally with the chemical structure, governs physico-mechanical properties of thermosets [5]. Therefore, it is of great scientific and technological interest to analyze and understand the structure and properties of crosslinked poly(methyl methacrylate). Especially, easily accessible results as well as simple calculations leading to

rapid and accurate conclusions are of the highest interest.

One of the experimental techniques most frequently used in the characterisation of the structure of crosslinked polymers is dynamic mechanical analysis (DMA). Variation of loss tangent ($\tan\delta$) with temperature yields directly the value of glass transition temperature (T_g), whereas storage modulus within the rubbery plateau (E'_{rubbery}) can be used to evaluate network parameter (M_c) – the molecular weight between crosslinks [16]. Classical theory of rubber elasticity, which is often used for this purpose, assumes that the elastic modulus is independent of the network chemical structure and depends primarily on the tightness of the network structure. The E'_{rubbery} correlates with M_c according to the following formula [9]

$$M_c = \frac{3RTd}{E'_{\text{rubbery}}} \qquad (1)$$

where T is the absolute temperature at which the modulus is determined, d – polymer density, and R – the universal gas constant.

The M_c can be easily transferred into the crosslink density (q) with the following relationship [1]

$$M_c = \frac{MW}{q} \qquad (2)$$

where MW is the monomer molecular weight.

Some less known application of DMA, dealing with the degree of crystallinity of polymers, had been reported by Khanna et al. [12]. The method was based on the comparison of differences in storage modulus values ($\Delta \log E'$) below and above T_g for crystalline linear polymers and for an amorphous one, to yield directly the degree of crystallinity of the former. If one did the same for a polymer network, assuming chemical crosslinks work similarly to crystallites, that can be recognized as physical crosslinks [17], another physical interpretation of those data may be considered. For instance, it could be thought as a measure of polymer network crosslink density. The following formula, developed for estimating the degree of crystallinity by Khanna, was proposed in this work for assessing the degree of crosslinking (DX)

$$DX = 1 - \frac{(\Delta \log E')_{\text{sample}}}{(\Delta \log E')_{\text{PMMA}}} \qquad (3)$$

where the non-crosslinked bulk PMMA was used as a reference amorphous material (($\Delta \log E'$)$_{\text{PMMA}}$ = 3.22).

The values of $\Delta \log E'$ measured for a series of poly(methyl methacrylate)s crosslinked with a varied amount of triethylene glycol dimethacrylate (TEGDMA) have been taken to calculate the degree of crosslinking of the network (DX).

2. Materials and methods

The X-PMMAs were received in bulk. The moulds built of two glass plates, a spacer 2 mm thick and clamps were filled by use of a syringe with mixtures of methyl methacrylate (MMA, Acros, Belgium) and triethylene glycol dimethacrylate (TEGDMA, Sigma-Aldrich, USA) – in the amounts of: 1, 2, 5, 10 and 20 mol.%, with 1 wt.% of benzoyl peroxide (BPO, Acros, Belgium) – the initiator. The moulds were placed in a water bath and temperature was raised gradually from 56 to 85 °C for 4.5 hrs. After that, the moulds were transferred to a drying oven and the temperature was raised from 85 to 120 °C within 18 hrs.

The rectangular samples of polymers (length × width × thickness: 50 mm × 5 mm × 2 mm) were examined by using Dynamic Mechanical Analysis (Polymer Laboratories MK II DMA apparatus, UK). Experiments were performed in bending mode and a frequency of 1 Hz, over the temperature range from 20 to 200 °C. The T_g was taken as the temperature at the $\tan\delta = f(T)$ peak maximum. Values of storage modulus (E') were read off directly from variations of $\log E'$ with temperature, 40 degrees before β and 40 degrees above α transition. The network parameter (M_c) was calculated according to equation (1) and transferred into crosslink density (q) according to equation (2). The degree of crosslinking (DX) was calculated by use of equation (3).

The polymer densities (d) were determined according to the Archimedes' principle, on the Mettler Toledo XP Balance with 0.01 mg accuracy (Switzerland) with the density determination kit at 25 °C. Water was used as the immersing liquid.

1H NMR experiments (300 MHz spectrometer, Varian UNITY/INOVA, USA) were performed in the deuterated chloroform solution (Acros, Belgium), using *tetramethylsilane* (TMS) as a reference (Sigma-Aldrich, USA). Powdered samples of X-PMMAs were soaked in CDCl$_3$ for 1 week. Then the extract was filtrated and the filtrate was examined with 1H NMR.

FT IR spectra were recorded on a Bio-Rad FTS 175C spectrometer (Bio-Rad Laboratories, Germany), with 128 scans at resolution of 1 cm^{-1}. The absorption intensity of selected peaks was measured after the baseline correction in the 2000–800 cm^{-1} region. Monomers were analyzed as very thin films formed

onto potassium bromide pellet. The cured samples were pulverized into fine powder with a planetary ball mill (Pulverisette, Fritsch GmbH, Germany) and next sifted to a particle diameter less than 24 μm. The samples of those polymers were admixed with potassium bromide and examined as pellets. The degree of conversion (*DC*) in polymers was calculated by relating the absorbance of the double bonds stretching vibrations to the peak assigned to the carbonyl stretching vibration – the internal standard, as follows [4]

$$DC = 1 - \frac{(A_{C=C} / A_{C=O})_{\text{polymer}}}{(A_{C=C} / A_{C=O})_{\text{monomer}}} \qquad (4)$$

where $A_{C=C}$ is the absorption of the peak at 1637 cm^{-1}, referring to the C=C stretching vibrations and $A_{C=O}$ is the absorption of the peak at 1718 cm^{-1}, referring to the C=O stretching vibrations.

The results were subjected to statistical analysis with a Statistica 10 software. The distributions of the residuals were tested with Shapiro–Wilk test and the equality of variances were tested with Levene test. When the distributions of the residuals were normal and the variances were equal the one-way analysis of variance ANOVA ($\alpha = 0.05$) was used, and if alternative hypothesis was accepted the HSD Tukey post hoc test was used to determine the differences between mean values ($\alpha = 0.05$). When the distributions of the residuals were not normal and/or the variances were not equal the Kruskal–Wallis tests was used ($\alpha = 0.05$).

3. Results

Five polymer networks of varied crosslink density were obtained by the thermal copolymerization in bulk of methyl methacrylate (MMA) with triethylene glycol dimethacrylate (TEGDMA) (Fig. 1). The TEGDMA content in the polymerizing mixture, being of 1, 2, 5, 10 and 20 mol.% allowed the polymer network crosslink density to be controlled.

DMA was used to determine glass temperature and dynamic mechanical properties of the X-PMMA networks. The curves of the loss tangent and bending storage modulus as a function of temperature were obtained and analyzed.

The tanδ curves (Fig. 2) showed two distinct relaxations, which appeared as narrow peaks. They were labeled as β and α. The peak maximum corresponding to β transition (T_β) was less evident and it was centered at about 105 °C. Transition a was recognized
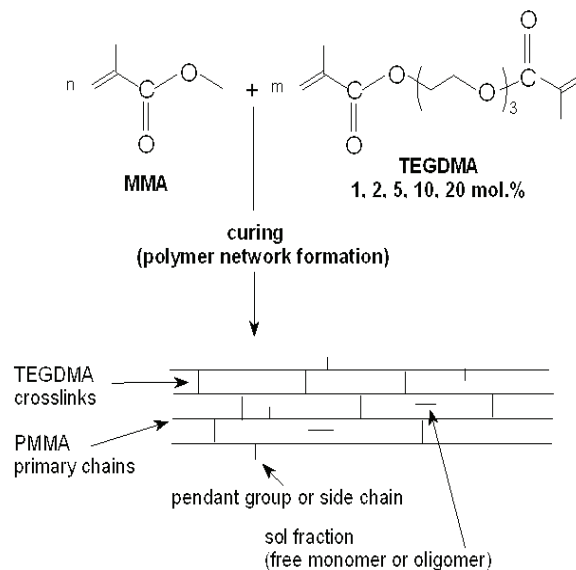

Fig. 1. The chemical structure of the monomers used in the study and the general representation of the molecular structure of the polymer networks formed
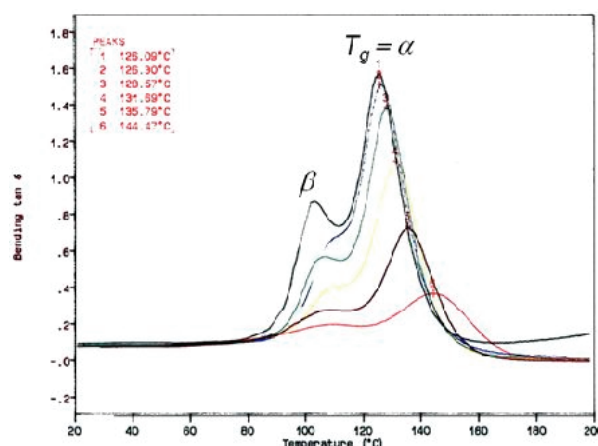

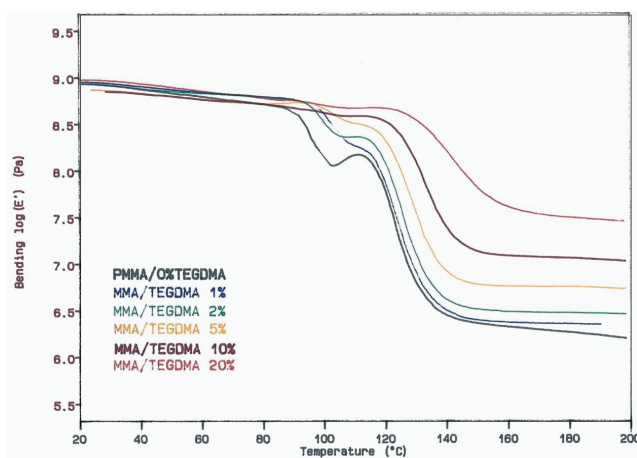Fig. 2. The set of tanδ curves for X-PMMA networks examined

Fig. 3. The set of logE' curves for X-PMMA networks examined

Table 1. The T_g and T_β of X-PMMAs (mean values with standard deviations)
and one-way AVOVA test results ($\alpha = 0.05$)

	TEGDMA mol.% fraction					
	0	1	2	5	10	20
T_β ($p = 0.2144$)	102.8 ± 3.9	107.9 ± 4.2	106.9 ± 4.4	110.4 ± 4.8	108.3 ± 4.5	109.4 ± 4.8
T_g ($p < 0.0001$)	126.1 ± 5.0^A	126.3 ± 4.9^A	128.6 ± 4.3^{AB}	131.7 ± 4.5^{AB}	135.8 ± 4.5^{BC}	144.5 ± 5.2^C

Notes: * Groups with the same uppercase superscript letters; (A–C) for each row are not significantly different at the $p < 0.05$ level.

Table 2. The dynamic storage modulus values of PMMA and X-PMMAs (mean values with standard deviations)
with the results of one-way ANOVA ($\log E'_{glassy}$ and E'_{glassy})* or Kruskal–Wallis ($\log E'_{rubbery}$ and $E'_{rubbery}$) tests results ($\alpha = 0.05$)

	TEGDMA mol.% fraction					
	0	1	2	5	10	20
$\log E'_{glassy}$ (Pa) ($p = 0.0078$)	9.18 ± 0.05^A	9.18 ± 0.05^A	9.19 ± 0.04^A	9.06 ± 0.06^B	9.11 ± 0.07^{AB}	9.20 ± 0.06^A
E'_{glassy} (MPa) ($p = 0.0087$)	1513.6 ± 174.3^{AB}	1513.6 ± 180.03^{AB}	1548.8 ± 127.1^A	1148.2 ± 148.06^B	1288.3 ± 186.5^{AB}	1584.9 ± 212.1^A
$\log E'_{rubbery}$ (Pa) ($p < 0.0001$)	5.96 ± 0.05	6.50 ± 0.06	6.69 ± 0.03	6.93 ± 0.02	7.25 ± 0.04	7.67 ± 0.06
$E'_{rubbery}$ (MPa) ($p < 0.0001$)	0.91 ± 0.11	3.16 ± 0.47	4.90 ± 0.34	8.51 ± 0.39	17.78 ± 1.70	46.77 ± 6.64

Notes: * Groups with the same uppercase superscript letters; (A–B) for each row are not significantly different at the $p < 0.05$ level.

as the glass temperature ($T_\alpha = T_g$). It was better resolved and its maximum was centered at about 130 °C. T_β as well as T_g shifted to higher temperatures and the $\tan\delta$ peak lost intensity with increasing TEGDMA content. The DMA transition temperatures of X-PMMAs are reported in Table 1.

Plots of $\log E'$ versus temperature are summarized in Fig. 3, whereas the detailed information for the storage modulus in the glassy (E'_{glassy}) and viscoelastic ($E'_{rubbery}$) states are presented in Table 2.

The E'_{glassy} values were similar and did not depend on the TEGDMA content. The $E'_{rubbery}$ increased significantly as the TEGDMA content increased. The drops of modulus during β and α transitions corresponded to peak maxima in the $\tan\delta$ curves. The less crosslinked network as well as PMMA delivered more evident β relaxation than X-PMMAs having higher crosslink density. After the initial drop in E' caused by β transition, a slight increase in E' was observed. After that, the E' decreased due to the glass transition.

DMA results for E' were used to calculate M_c, q and DX. For this purpose equations (1), (2) and (3) were used, respectively. Additionally, assuming crosslinks as volumeless junction points, $M_{c \, theor}$ was calculated according to the following formula

$$M_{c\_theor} = \frac{MW}{X \times f} \qquad (5)$$

where MW is the MMA molecular weight (100.12 g/mol), X – the molar fraction of TEGDMA, and f – the number of functionalities in the TEGDMA molecule ($f = 2$). In Table 3, the results for $M_{c \, exp}$, $M_{c \, theor}$, q and DX are presented.

The decrease in $M_{c \, exp}$ and the increase in q were accompanied by the increase of the TEGDMA content. The uncrosslinked PMMA had the finished value of $M_{c \, exp}$, whereas $M_{c \, theor}$ was unfinished.

The $M_{c \, exp}$ values determined in DMA experiments for X-PMMA were generally higher than the theoretical $M_{c \, theor}$ values. Exceptionally, the experiment on X-PMMA crosslinked with 1 mol.% of TEGDMA resulted in the opposite result. The value of $M_{c \, exp}$ was slightly higher than the $M_{c \, theor}$ value.

Table 3. The values of $M_{c\,\mathrm{exp}}$, $M_{c\,\mathrm{theor}}$, q and DX for X-PMMAs (mean values with standard deviations)
with the results of one-way ANOVA (d and DX)* or the Kruskal–Wallis ($M_{c\,\mathrm{exp}}$ and q_{exp}) test results ($\alpha = 0.05$)

	TEGDMA mol.% fraction					
	0	1	2	5	10	20
$M_{c\,\mathrm{theor}}$ (g/mol)	∞	5000	2500	1050	550	300
q_{theor}	–	0.02	0.04	0.09	0.18	0.33
d (g/cm^3) ($p = 0.0589$)	1.17±0.01	1.17±0.01	1.18±0.02	1.18±0.01	1.19±0.02	1.20±0.02
$M_{c\,\mathrm{exp}}$ (g/mol) ($p < 0.0001$)	14455±1703	4283±573	2711±194	1569±79	773±71	307±62
q_{exp} ($p < 0.0001$)	0.007±0.001	0.024±0.003	0.036±0.003	0.061±0.003	0.134±0.013	0.338±0.079
DX ($p < 0.0001$)	-	0.17±0.02 [A]	0.22±0.02 [A]	0.34±0.02 [B]	0.42±0.03 [C]	0.52±0.03 [D]

Notes: * Groups with the same uppercase superscript letters; (A–D) for each row are not significantly different at the $p < 0.05$ level.

The FTIR spectroscopy was used to assess the amount of unreacted double bonds in X-PMMA systems under study. Figure 4 presents examples of FTIR spectra of the mixture of MMA with TEGDMA monomers and its cured form. In Table 4, the values of the DC are summarized.
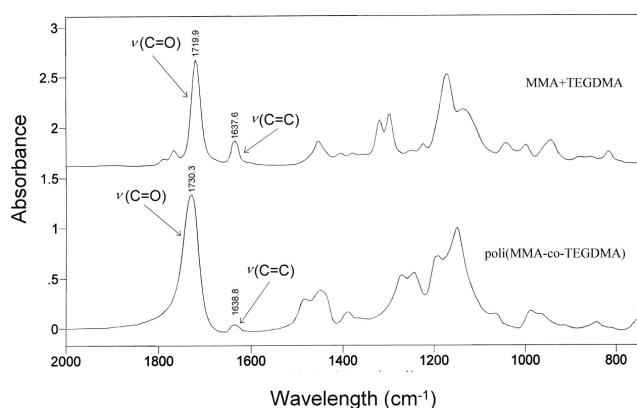

Fig. 4. The exemplary FTIR spectra of the mixture of MMA with 5 mol.% of TEGDMA and its cured form

As shown by examples in Fig. 5, the presence of sol fraction in X-PMMAs under study was detected in 1H NMR experiments, by analyzing the extracts of X-PMMAs in CDCl$_3$.
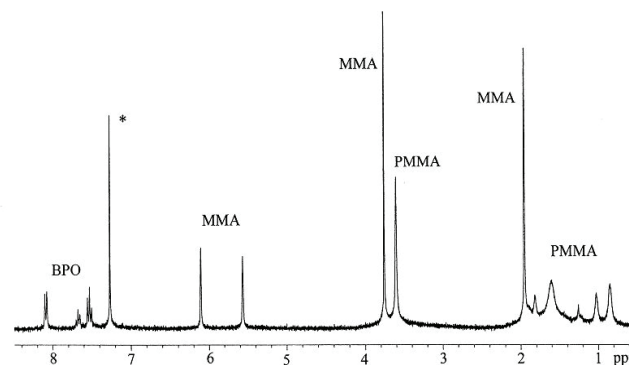

Fig. 5. Exemplary 1H NMR spectrum of sol fraction in X-PMMA, cured with 5% of TEGDMA

4. Discussion

As the data from Table 1 show, the increase in the crosslinker content causes an increase of the polymer network stiffness, which may be illustrated by the linear increase in T_g (R = 0.993, Fig. 6).

It might also be noted that the uncrosslinked PMMA had the T_g of 126.5 °C, which is in accordance with cited data obtained with the same technique [7]. This value is, however, higher than the T_g value mostly reported for this polymer, of 105 °C [13],

Table 4. The DC (mean values with standard deviations) in X-PMMAs under study determined by FTIR and one-way AVOVA test results ($\alpha = 0.05$)

	TEGDMA mol.% fraction					
	0	1	2	5	10	20
DC ($p = 0.6068$)	0.85 ± 0.04	0.85 ± 0.03	0.87 ± 0.04	0.85 ± 0.04	0.87 ± 0.03	0.89 ± 0.04

showing that DMA produces higher T_g values than other techniques, such as differential scanning calorimetry.
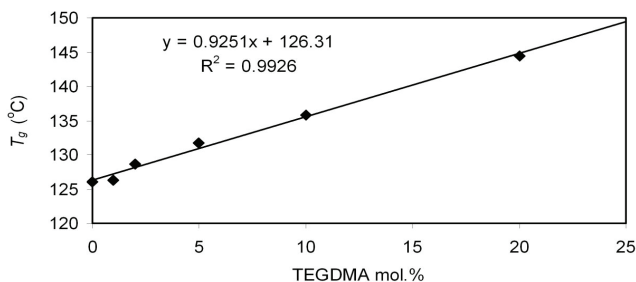

Fig. 6. The correlation between the T_g
and the TEGDMA content

The small peak in the $\tan\delta = f(T)$ plot, preceding T_g, called β transition, may reflect the rotations of methacrylate groups in unreacted MMA or TEGDMA monomers. However, its decreasing intensity with increasing TEGDMA content as well as the accompaniment of a small increase in modulus suggest that it would be rather the post-curing reaction with the aid of double bonds. This might be attributed to the incomplete conversion of double bonds in the material. It points out that after β transition the system gained higher level of crosslinking as the temperature increased and it was manifested by the increase in modulus.

The presence of unreacted double bonds in polymers under study has been proven by FTIR spectroscopy (Fig. 4, Table 4), whereas the presence of sol fraction by 1H NMR (Fig. 5).

The higher the TEGDMA content was, the higher the DC determined by utilizing FTIR technique. The DC was determined in respect to the C=O band absorption, used as an internal standard, and ranged from 0.85 to 0.89. The actual values of DC may be higher, since the carbonyl internal standard produces underestimated values of DC [4]. The differences in DC in X-PMMAs probably result from kinetics of the radical polymerization between two kinds of monomer or from the varied behavior of absorption in carbonyl in MMA and TEGDMA [19].

1H NMR spectra of sol fraction extracted from powdered X-PMMA samples confirmed the presence of sol fraction in X-PMMAs under study. As shown in Fig. 5, an exemplary spectrum of X-PMMA consists of peaks corresponding to the initiator (BPO), MMA monomer as well as PMMA. There were no signals from TEGDMA monomer, which means that the whole amount of this monomer has been built into the insoluble network structure with at least one of the double bonds. The peaks corresponding to the metha-

crylate double bonds may be explained by the presence of unreacted monomer, however they may also originate from the termination of the radical chain by disproportionation.

Tanδ peak loss intensity with increasing TEGDMA content suggests decreasing segmental motion between crosslinks with decreasing length between them, i.e., increasing crosslink density. It was confirmed by the E' behavior in the rubbery region. Using $E'_{rubbery}$ values, M_c and q were determined.

The theoretical as well as experimental network parameters calculated from the storage modulus in the rubbery plateau region ($E'_{rubbery}$) decreased with increased TEGDMA content (Table 2).

Finite M_c measure of the uncrosslinked PMMA may be explained by the presence of trapped entanglements of macrochains. The smaller value of experimental M_c in respect to the theoretical one in the case of X-PMMA crosslinked with 1 mol.% of TEGDMA resulted from the greater increase in modulus than can be predicted according to the theory of rubber elasticity. This discrepancy may be attributed to the higher possible conformations that the chain can achieve in the less crosslinked system, allowing for higher segmental motion. Hence, the formation of entanglement is favored. The opposite situation, observed for networks crosslinked with at least 2 mol.% of TEGDMA results from lower modulus than could be predicted. The most probable reason might be incomplete conversion of double bonds in the crosslinker, which generates side groups or side chains as well as the presence of loops, which does not transform stress.
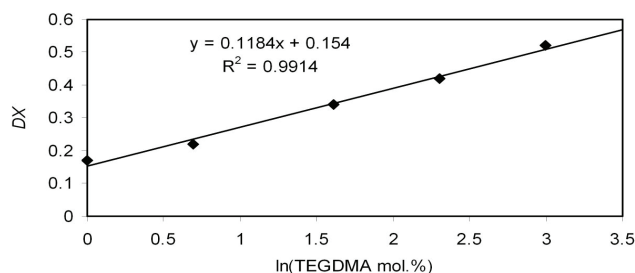

Fig. 7. The correlation between the DX
and the TEGDMA content

In the next step, the Khana equation was adopted to the assessment of the degree of crosslinking (DX). For this purpose the values of storage modulus below and above T_g were read off the $\log E'_{rubbery} = f(T)$ plots. From Table 3, it can be seen that the DX of X-PMMAs increases as the TEGDMA content increases. Moreover, this relation has a linear relation-

ship on the semi-logarithmic scale ($R = 0.991$), as it is shown in Fig. 7.

5. Conclusions

The MMA curing is an effect of its copolymerization with TEGDMA, in which the latter one serves as the crosslinker. Therefore, when the TEGDMA content in the network increased, its network parameter dropped and crosslink density rose. This resulted in the increase of glass temperature and storage modulus in the rubber plateau region.

The direct measure of the difference between storage modulus in the glassy and elastic regions might serve as a direct indicator of the crosslink density in crosslinked poly(methyl methacrylates).

Acknowledgments

References

[1] ALGER M.S.M., *Polymer Science Dictionary*, London and New York Elsevier Science Publishers, 1989.

[2] ALI U., KARIM K.J., BUANG N.A., *A Review of the Properties and Applications of Poly (Methyl Methacrylate) (PMMA)*, Polym. Rev., 2015, 55(4), 678–705.

[3] ARORA M., CHAN E.K.S., GUPTA S., DIWAN A.D., *Polymethylmethacrylate bone cements and additives: A review of the literature*, World J. Orthop., 2013, 4(2), 67–74.

[4] BARSZCZEWSKA-RYBAREK I., *Quantitative determination of degree of conversion in photocured poly(urethane-dimethacrylate)s by FTIR spectroscopy*, J. Appl. Polym. Sci., 2012, 123(3), 1604–1611.

[5] BARSZCZEWSKA-RYBAREK I.M., *A New Approach to Morphology Studies on Diacrylate Polymer Networks Using X-Ray Powder Diffraction*, Macromol. Chem. Phys., 2013, 214(9), 1019–1026.

[6] CHLADEK G., ZMUDZKI J., BASA K., PATER A., KRAWCZYK C., PAKIEŁA W., *Effect of silica filler on properties of PMMA resin*, Arch. Mater. Sci. Eng., 2015, 71(2), 63–72.

[7] CLARK R.L., *Dynamic mechanical thermal analysis of dental polymers. II. Bis-phenol A-related resins*, Biomaterials, 1989, 10, 549–552.

[8] DEB S., AIYATHURAI L., ROETHER J.A., LUKLINSKA Z.B., *Development of high-viscosity, two-paste bioactive bone cements*, Biomaterials, 2005, 26, 3713–3718.

[9] FLORY P.J., *Molecular theory of rubber elasticity*, Polym. J., 1985, 17, 1–12.

[10] HILD G., *Model networks based on "endlinking" processes: synthesis, structure and properties*, Prog. Polym. Sci., 1998, 23, 1019–1149.

[11] KETTEL M.J., SCHAEFER K., PICH A., MOELLER M., *Functional PMMA nanogels by cross-linking with cyclodextrin methacrylate*, Polymer, 2016, 86, 176–188.

[12] KHANNA Y.P., *Estimation of polymer crystallinity by dynamic mechanical techniques*, J. Appl. Pol. Sci., 1989, 37, 2719–2726.

[13] LEE W.A., RUTHERFORD R.A., [in:] *Polymer Handbook*, J. Brandrup, E.H. Immergut (ed.), J. Wiley & Sons, New York 1975.

[14] MACURA-KARBOWNIK A., CHADEK G., ŻMUDZKI J., KASPERSKI J., *Chewing efficiency and occlusal forces in PMMA, acetal and polyamide removable partial denture wearers*, Acta Bioeng. Biomech., 2016, 18(1). DOI: 10.5277/ABB-00357-2015-03.

[15] MEMON M.S., YUNUS N., RAZAK A.A., *Some mechanical properties of a highly cross-linked, microwave-polymerized, injection-molded denture base polymer*, Int. J. Prosthodont., 2001, 14(3), 214–218.

[16] MENARD K.P., *Dynamic Mechanical Analysis. A Practical Introduction*, Boca Raton CRC Press, 2008.

[17] NMAB Committee on Organic Polymer Characterization. Polymer Characterization: Report. Washington D.C. National Academy of Science, 1977.

[18] REIS K.R., BONFANTE G., PEGORARO L.F., CONTI P.C., OLIVEIRA P.C., KAIZER O.B., *In vitro wear resistance of three types of polymethyl methacrylate denture teeth*, J. Appl. Oral. Sci., 2008, 16(3), 176–80.

[19] SIDERIDOU I., TSEREKI V., PAPANASTASIOU G., *Effect of chemical structure on degree of conversion in light-cured dimethacrylate-based dental resins*, Biomaterials, 2002, 23, 1819–1829.

[20] ŚMIGA-MATUSZOWICZ M., KORYTKOWSKA-WAŁACH A., *Polymeric in situ forming systems for biomedical applications*. Part I. *Injectable implants*, Polimery, 2015, 60, 149–159.

[21] WOOL R.P., *Polymer entanglements*, Macromolecules, 1993, 26(7), 1564–1569.