

# New Polymeric Nanocomposites Based on Polyhedral Oligomeric Silsesquioxanes

NICOLETA MIHAELA SULCA<sup>1\*</sup>, ADRIANA LUNGU<sup>1</sup>, ROXANA POPESCU<sup>1</sup>, SORINA ALEXANDRA GAREA<sup>1</sup>, HORIA IOVU<sup>1</sup>

<sup>1</sup>University Politehnica of Bucharest, 149 Calea Victoriei, 010072, Bucharest, Romania

*New polymeric nanocomposites based on nanostructured reinforcing agents as Polyhedral Oligomeric Silsesquioxanes (POSS) with methacrylic groups were synthesized and the influence of POSS type was studied. As polymer matrix a mixture of functionalized POSS and triethylene glycol dimethacrylate (TEGDMA) was used by replacing the classical diglycidyl methacrylate monomer (BisGMA) with various POSS functionalized with methacrylic groups. The obtained nanocomposites were characterized by spectroscopic methods (FT-IR, RAMAN), thermal analysis (TGA, DMA) and scanning electron microscopy (SEM).*

*Keywords: polyhedral oligomeric silsesquioxanes, nanocomposite, thermostability, FT-IR, RAMAN, TGA, DMA, SEM.*

Polymers reinforced with well defined nanosized inorganic clusters (i.e., polymeric nanocomposites) have attracted a tremendous degree of interest because of their potential applications. Recently, polyhedral oligomeric silsesquioxane (POSS) – based hybrid polymers were reported in the literature [1, 2, 16]. POSS compounds exhibit inorganic/organic hybrid architectures due to the inner inorganic cage composed of silicone and oxygen ( $\text{SiO}_{1.5}$ )<sub>n</sub> and organic radicals as substituents to these cages (R)<sub>n</sub>. The unique ‘Si–O’ cage structure can be viewed as a discrete, chemically modified particle of silica having an inner inorganic cage structure that is rigid and exhibits a completely defined size (1.53 nm). Unlike silica, which requires surface modification for use as a filler, the outer surface of POSS molecule is substituted by eight organic groups (fig. 1). The organic group may be inert to further chemical reactions (e.g., methyl, cyclohexyl, phenyl, etc.) or may be polymerizable by different mechanisms. The functional groups can be selected to copolymerize with organic monomers in order to obtain various POSS-based hybrid polymers. For example, a monofunctional POSS can be grafted onto macromolecular chains by co-polymerization or reactive blending (pendant-type hybrid polymers), a difunctional POSS is used to prepare backbone type polymers (POSS building blocks into macromolecular backbones), and the multifunctional POSS is suitable for the crosslinking-type hybrid polymers (POSS-containing thermosetting nanocomposites) [3, 4, 17].

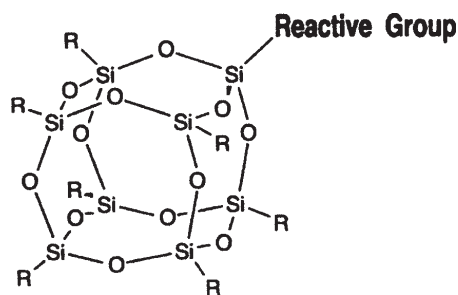


Fig. 1. POSS structure

The hybrid structure of POSS particles, with a silica core and a variable organic shell, offers a precise way to vary the polymer–nanoparticle interaction and thereby to achieve either plasticization or reinforcement, depending on the application [5, 6]. Therefore the cage-like structures of POSS allow the building of the materials with precise control of the nanoarchitecture.

The nanosize POSS species are chemically bonded to the polymeric matrix and homogeneously dispersed at molecular level, thus effectively improving the physical properties of the nanocomposites. The incorporation of POSS derivatives into polymeric materials may help to improve the mechanical properties, to increase the thermal stability, oxidation resistance and surface hardening as well as to reduce the flammability and the viscosity during processing [7-10].

The methacrylate oligomers: bisphenol A glycerolate dimethacrylate (BisGMA) and triethylene glycol dimethacrylate (TEGDMA) have been chosen for their similar chemistry, which allows comparison of the POSS influence on the structures and the properties, and because of their use in several applications.

The aim of this study was to explore new polymeric nanocomposites, in which POSS completely substitutes the commonly used dimethacrylate based monomer BisGMA from the conventional dimethacrylate resins systems BisGMA/TEGDMA. The products were characterized by a combination of spectroscopic (FT-IR, RAMAN), thermal (TGA, DMA) and microscopy techniques.

For this purpose, two different types of oligomeric nanocages (mono- and octafunctional) have been used: one POSS with isobutyl groups on seven of the cage corners POSS-(1-Propylmethacrylate)-Heptaisobutyl substituted (HISO-POSS) and one with seven cyclopentyl groups POSS-3-[(3, 5, 7, 9, 11, 13, 15-Heptacyclopentylpentacyclo[9.5.1.1<sup>3,9</sup>.1<sup>5,15</sup>.1<sup>7,13</sup>]octasiloxan-1-yloxy)dimethylsilyl]propyl methacrylate (CPENTYL-POSS). The remaining corner is substituted with propyl-methacrylate. The difficulty in working with crystallized POSS fillers when dispersed in homopolymers led to the selection of non-crystallizable POSS for the present study.

\* Tel.: 0729319985

To further improve the dispersion in TEGDMA, an octafunctional POSS with acrylic groups was chosen – Methacryl substituted POSS, cage mixture, n=8, 10, 12 (MA-POSS). MA-POSS is polydisperse and therefore non-crystallizable composed of T<sub>8</sub>, T<sub>10</sub> and T<sub>12</sub> cages mixtures. The MA-POSS seems to be the best candidate, because of the presence of multiple reactive groups (C=C), and the rigid, bulky structure. The highly cross-linked structure derived from C=C curing can restrict the motion of TEGDMA molecules, which enhances the thermo- mechanical properties [11-13].

These types of POSS were chosen in order to have different functionalities (crosslinking points within the polymer network, fig. 2) and solubility for gaining a wide range of dispersion of the POSS particles, from molecular level to micro-aggregates or nano-aggregates with either a crystalline or an amorphous character.

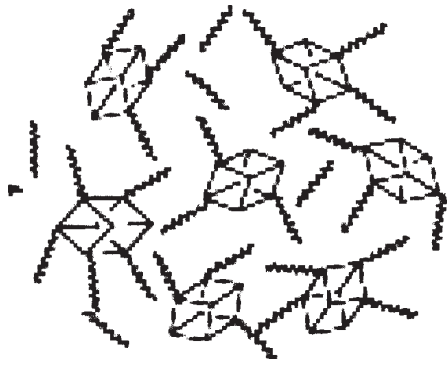
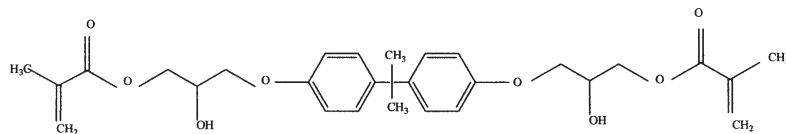
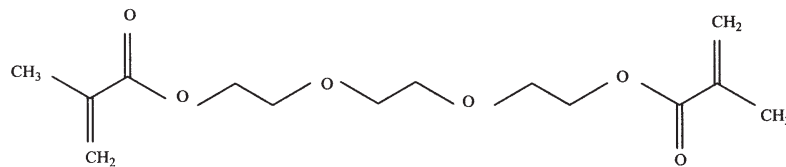


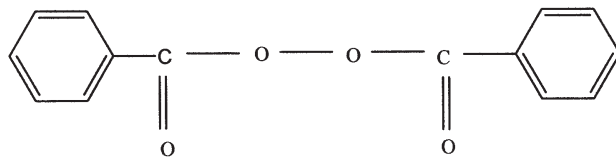
Fig.2. The POSS – based nanocomposite structure



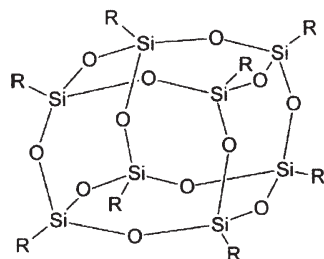
BisGMA



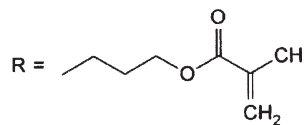
TEGDMA



Benzoyl peroxide



MA-POSS



## Experimental part

### Materials

All the raw materials BisGMA, TEGDMA, benzoyl peroxide (PB) were purchased from Sigma-Aldrich Chemicals and used as received. Three types of POSS reinforcing agents were used for nanocomposites synthesis: MA-POSS, HISO-POSS and CPENTYL - POSS.

The characteristics of the monomers and of the POSS compounds are shown in table 1, and table 2 respectively.

Table 1

THE MAIN CHARACTERISTICS OF THE MONOMERS USED AS A POLYMER MATRIX

Vinyl ester monomers	MW (g/mol)	Viscosity (Pa x s)
BisGMA	512.61	1369
TEGDMA	286.33	0,008

Table 2

THE MAIN CHARACTERISTICS OF THE USED POSS

POSS	MW	m.p. (°C)	$\rho$ (g/cm <sup>3</sup> )
MA-POSS	1433.9	-	1.22
HISO-POSS	943.6	108 - 112	-
CPENTYL-POSS	1101.8	243 - 249	-

The chemical structures of the monomers and reinforcing agents are given in figure 3.

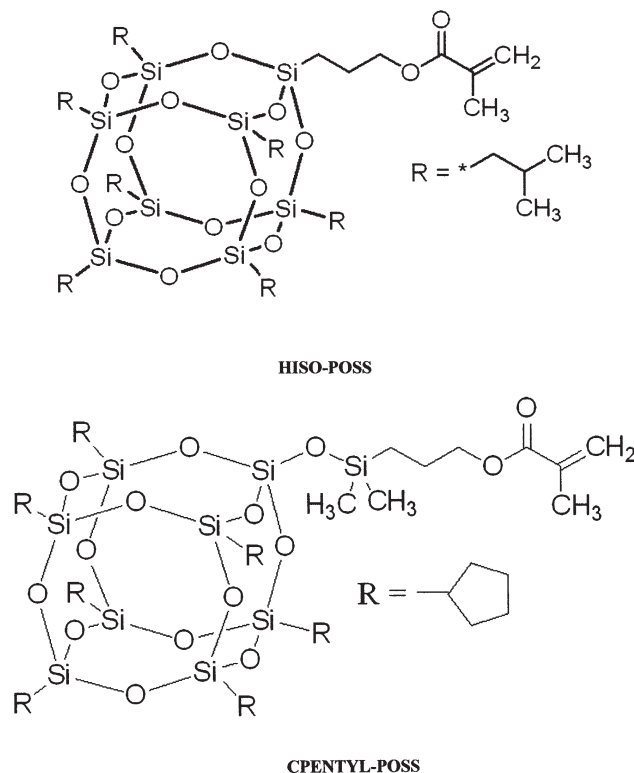


Fig. 3. The chemical structures of the monomers and reinforcing agents

**Nanocomposites synthesis**

Three types of composites based on BisGMA and TEGDMA monomers and MA-POSS, HISO-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. Then, the reinforcing agent (50%) was added and mixed into the resin. A good dispersion was achieved by using an ultrasonic device for 15 min at room temperature in order to uniformly disperse fillers into matrices. Benzoyl peroxide (1% w/w) was added to the monomer, and the mixture was ultrasonicated until it was dissolved. In order to minimize the air bubbles, the samples were degassed for 20 min. The curing reaction is performed at 80°C, 24h.

The most important steps in the nanocomposites synthesis are shown in figure 4.

**Characterization**

The FT-IR Spectra were recorded on a Shimadzu 8900 spectrometer using 30 scans with a resolution of 4 cm<sup>-1</sup> in 400-4000 cm<sup>-1</sup> region. The samples were run from KBr pellets.

Raman spectra were registered on a DXR Raman Microscope from Thermo Scientific using a 532 nm laser

**Table 3**  
THE MAIN SYSTEMS USED FOR PRODUCING NANOCOMPOSITES

No.	System	Ratio (% w)
1	BisGMA: TEGDMA	50:50
2	MA-POSS: TEGDMA	50:50
3	HISO-POSS: TEGDMA	50:50
4	CPENTYL- POSS : TEGDMA	50:50

line and a number of 50 scans. The laser beam was focused with the 10X objective of the Raman Microscope.

The TGA curves were registered on a Q500 TA Instrument at 10°C/min heating rate, from 20°C to 600°C.

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 temperature region 25°C - 300°C.

The morphology of composites was examined by scanning electron microscopy (SEM) using an HITACHI S2600N equipment. Prior to SEM examination, the specimens were sputter-coated with silver in order to

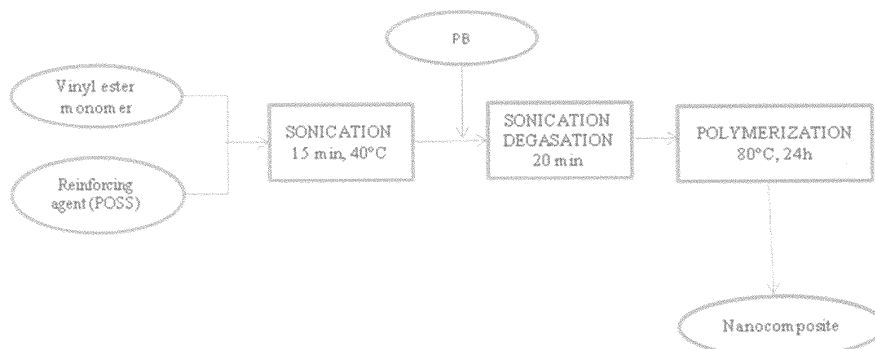
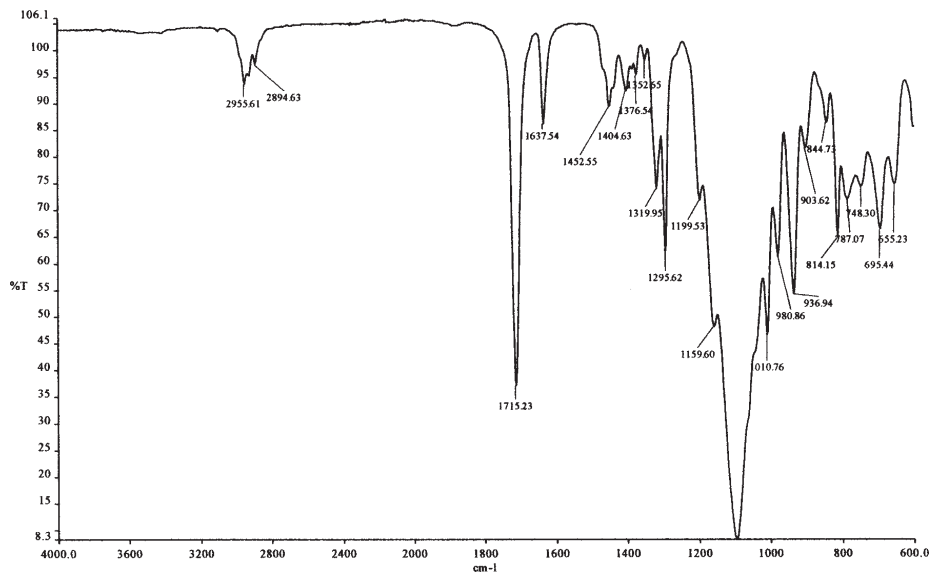
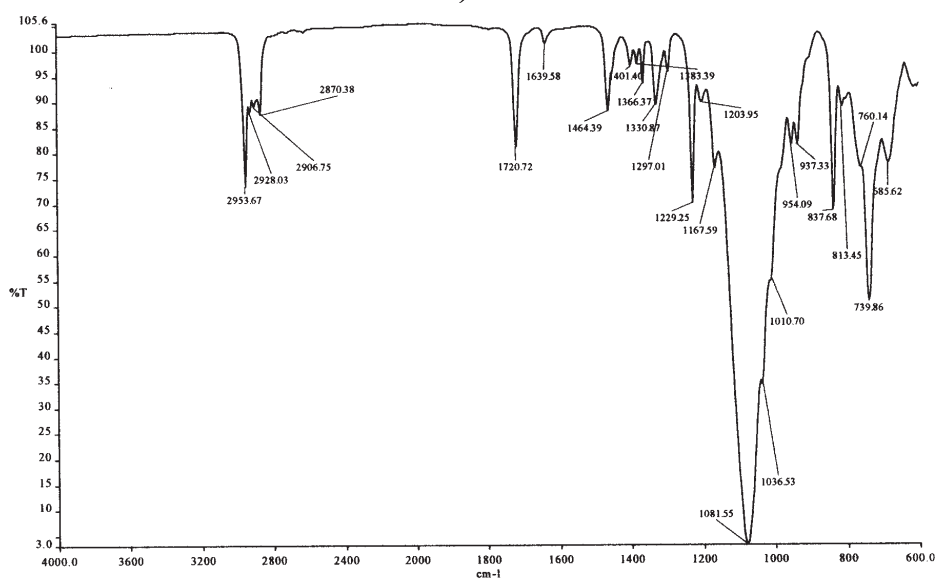


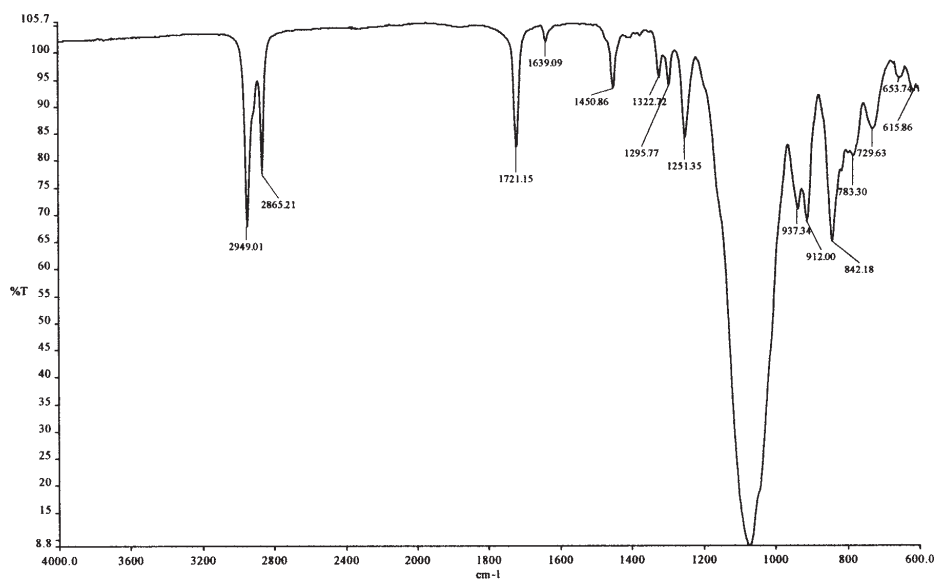
Fig. 4. The synthesis process of nanocomposite based on vinyl ester resin initiated with PB and reinforced with POSS



a)



b)



c)

Fig.5. The FT-IR spectrum of a) MA-POSS; b) HISO-POSS; c) CPENTYL-POSS

Table 4  
THE FTIR SPECTRAL ASSIGNMENTS FOR THE USED POSS

Spectral assignment/ Wavelength (cm <sup>-1</sup> )	MA-POSS	HISO -POSS	CPENTYL-POSS
$\nu_{as}$ CH <sub>3</sub>	2955	2953	2949
$\nu_{as}$ CH <sub>2</sub>	2928	2928	-
$\nu_s$ CH <sub>2</sub>	2894	2870	2865
$\nu$ C=O	1715	1720	1721
$\nu_{C=C}$ methacrylic	1637	1639	1639
$\delta_{as}$ C-H	1452	1464	1450
$\delta_s$ C-H	1404	1401	1400
$\nu$ Si-C	1295	1296	1295
$\nu$ C-O-C	1160	1168	-
$\nu_{Si-O-Si}$ from the polyhedral cage	1100	1081	1080

avoid charge accumulation. The SEM images have been achieved at electron acceleration voltage of 25 kV, up to 5  $\mu$ m resolution with a magnification between 1000x and 10.000x. For all the samples a selection of the most significant micrographs was done (1000x and 3000x magnification, 10 and 50  $\mu$ m resolution). Then, the samples were qualitatively analysed through EDAX (energy dispersive X-ray analysis). Due to Ag coating of the samples, all EDAX spectra show the Ag peak.

### Results and discussions

For the synthesis process of nanocomposite, the main idea was to replace the typical monomer BisGMA with POSS including MA groups in order to increase the mechanical and thermal properties and also to decrease the high viscosity given by BisGMA. Three types of samples based on replacing BisGMA with POSS were prepared according to table 3. As a reference the classical mixture BisGMA was used.

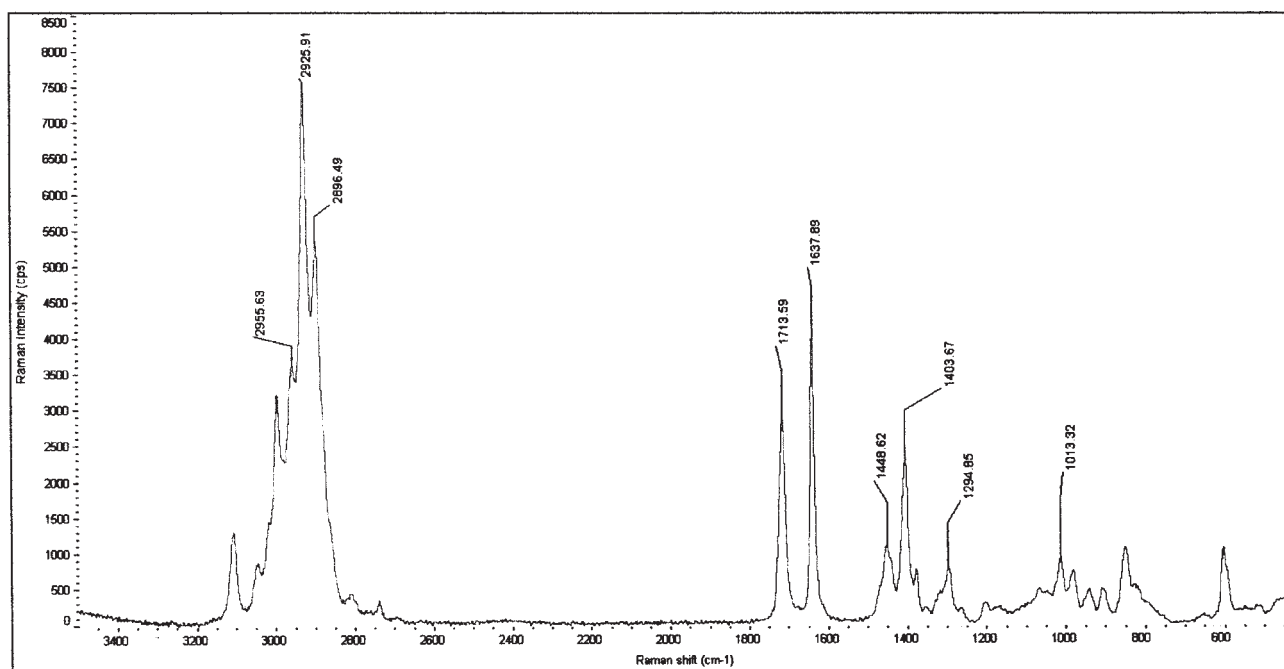
### POSS Analyses

Very few information concerning the analysis of POSS structure may be found in the literature [14, 15].

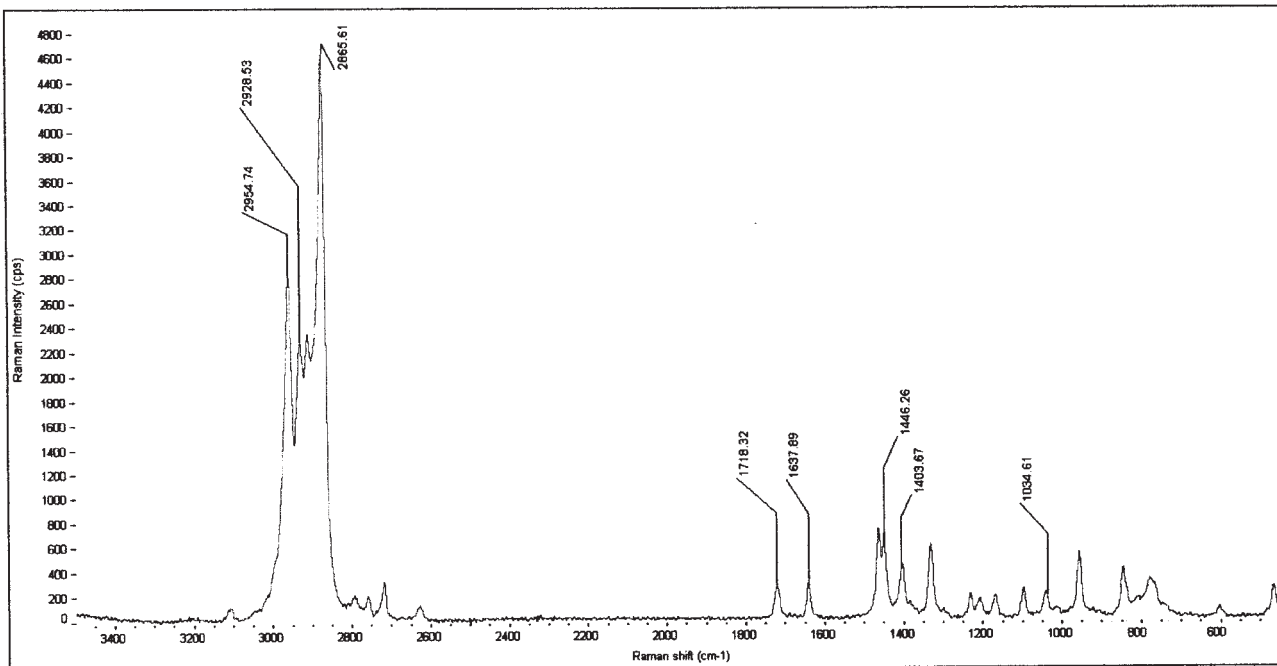
From the FT-IR Spectra of MA-POSS, HISO-POSS and CPENTYL-POSS one may notice the characteristic band at 1080 -1100 cm<sup>-1</sup> assigned to the stretching vibration of Si-O-Si bond from the cage which is dependent on the substituents bonded to the cage (1100, 1081 and 1080 cm<sup>-1</sup>, tabel 4). The same dependence is observed for the bond assigned to Si-C band. All the other bands are assigned to the vibration of the bonds from the organic chains linked to the Si atoms.

The RAMAN spectra (fig. 6, table 5) prove the presence of the same important peaks.

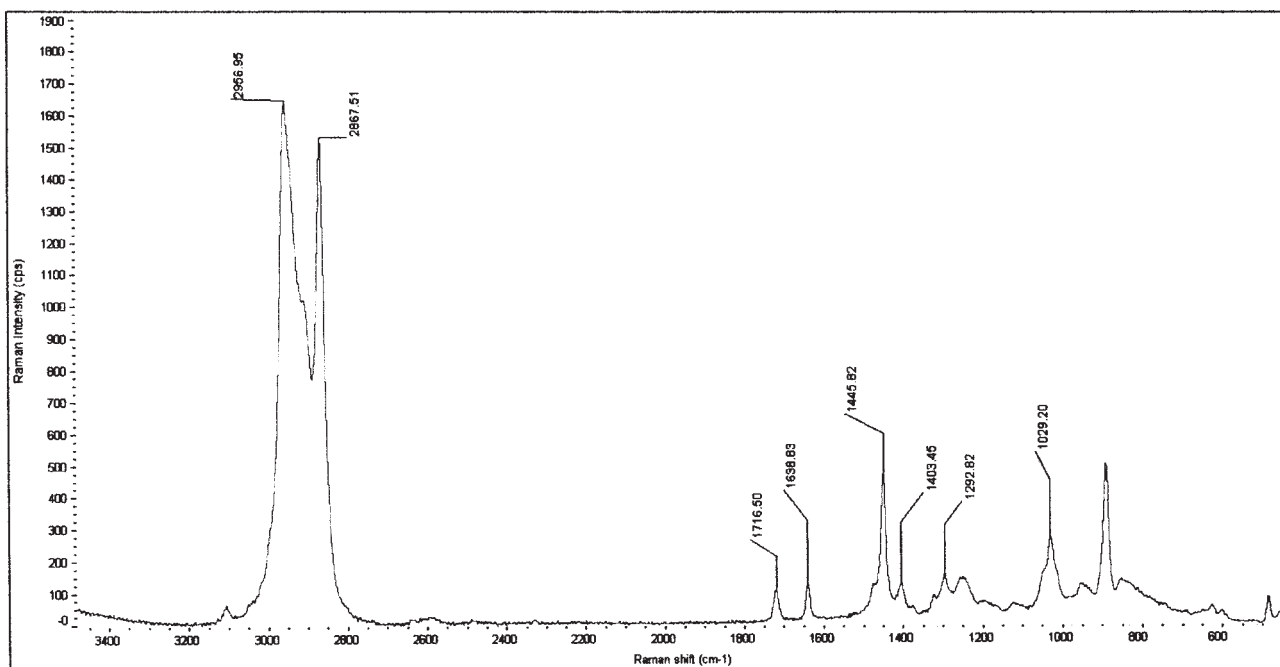
From the TGA curves of different POSS (fig. 7, table 6) one may notice that CPENTYL-POSS exhibits the highest thermostability and HISO-POSS the lowest one. This behavior could be attributed to the formation of a crosslinked silicate network, probably due to the structure of MA-POSS which includes eight methacrylic groups.



a)



b)



c)

Fig. 6. The Raman spectra of a) MA-POSS; b) HISO-POSS; c) CPENTYL-POSS

### Nanocomposites characterization

FTIR spectra of the obtained nanocomposites are shown in figure 8.

A sharp and strong peak due to Si-O-Si stretching of the silsesquioxanes cage appears at 1090 - 1100  $\text{cm}^{-1}$ . The main peaks of C=C and Si-O-Si are revealed in all nanocomposites spectra. The curing process significantly reduces the intensity of main peak of the C=C group (1635  $\text{cm}^{-1}$ ) of 50% BisGMA-50% TEGDMA copolymer. The FTIR spectrum of POSS\_TEGDMA including 50% POSS, also demonstrates the disappearance of the C=C, no matter what kind of POSS is used (MA-POSS, HISO-POSS or CPENTYL-POSS) (fig. 8).

The RAMAN spectra (fig. 9) also show the decrease of the intensity of C=C signal from the methacrylic unit

which means that a high yield of reaction between the two monomers occurred.

By TGA one may study the influence of the polyhedral cage against the thermal stability of the POSS based nanocomposites.

From table 7 one may notice that by replacing BisGMA with MA-POSS the thermostability slowly increases, considering the initial temperature at which the mass loss starts. This may be due to the highly crosslinked structure formed by the reaction between the eight MA groups from MA-POSS with the MA groups from TEGDMA which is more difficult to be thermally destroyed. However for the other two POSS types, HISO-POSS and CPENTYL-POSS the thermostability decreases. The nanocomposite based on



**Table 5**  
THE MAIN RAMAN SPECTRAL ASSIGNMENTS FOR THE USED POSS

Spectral assignment/ Wavelength (cm <sup>-1</sup> )	MA-POSS	HISO -POSS	CPENTYL-POSS
$\nu_{as}CH_3$	2955	2954	2956
$\nu_{as}CH_2$	2925	2928	-
$\nu_sCH_2$	2896	2865	2867
$\nu C=O$	1714	1718	1716
$\nu_{C=C}$ methacrylic	1637	1637	1638
$\delta_{as}C-H$	1448	1446	1445
$\delta_sC-H$	1403	1403	1403
$\nu_{Si-C}$	1294	-	1292
$\nu_{Si-O-Si}$ from the polyhedral cage	1013	1034	1029

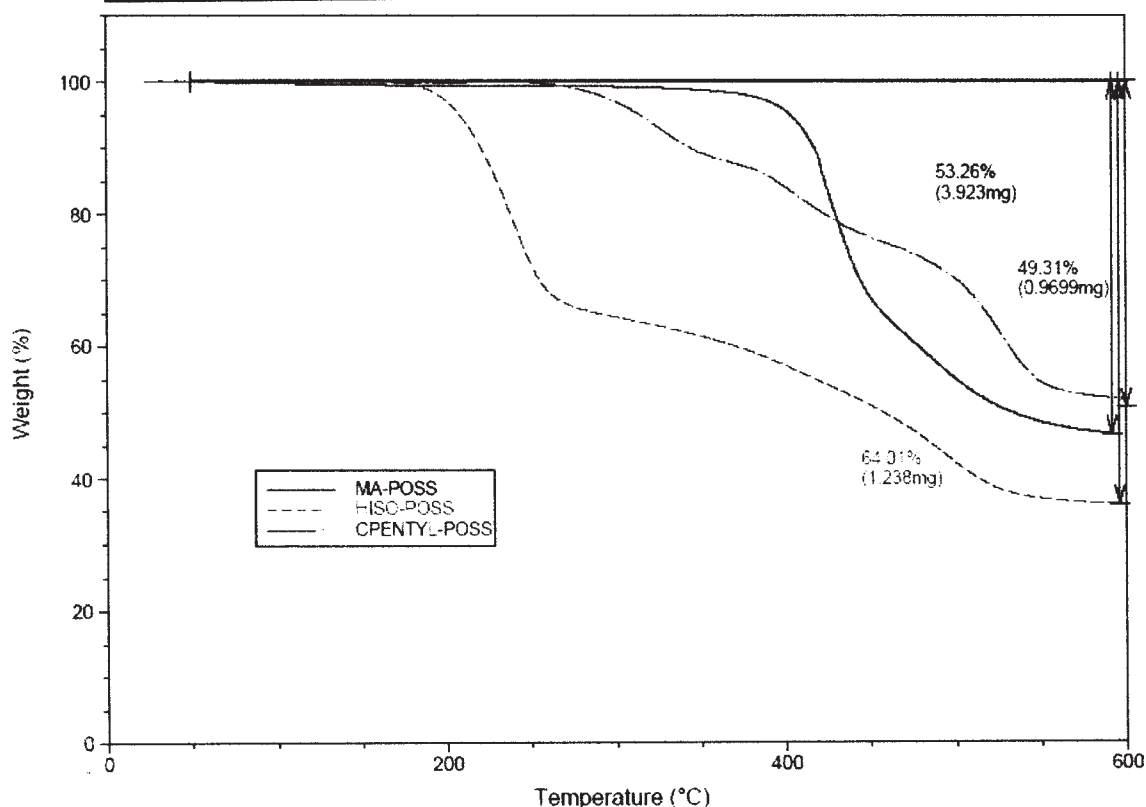


Fig. 7. The TGA curves for different POSS

**Table 6**  
THE THERMOSTABILITY OF THE REINFORCING AGENTS

POSS Type	T <sub>onset</sub> (°C)	T <sub>max</sub> (°C)	Weight loss (%)
MA-POSS	348	423	53
HISO-POSS	169	240; 492	64
CPENTYL-POSS	243	326; 404; 527	49

HISO-POSS exhibits the lowest thermostability probably due to a lower density of the crosslinked structure [TEGDMA-(HISO-POSS)], the modified POSS (HISO-POSS) exhibiting only one MA group able to complete the copolymerization reaction with TEGDMA.

The T<sub>g</sub> value, obtained by DMA, (table 7) for the BisGMA-TEGDMA copolymer is higher than the T<sub>g</sub> values of both Bis-GMA and TEGDMA homopolymers, but if Bis-GMA is replaced with HISO-POSS the T<sub>g</sub> value decreases with approximatively 40°C. This may be due to the formation of a less compact structure

because of the polyhedral cages. Also, the obtained structure (HISO-POSS\_TEGDMA) is more similar with TEGDMA homopolymer according to the initial structure of HISO-POSS which includes only one active MA group.

The systems based on 50%MA-POSS and 50%CPENTYL-POSS respectively were not able to be studied by DMA because they are too brittle.

Figure 11 displays SEM images of the fracture surfaces of the reference dimethacrylate resin (50% Bis-GMA\_50% TEGDMA) and 50% CPENTYL-POSS\_50%TEGDMA composite. These surfaces show no macro-phase separation or evidence of aggregates of CPENTYL-POSS within the limits of SEM detection. A variety of magnifications were employed to examine the morphology.

The dispersed phase domains and the matrix regions were analyzed by EDAX, to determine the local silicon content in the SEM images. EDAX elemental analyses of phase domains in a nanometer-size region cannot be

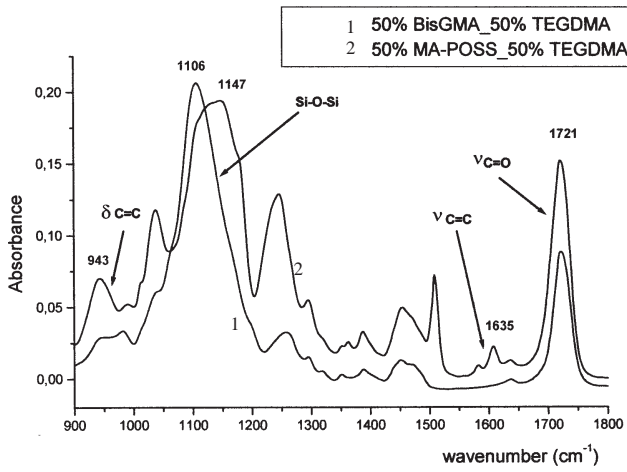
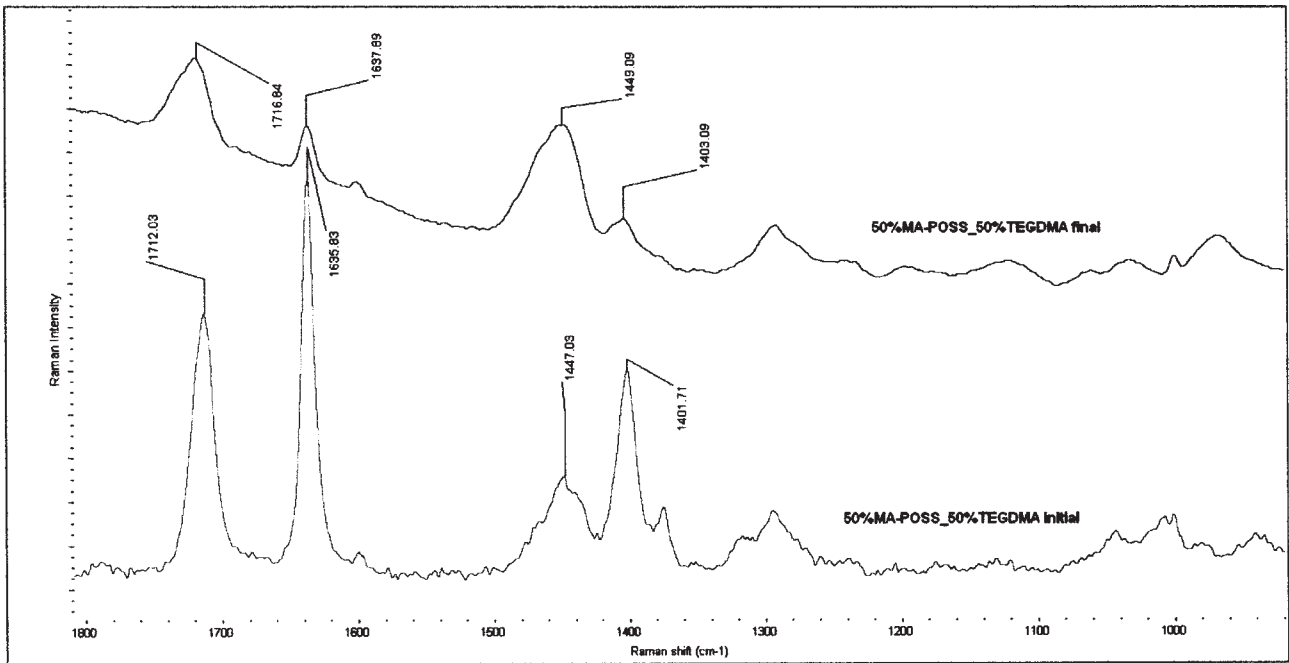
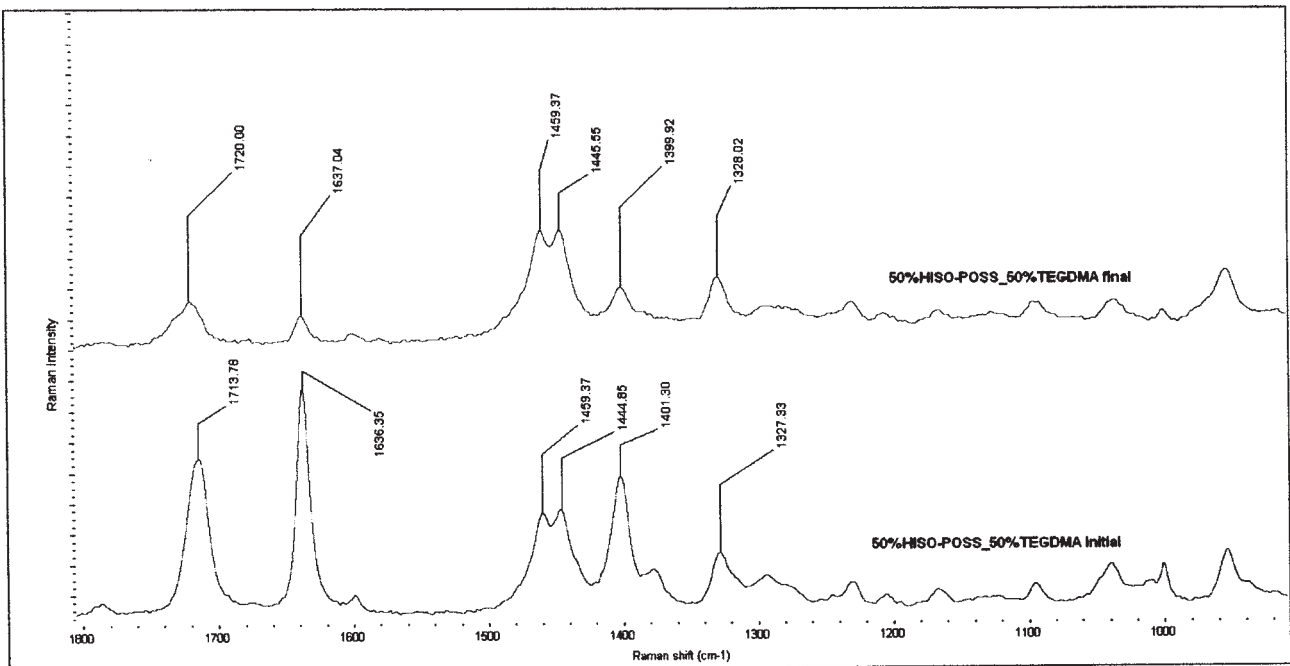


Fig. 8. The FTIR spectra for the nanocomposite 50%MA-POSS\_50%TEGDMA

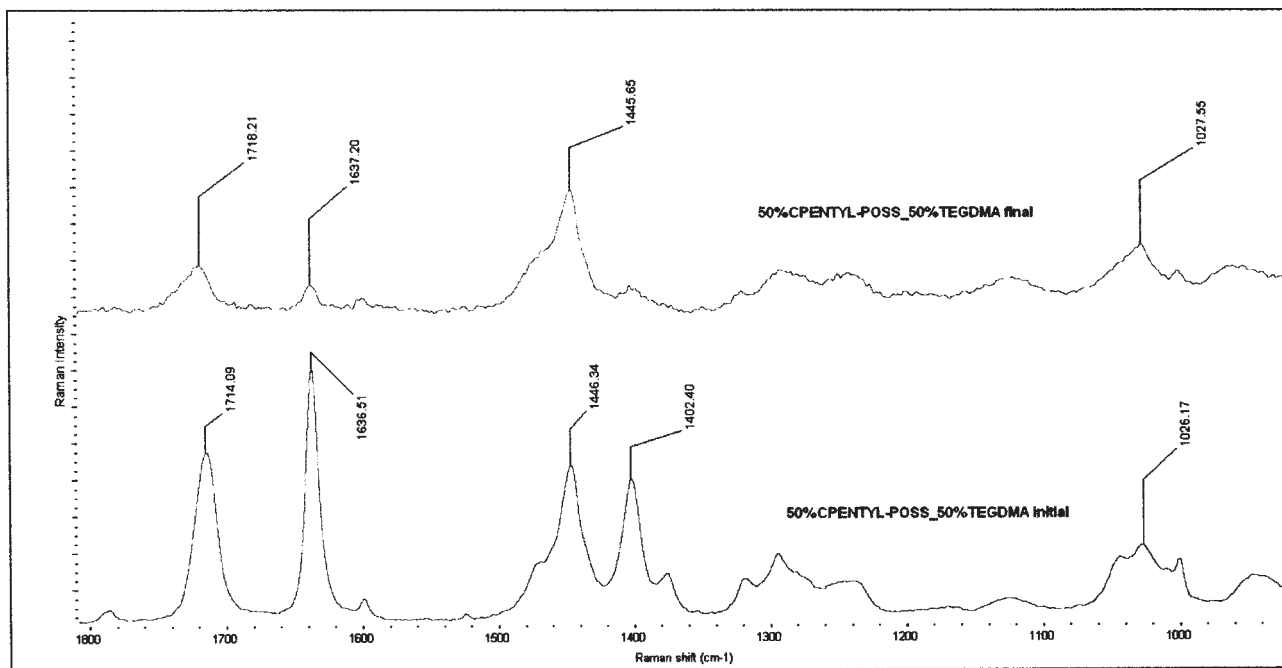


a)



b)





c)

Fig. 9. The RAMAN spectra for the composites with various types of POSS  
 a) 50%MA-POSS\_50%TEGDMA; b) 50%HISO-POSS\_50%TEGDMA; c) 50%CPENTYL-POSS\_50%TEGDMA

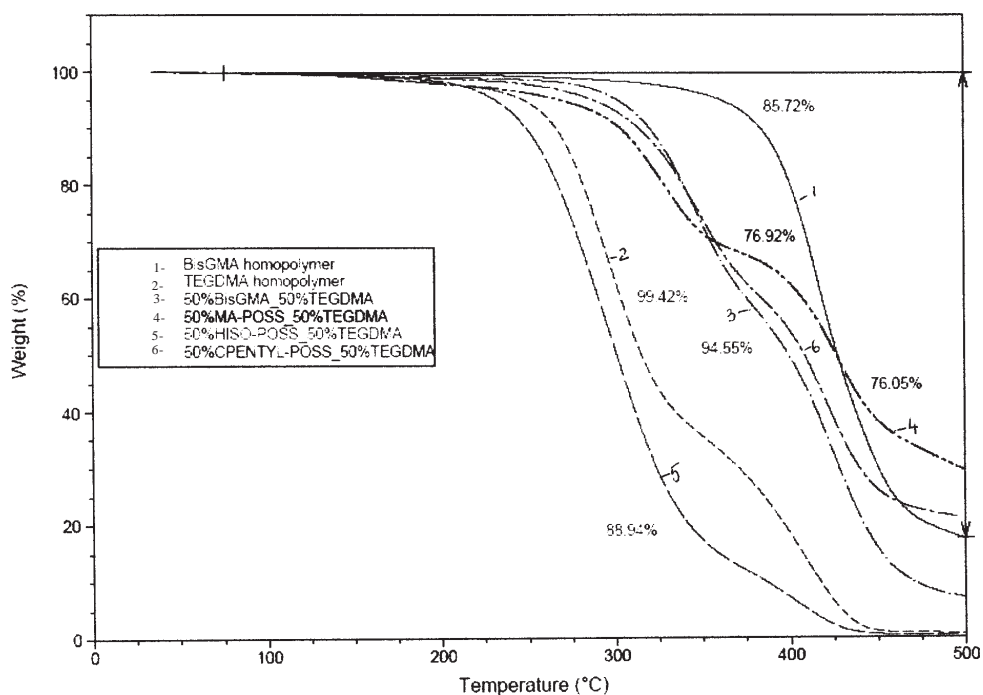


Fig. 10. The TGA curves for the nanocomposites initiated with benzoyl peroxide (80°C; 24h)

**Table 7**  
 THE SIGNIFICANT TEMPERATURES FROM THE DTG CURVES FOR THE NANOCOMPOSITES INITIATED WITH BENZOYL PEROXIDE

Sample	T <sub>onset</sub> (°C)	T <sub>max</sub> (°C)	T <sub>g</sub> (°C)	Weight loss (%)
100%BisGMA	275	416	147	85
100%TEGDMA	220	287; 396	123	99
50%BisGMA -50%TEGDMA	260	347; 425	175	94
50% MA-POSS - 50%TEGDMA	280	327; 427	-	77
50% HISO-POSS- 50%TEGDMA	200	310; 416	132	100
50%CPENTYL-POSS- 50%TEGDMA	210	353; 424	-	76

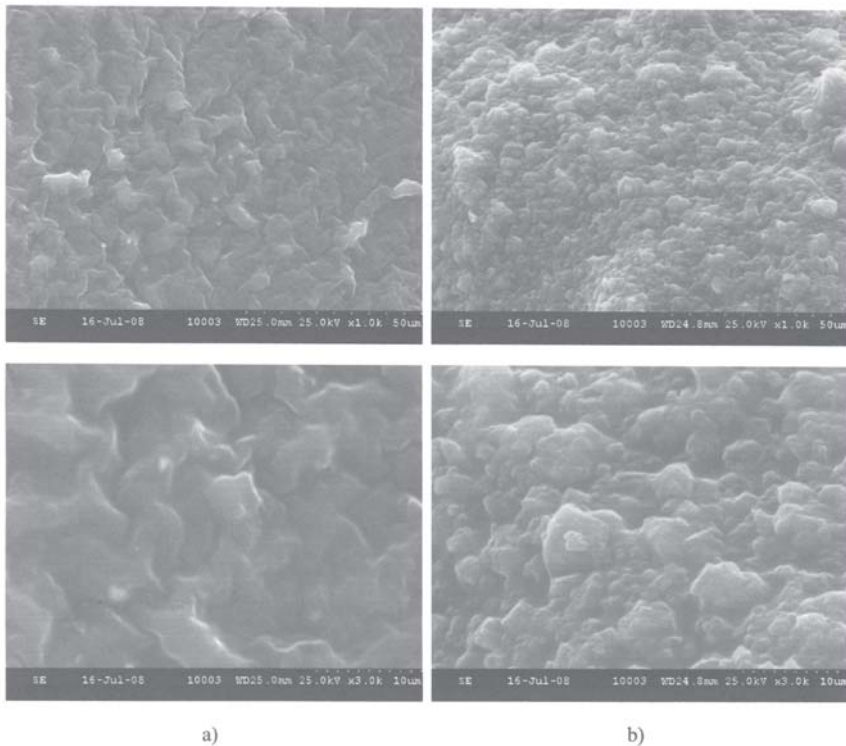


Fig. 11. SEM micrographs of fractured surface for:  
 a) 50% BisGMA\_50% TEGDMA;  
 b) 50% CPENTYL-POSS\_50% TEGDMA

sample	total % Si in SEM image	% Si at specific location
BisGMA_TEGDMA (no POSS)	-	-
MA-POSS_TEGDMA	63.57	59.44
HISO-POSS_TEGDMA	70.93	72.15
CPENTYL-POSS_TEGDMA	69.20	68.88

**Table 8**  
 SILICON CONTENT FROM EDAX SPECTRA

accurately measured. From this analyses it was determined the total amount of silicon in a SEM image and the amount of silicon at specific location (table 8).

### Conclusions

New nanocomposites based on modified POSS were successfully synthesized by replacing the classical monomer Bis-GMA with POSS having different groups bonded to the polyhedral cages.

Using a modified POSS with multiple MA groups, like MA-POSS, the properties of the obtained nanocomposite are improved, e.g. the Tg value and the thermostability. These improvements are also due to rigidity induced by the polyhedral cages which confirms that the MA-POSS acts both as a comonomer for the reaction with TEGDMA and also as a true reinforcing agent within the obtained nanocomposite.

In the case of HISO-POSS and CPENTYL-POSS the obtained properties for the nanocomposites are lower than for BisGMA-TEGDMA system because of the incomplete copolymerization reaction with only one MA group from the modified POSS.

The micro-morphology and aggregation state of nanocomposites will be further investigated using TEM and XRD.

### References

- WEICKMANN, H., DELTO, R., THOMANN, R., BRENN, R., DOLL, W., MULHAUPT, R., *J Mater Sci*, **42**, 2007, p. 87
- FONG, H., DICKENS, S. H., FLAIM, G. M., *Dental Materials*, **21**, 2005, p. 520

- LEE, Y.-J., HUANG, J.-M., KUO, S.-W., LU, J.-S., CHANG, F.-C., *Polymer*, **46**, 2005, p. 173
- ZHAO, C., YANG, X., WU, X., LIU, X., WANG X., LU L., *Polymer Bulletin*, **60**, 2008, p. 495
- ZHANG, Z., LIANG, G., WANG X., *Polymer Bulletin*, **58**, 2007, p. 1013
- LIN, H.-C., KUO, S.-W., HUANG, C.-F., CHANG, F.-C., *Macromol. Rapid Commun.*, **27**, 2006, p. 537
- JOTHIBASU, S., PREMKUMAR, S., ALAGAR M., *High Performance Polymers*, **00**, 2007, p. 1
- CHEN, W.-Y., HO, K. S., HSIEH, T.-H., CHANG, F.-C., WANG, Y.-Z., *Macromol. Rapid Commun.*, **27**, 2006, p. 452
- MATEJKA, L., STRACHOTA, A., PLESTIL, J., WHELAN, P., STEINHART, M., SLAOF, M., *Macromolecules*, **37**, 2004, p. 9449
- LIU, Y., ZHENG, S., NIE K., *Polymer*, **46**, 2005, p. 12016
- ZHENG, L., WADDON, A. J., FARRIS, R. J., COUGHLIN, E. B., *Macromolecules*, **35**, 2002, p. 2375
- WADDON, A. J., ZHENG, L., FARRIS, R. J., COUGHLIN, E. B., *Nanoletters*, **10**, 2002, p. 1149
- WADDON, A. J., COUGHLIN, E. B., *Chem. Mater.*, **15**, 2003, p. 4555
- FU, B. X., HSIAO, B. S., PAGOLA, S., *Polymer*, **42**, 2001, p. 599
- XU, H., KUO, S.-W., LEE, J.-S., *Macromolecules*, **35**, 2002, p. 8788
- PETREA, C., GÂREA, S.A., IOVU, H., *Mat. Plast.*, **45**, nr. 1, 2008, p. 34
- GAREA, S.A., CONSTANTIN, F., VOICU, G., IOVU, H., **45**, nr. 4, 2008, p. 414

Manuscript received: 1.10.2008