U.P.B. Sci. Bull., Series B, Vol. 73, Iss. 3, 2011 ISSN 1454-2331

COMPARISON BETWEEN OCTA - OR MONOFUNCTIONAL POSS INTERACTIONS WITH DIMETHACRYLATE MONOMERS

Adriana LUNGU [1], Nicoleta M. FLOREA[2], Geta VOICU[3], Horia IOVU[4]

A fost realizat un studiu sistematic al reacției de fotopolimerizare între doi monomeri dimetacrilați (BisGMA şi TEGDMA) în prezența unor compuşi de tip POSS (octa- sau monofuncțional). Scopul principal al acestui studiu a fost obținerea de noi materiale compozite hibride cu proprietăți îmbunătățite. S-au folosit doi compuşi de tip POSS pentru a substitui, parțial sau total, monomerul de bază BisGMA. Compozitele hibride rezultate au fost caracterizate prin diferite metode (FTIR, RAMAN, TGA, DMA, XRD).

A systematic study on the photopolymerization reaction of two dimethacrylate monomers (BisGMA and TEGDMA) in the presence of POSS compounds (octa- or monofunctional) was performed. The main purpose was to investigate new possibilities to obtain novel hybrid composites with enhanced properties. Two different POSS compounds were explored to substitute, partially or completely, the base monomer BisGMA. The obtained hybrid composites were advanced characterized by various methods (FTIR, RAMAN, TGA, DMA, XRD).

Keywords: polyhedral oligomeric silsesquioxanes, hybrid composites, photopolymerization

1. Introduction

Dental composites typically consist of a methacrylate – based matrix and glass or ceramic fillers. Compared to dental amalgams, the composites possess better esthetic property, have less safety concern, and have shown satisfactory clinic results.

In general, Bisphenol A glycerolate dimethacrylate (BisGMA) - Triethyleneglycol dimethacrylate (TEGDMA) based dental restorative composites have shown relatively good clinical results. BisGMA is an important dental

---

[1] Postdoctoral Researcher, Dept. of Polymer Science and Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: adriana_lungu2006@yahoo.com

[2] PhD Student, Dept. of Polymer Science and Engineering, University of POLITEHNICA of Bucharest, Romania

[3] Lecturer, Dept. of Science and Engineering of Oxidic Materials, University POLITEHNICA of Bucharest, Romania

[4] Prof., Dept. of Polymer Science and Engineering, University POLITEHNICA of Bucharest, Romania

monomer and is very viscous, honey-like liquid. To improve handling capabilities, a diluent monomer, TEGDMA, is added to decrease the resin viscosity. In the BisGMA/TEGDMA composites, BisGMA enhances the resin reactivity, whereas TEGDMA leads to an increased vinyl conversion. However, there are still several physical properties (thermostability, glass transition temperature) which need to be improved [1].

Polyhedral oligomeric silsesquioxane (POSS) is a novel organic/inorganic hybrid monomer, and may provide a potential solution to significantly improve some properties of hybrid dental composites. POSS units are three-dimensional, cube-shaped species with diameters between 1 to 3 nm, characterized by an inorganic inner siloxane core $(SiO_{1.5})_x$ surrounded by organic substituents. These may be simple organic groups, or modified to exhibit a wide range of polarities and reactivity, which make POSS nanoparticles compatible with polymers, biological systems and surfaces [2–4]. The incorporation may be done through blending, grafting or co-polymerization process [5]. Unlike silica, which requires surface modification for use as filler, each POSS molecule contains covalently bonded functional groups that can be copolymerized during photocuring.

Earlier results showed that incorporation of POSS into different polymeric matrices could exhibit various influences on the properties of the final material due to the POSS–polymer matrix interactions, as well as the size and the mass of the POSS cage. The availability of POSS macromers functionalized with one or more reactive groups (such methacrylate) made polymerization techniques a useful strategy to obtain new hybrid materials, in which POSS cages are incorporated in, or even are part of the polymer backbone [6-9].

The present work reports a systematic study on the photopolymerization reaction of the two dimethacrylate monomers (BisGMA and TEGDMA) in the presence of POSS compounds (octa- or monofunctional) which was performed in order to investigate new possibilities to improve physical and chemical properties of dental materials. The two different POSS compounds were explored to substitute, partially or completely, BisGMA to obtain novel hybrid composites with enhanced properties.

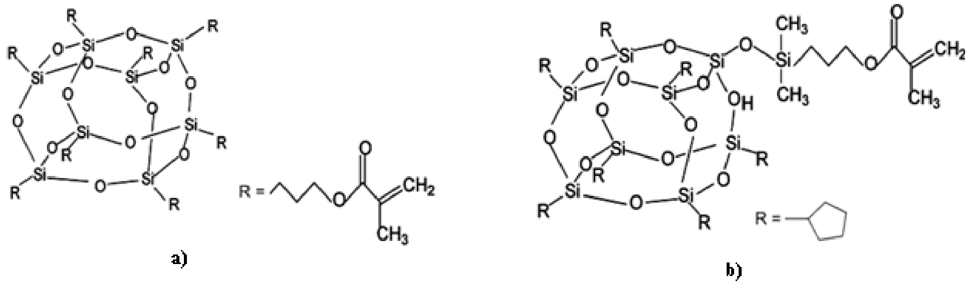
2. Materials and methods

2.1 Materials

Two different POSS compounds were selected: one octafunctional **MA-POSS** (Octapropylmethacryl - octasiloxane cage mixture, n=8, 10, 12) and one monofunctional-POSS, **CPENTYL-POSS** (Heptacyclopentyl - octasiloxane - yloxy) dimethylsilyl] propyl methacrylate) (Fig. 1). As polymeric matrix two dimethacrylate monomers: bisphenol A glycerolate dimethacrylate **(BisGMA)** and triethyleneglycol dimethacrylate **(TEGDMA)** (Fig. 2) were used**.**

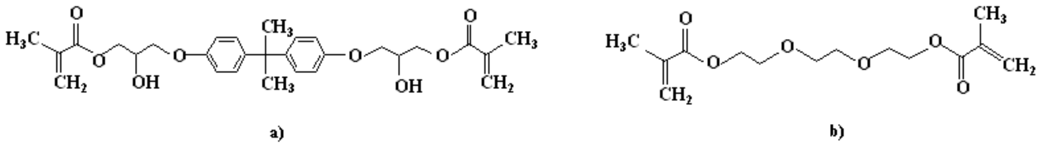
POSS hybrid composites were cured by photo-initiated free radical polymerization using camphorquinone (CQ) and ethyl-4-(N,N’-dimethylamino) benzoate (4EDMAB).

All chemicals were purchased from Sigma-Aldrich Chemicals and used as received.



a) b)

Fig. 1. The chemical structure of POSS compounds: a) MA-POSS, b) CPENTYL-POSS



a) b)

Fig. 2. The chemical structure of polymeric matrices: a) BisGMA, b) TEGDMA

2.2 Hybrid composites synthesis

Two types of composites based on BisGMA and TEGDMA monomers and MA-POSS and CPENTYL-POSS reinforcing agents were synthesized. The polymer phase was prepared by mixing the functionalized POSS with the monomers, until the mixture was homogeneous. A good dispersion was achieved by using an ultrasonic device for 15 min at room temperature in order to uniformly disperse fillers into matrices.

CQ (0.2% w) and 4EDMAB (0.8% w) were added to each resin system to allow for visible light curing. After photopolymerization, the obtained samples are left in a Teflon mould for 24 h at room temperature and then characterized [10].

The formulations of the resin systems investigated are described in table 1 [11]. Besides octa-POSS, we have also used a mono-POSS in order to check the influence of POSS substituents on the thermal properties of the composites.

Table 1

POSS based hybrid composites

No.	**Sample code**	**POSS*, % w.**	**BisGMA, % w.**	**TEGDMA, % w.**
1	P0/B50/T50	**0**	**50**	**50**
2	P2/B48/T50	2	48	50
3	P10/B40/T50	10	40	50
4	P25/B25/T50	25	25	50
5	P50/B0/T50	**50**	**0**	**50**

*POSS could be MA-POSS or CPENTYL-POSS

The POSS compound was explored to substitute, partially or completely, the monomer BisGMA to obtain novel hybrid composites with improved properties, according to a recent study. For testing this hypothesis, the concentration of diluent monomer (TEGDMA) was maintained at a constant level in all resin formulations. Fig. 3 shows photographs of POSS based hybrid composites with different POSS loadings. At the same thickness, the samples with MA-POSS exhibit excellent optical transparency while specimens with CPENTYL-POSS become highly opaque as the POSS content increases.

a) b)

Fig. 3. Hybrid composites with different POSS types:
a) MA-POSS/BisGMA/TEGDMA; b) CPENTYL-POSS/BisGMA/TEGDMA

2.3 Characterization

Fourier Transformed Infrared Spectrometry (FTIR)

FTIR spectra were recorded on a VERTEX 70 BRUCKER FT-IR spectrometer equipped with a attenuated total reflectance (ATR) accessory. All FTIR measurements were performed in the ATR-FTIR cell on Ge crystal, at room temperature. The FTIR spectra were recorded using 32 scans, with a resolution of 4 cm^{-1} in 600-4000 cm^{-1} wave number region.

Raman spectroscopy

Raman spectra were recorded on a DXR Raman Microscope from Thermo Scientific using a 532 nm laser line and a number of 50 scans. The laser beam was focused with the 10X objective of the Raman Microscope.

Thermogravimetric Analysis (TGA)

The TGA curves were recorded on a Q500 TA Instrument at 10°C/min heating rate, from 20°C to 500°C, under nitrogen atmosphere.

Dynamic Mechanical Analysis

The DMA tests were run on a TRITEC 2000 equipment using 5°C/min heating rate at three different frequencies (0.316, 1, 3.16 Hz) in the range 25°C - 200°C.

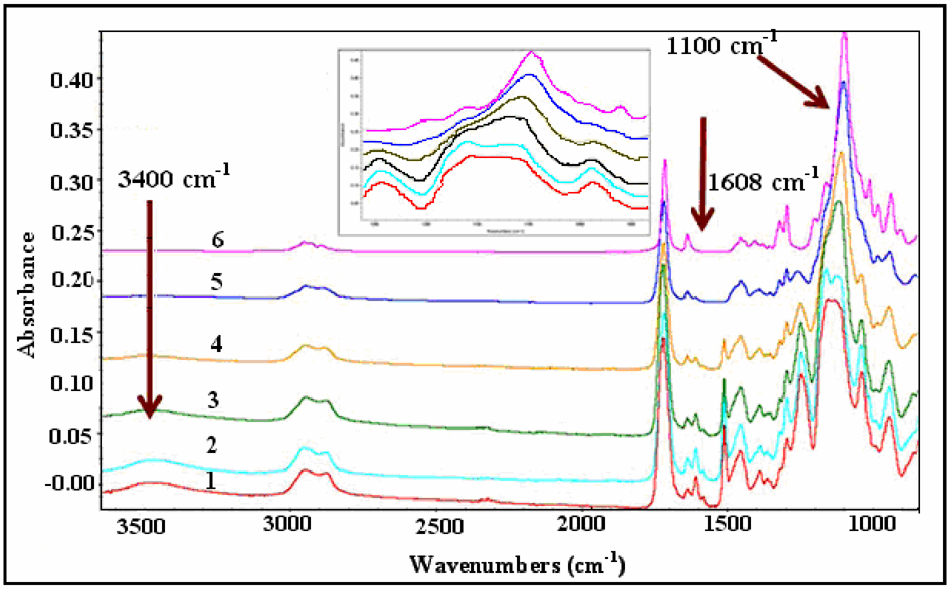
X-Ray Diffraction (XRD)

The XRD spectra were recorded on a XRD-6000 SHIMADZU diffractometer, with CuK alpha radiation. The scanned range was 2θ = 5 - 65°, with a scan speed of 2°/min.

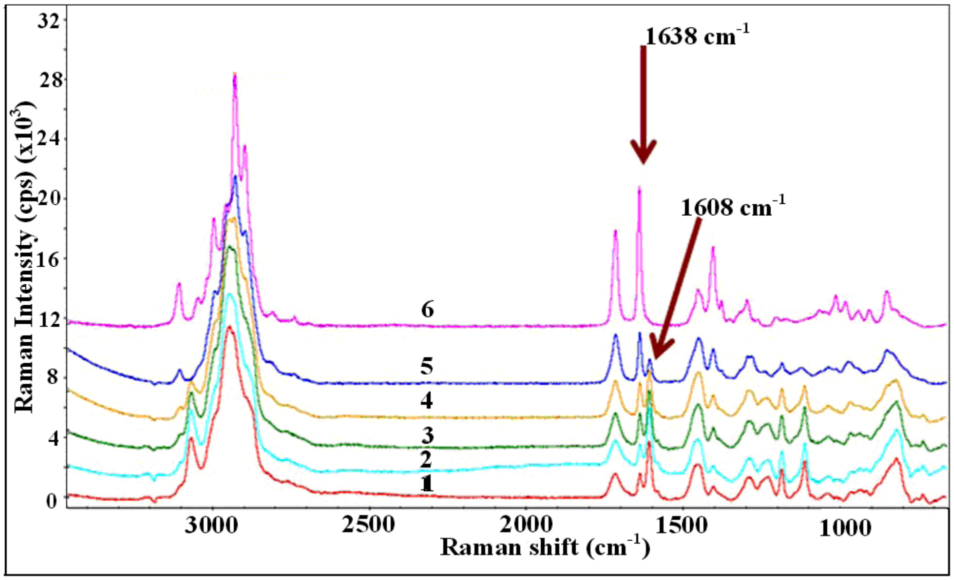
3. Results and discussion

3.1 The influence of POSS concentration on FTIR and RAMAN spectra

First the chemical composition of the POSS based composites was studied by FTIR and RAMAN spectroscopy. These techniques provided valuable information about the structure of the obtained hybrid composites.



a)



b)

Fig. 4. FTIR (a) and Raman (b) spectra for hybrid composites with **MA-POSS**: (1) P0/B50/T50, (2) P2/B48/T50, (3) P10/B40/T50, (4) P25/B25/T50, (5) P50/B0/T50, (6) MA-POSS

Two distinct BisGMA absorption bands were monitored in the FTIR spectra for POSS hybrid composites: 3400 cm^{-1} corresponding to -OH groups and 1608 cm^{-1} assigned to C=C aromatic ring stretching vibrations (Fig. 4a). As the BisGMA content decreases, the selected peaks diminish in intensity consecutively.

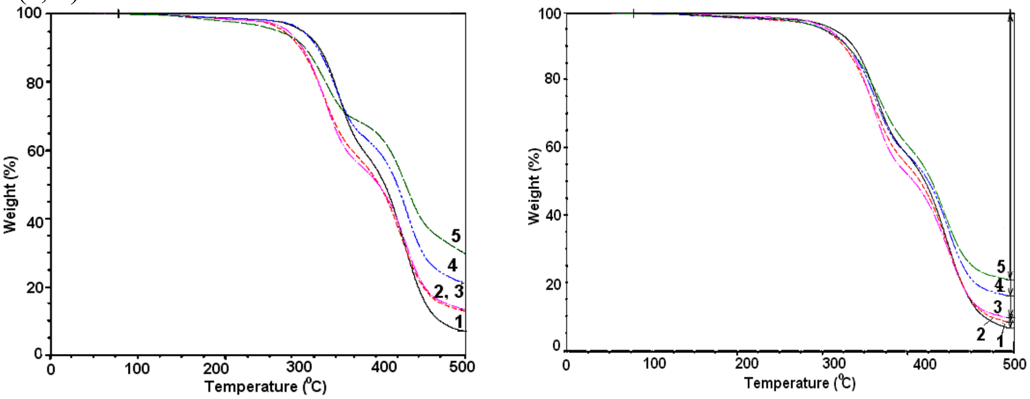
Also, a strong absorption band appears in the FTIR spectra in the range 1070 cm^{-1} and 1100 cm^{-1} assigned to the asymmetric stretching vibration of Si-O-Si groups from the inorganic cage (inset Fig. 4a). At 0% POSS concentration this band is broadly defined. As the POSS concentration increases, Si-O-Si band becomes progressively narrower and shifts to lower wavelengths due to the strong Si-O-Si vibration from the inorganic compound. At 50% POSS concentration Si-O-Si absorption band is similar to that of the neat POSS compound. These issues were observed regardless of the type of POSS used (MA-POSS or CPENTYL-POSS).

The absorption band assigned to C=C bond (1638 cm^{-1}) was detected in the RAMAN spectra. As the C=C bond from the methacrylic groups is nonpolar, the absorption band exhibits a higher intensity in the Raman spectra than in FTIR spectra and may be used to study the polymerization kinetic [13]. The RAMAN spectra for hybrid composites show that the peak at 1638 cm^{-1} exhibits a higher intensity as the POSS concentration increases, due to the presence of multiple C=C bonds.

3.2 TGA characterization

The influence of POSS type and concentration on the composites thermostability

The influence of the polyhedral cages on the thermal stability of the POSS based composites was studied. The thermograms of the MA-POSS and CPENTYL-POSS based composites at different concentrations are showed in Fig. 5 (a, b).



a) b)

Fig 5. Thermal decomposition curves of hybrid composites based on
a) MA-POSS and b) CPENTYL-POSS
(1) P0/B50/T50, (2) P2/B48/T50, (3) P10/B40/T50, (4) P25/B25/T50, (5) P50/B0/T50

For the POSS hybrid composites it was observed that the residual mass increases as POSS concentration is higher.

The residual mass is increasing from 13% for the MA-P2/B48/T50 composites to 39% for the MA-P50/B0/T50 composites (Fig. 5a). This improvement in thermal properties can be corroborated with the interactions between polymeric matrix and POSS compounds.

The CPENTYL-POSS hybrid composites exhibit a similar thermal behavior: the residual mass is increasing from 11% for the CPENTYL-P2/B48/T50 composites to 28% for the CPENTYL-P50/B0/T50 composites (Fig. 5b).

It can be noticed that the formulations with MA-POSS exhibit a higher thermostability compared with the CPENTYL-POSS hybrid composites [14]. POSS-MA seems to be the best candidate to form a highly crosslinked network due to the presence of multiple C=C bonds. The rigid and bulky structure of the

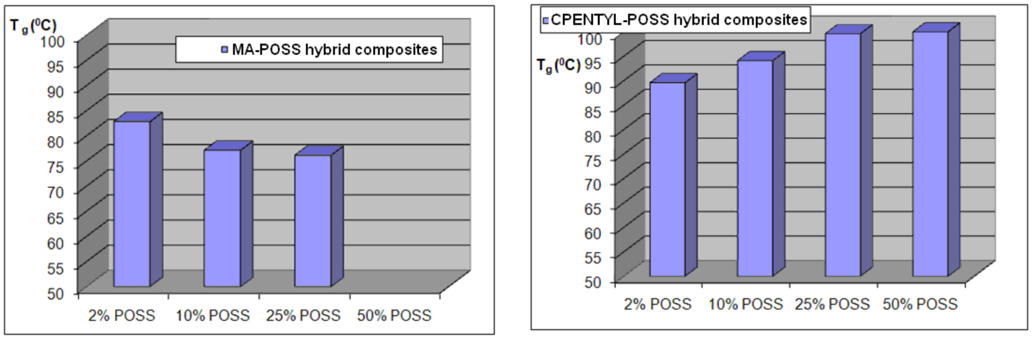
Si-O-Si cages reduces the mobility of the polymeric macromolecules, leading to improved thermal properties.

The improvement of the thermostability of the hybrid composites based on MA-POSS and CPENTYL-POSS compared with the polymeric matrix can be explained by the thermal behavior of neat POSS compounds [15]. Having a good thermal stability, the introduction of POSS into the polymeric network leads to an increased thermal resistance of the obtained hybride composites. The size and the weight of POSS lead to a superstructure which influences the thermal properties. This fact proves that the election of the POSS compound is an important step in hybrid composites synthesis.

3.3 DMA characterization

The influence of POSS type and concentration on the T_g values

In order to establish if the POSS type or concentration exhibits any influence on the T_g, DMA tests were performed (Fig. 6). For some hybrid composites, e. g. MA-P50/B0/T50, DMA tests could not be recorded because the samples were too brittle.



a) b)

Fig. 6. T_g values for hybrid composites based on MA-POSS (a) and CPENTYL-POSS (b)

For the reference sample (P0/B50/T50), T_g was found to be 85°C.

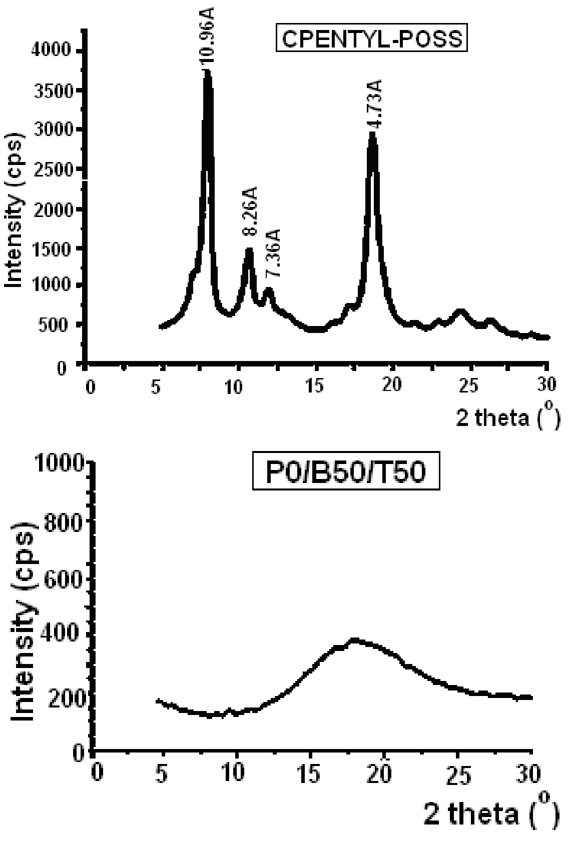
For MA-POSS hybrid composites Tg values decrease as the POSS concentration increases. This behavior is probably due to the POSS cages and the organic substituents, which can provide voids within the polymeric matrix. Another important reason which may lead to the decreasing of Tg is the presence in the system of some free POSS molecules, which are not linked by covalent bonds with polymeric matrix. This residual POSS molecules lead to defects in the perfect crosslinked structure of the composite material. Thus, the POSS compound acts more like a plasticizer than a reinforcing agent in the final structure of the composites [13].

In the case of the CPENTYL-POSS based composites T_g increases as the amount of POSS is higher, probably due to the strong interactions between POSS and polymer, which control the mobility of the macromolecular segments. Thus, the incorporation of POSS cages functionalized with bulky substituents (cyclopentyl) is followed by an increase of T_g [13].

3.4 Characterization of crystal structure of POSS composites by XRD analysis

The morphology of the POSS hybrid composites was studied by XRD in order to determine the influence of POSS content on the microstructure and the crystalline POSS arrangement in the polymeric matrix.

XRD diffractograms were produced only for CPENTYL-POSS hybrid composites, where the POSS concentration gradually increases and progressively replace BisGMA (Fig. 7).



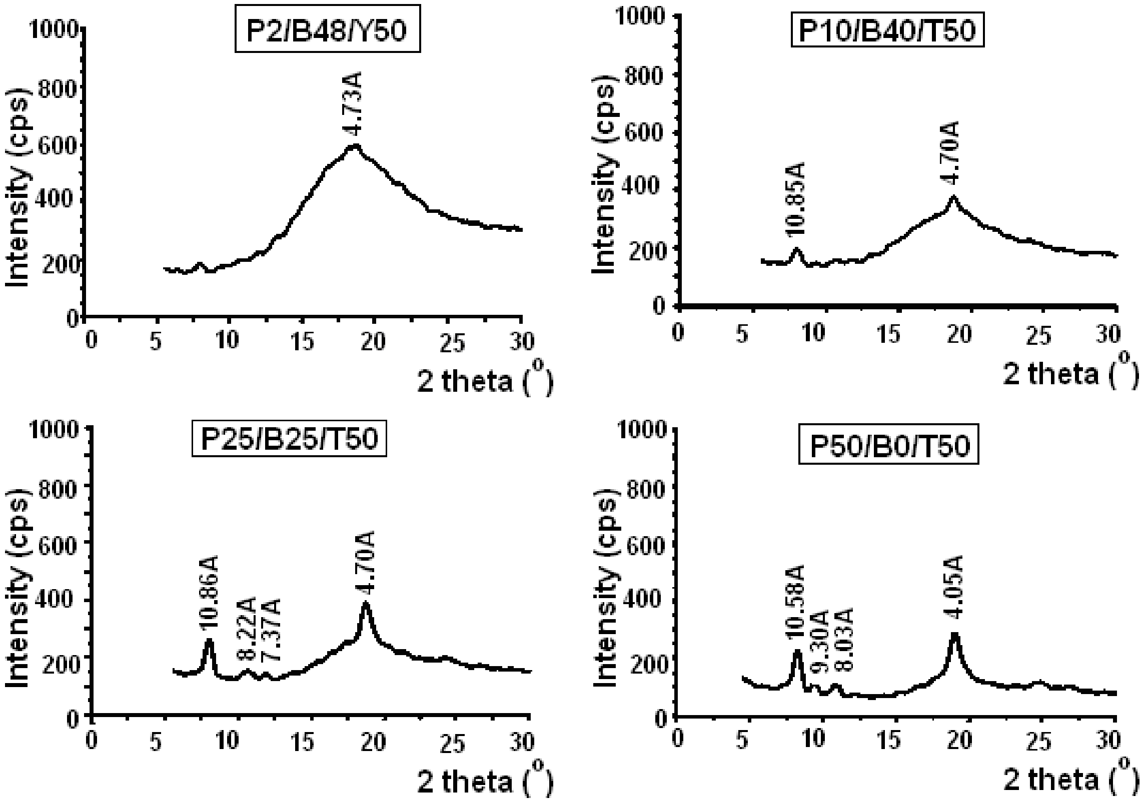


Fig. 7. XRD patterns for the CPENTYL-POSS hybrid composites

The diffraction peaks for pure CPENTYL-POSS are sharp and well defined indicating a high degree of crystallinity as we previously reported [14]. For pure CPENTYL-POSS, one may distinguish 5 distinct peaks at $2\theta = 8.05°$, 10.69°, 12.00°, 18.73° and 24.43°, which correspond to Bragg distances of 10.96 Å, 8.26 Å, 7.36 Å, 4.73 Å and 3.64 Å. The diffractogram of CPENTYL-POSS shows that the main diffraction peaks correspond to Miller index h k l = (1 0 1), (1 1 0), (1 0 2), (0 3 0; 1 1 3; 1 2 2) and (3 1 2). The Bragg distance 10.96 Å is due to the size of the POSS molecule. The other peaks are caused by the crystalline structure of POSS molecules. The nanocage structure, as well as the isotropic character, facilitate the crystalline phase [15-17].

As expected, for the sample without POSS (P0/B50/T50 copolymer) the lack of the crystallinity could be observed (an amorphous halo at $2\theta = 18{,}2°$ and no crystalline reflection peak). An important amorphous phase with a low degree of crystallinity could be detected also for P2/B48/T50.

As the POSS concentration increases (10%, 25%, 50%) distinct peaks appear meaning that the crystallinity degree is higher. For the hybrid composites

P25/B25/T50 and P50/B0/T50 a significant crystallinity degree was observed, XRD pattern being very similar to that of pure POSS.

MA-POSS hybrid composites were completely amorphous, even at high loadings. No POSS crystal peaks were identified confirming that MA-POSS does not segregate in the hybrid composites. The obtained results were in agreement with a recent study [11].

4. Conclusions

The partially or completely substitution of BisGMA with MA-POSS and CPENTYL–POSS leads to improved thermostability of final hybrid composites which is probably due to the interactions between polymeric matrix and POSS compounds.

The T_g value is strongly influenced by the POSS type. The best results in terms of T_g, were obtained for the CPENTYL-POSS based composites, and on the contrary very low T_g values were reached for the MA-POSS based composites.

For the hybrid composites with 25% and 50%CPENTYL-POSS an important crystallinity degree was observed, XRD pattern being very similar to that of pure POSS. Contrary to composites based on CPENTYL-POSS, MA-POSS composites were completely amorphous, even at high loadings. No POSS crystal peaks were identified confirming that MA-POSS does not segregate in the hybrid composite.

Acknowledgements

Authors recognise financial support from the European Social Fund through POSDRU/89/1.5/S/54785 project: "Postdoctoral Program for Advanced Research in the field of nanomaterials".

REFERENCES

[1] *L. Zhang, Y. Gao, Q. Chen, M. Tian, H. Fong,* Bis-GMA/TEGDMA dental composites reinforced with nano-scaled single crystals of fibrillar silicate, J Mater Sci, **vol. 45**, issue 9, may 2010, p. 2521-2524

[2] *P.T. Mather, H.G. Jeon, A. Romo-Uribe, T.S. Haddad, J. D. Lichtenhan*, Mechanical relaxation and microstructure of Poly(norbornyl-POSS) copolymers, Macromolecules, **vol. 32**, issue 4, february 1999, p. 1194-203

[3] *L. Zheng, R.J. Farris, E.B. Coughlin*, Novel polyolefin nanocomposites: synthesis and characterizations of metallocene-catalyzed polyolefin polyhedral oligomeric silsesquioxane copolymers, Macromolecules, **vol. 34**, issue 23, november 2001, p. 8034-8039

[4] *J. Deng, C.E. Farmer-Creely, B.D. Viers, A.R. Esker*, Unique rodlike surface morphologies in trisilanolcyclohexyl polyhedral oligomeric silsesquioxanes films, Langmuir, **vol. 20**, issue 7, march 2004, p. 2527-2530

[5] *T.S. Haddad, R. Stapleton, H.G. Jeon, P.T. Mather, J.D. Lichtenhan, S.H. Philips*, Polym Prep 1999;40:496-506

[6] *S. H. Philips, T. S. Haddad, S.J. Tomczak,* Curr Opin Solid State Mater Sci 2004;8:21-9

[7] *L. Zheng, A.J. Waddom, R.J. Farris, E.B. Coughlin*, X-ray characterizations of polyethylene polyhedral oligomeric silsesquioxane copolymers, Macromolecules, **vol. 35**, issue 6, march 2002, p. 2375-2379

[8] *J. Pyun, K. Matyjaszewski, J. Wu, K. Gyeong-Man, S.B. Chun, P.T. Mather*, ABA triblock copolymers containing polyhedral oligomeric silsesquioxane pendant groups: synthesis and unique properties, Polymer, **vol. 44**, issue 9, april 2003, p. 2739-2750

[9] *S.L. Schiavo, P. Mineo, P. Cardiano, P. Piraino*, Novel propylmethacrylate-monofunctionalized polyhedral oligomeric silsesquioxanes homopolymers prepared via radical bulk free polymerization, European Polymer Journal, **vol. 43**, issue 12, december 2007, p. 4898-4904

[10] *N.M. Sulca, A. Lungu, R. Popescu, S.A. Garea, H. Iovu*, New polymeric nanocomposites based on Polyhedral Oligomeric Silsesquioxanes, Mat Plast, **vol. 46**, issue 1, january 2009, p. 1-10

[11] *H. Fong, S.H. Dickens, G.M. Flaim*, Evaluation of dental restorative composites containing polyhedral oligomeric silsesquioxane methacrylate, Dental Materials, **vol. 21**, issue 6, june 2005, p. 520-529

[12] *W. Hedzelek, R. Wachowiak, A. Marcinkowska, L. Domka,* Infrared Spectroscopic Identification of chosen dental materials and natural teeth, Acta Physica Polonica A, **vol. 114**, issue 2, august 2008, p. 471-484

[13] *N.M. Sulca, A. Lungu, A.S. Garea, H. Iovu*, Monitoring the synthesis of new polymer nanocomposites based on different Polyhedral Oligomeric Silsesquioxanes using Raman Spectroscopy, J Raman Spectrosc, **vol. 40**, issue 11 , November 2009, p. 1634-1640

[14] *N.M. Sulca, A. Lungu, G. Voicu, A.S. Garea, H. Iovu*, Advanced characterization of polyhedral oligomeric silsesquioxanes used for nanocomposites synthesis, Mat Plast, **vol. 46**, issue 2, february 2009, p. 124-128

[15] *A. Lungu*, Materiale polimerice hibride pe baza de compusi nanostructurati, Phd thesis, 2009, University Politehnica of Bucharest

[16] *A.J. Waddon, L. Zheng, R.J. Farris, E.B. Coughlin*, Nanostructured polyethylene-POSS copolymers: control of crystallization and aggregation, Nanoletters, **vol. 2**, issue 10, october 2002, p. 1149-1155

[17] *A.J. Waddon, E.B. Coughlin*, Cristal structure of polyhedral oligomeric silsesquioxane (POSS) nanomaterials: a study by X-ray diffraction and electron microscopy, Chem. Mater**,** **vol. 15**, issue 24, December 2003, p. 4555-4561