Advanced Characterization of Polyhedral Oligomeric Silsesquioxanes Used for Nanocomposites Synthesis

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Three types of polyhedral oligomeric silsesquioxane (POSS) compounds were used to synthesize nanocomposites based on urethane dimethacrylate (UDMA). An advanced characterization of POSS compounds was done by X-Ray Photoelectron Spectroscopy (XPS) for chemical structure, X-Ray Diffraction (XRD) for crystalline phase and Differential Scanning Calorimetry (DSC) for thermal transitions. The POSS compounds generally influence the thermostability of UDMA-based nanocomposites acting both as a comonomer and reinforcing agent.

Keywords: polyhedral oligomeric silsesquioxanes, XPS, XRD, DSC, nanocomposites, TGA

Polyhedral oligomeric silsesquioxane (POSS) is a class of organic/inorganic hybrid nanomaterials made up of an inorganic silica $(RSiO_{1.5})_n$ core cage (n = 8, 10, 12). POSS compounds can be successfully incorporated into thermoplastics or thermosets polymers, being possible to enhance the final properties of the obtained nanocomposites. The core structure of the POSS can be modified by attaching either reactive or non-reactive functional groups to the Si atoms. The unreactive organic groups (R) are used for compatibilization of the POSS molecules with organic media (monomers or solvents), while the reactive groups (X) are required for grafting polymerization, e.g. R can be cyclohexyl, cyclopentyl, phenyl or a methyl, while X may include a vinyl, methacrylate group or an epoxy ring, etc. In general, to obtain molecular dispersion, some kind of chemical bonds between the POSS functional groups and the host polymer are required [1-3]. The degree of compatibility and reactivity can be tailored adequately designing the chemical structure pending from the stable silica-like core of the POSS. The reactive functionalities can generate covalent bonding with the base polymer, reducing in this way the repelling effect associated to the components mixture. Traditionally, copolymerization has been the most common approach used to form polymer–POSS nanocomposites [4].

The use of nanofillers is an excellent way to improve the mechanical and thermal behavior for a certain polymer without affecting the impact toughness or the transparency as it happens, using conventional fillers. The development of organic-inorganic nanocomposites with improved properties has attracted much interest in the past few years. Organic/inorganic nanocomposites have been regarded as new generation of high performance materials since they combine the advantages of the inorganic materials (rigidity, high stability, functionality) and the organic polymers (flexibility, dielectric, ductility and processability) receiving considerable attention due to their enhanced properties compared with the homogenous organic polymers [5].

The incorporation of POSS molecules into polymers can lead to a successful improvement of the flammability, thermal or polymer mechanical properties. The POSS derivatives have been shown to increase the glass transition temperature [6], modulus [7], decomposition temperature, and oxygen permeability [8, 9], while reducing the flammability [10] when incorporated into polymer matrices [11]. The thermo-mechanical properties of polymer–POSS nanocomposites systems are highly related to the final microstructure, which in turn depends on the type of interaction between the nanocages and the matrix. POSS nanocages can be dispersed at a molecular scale or they can act like microdispersed fillers [12].

In order to incorporate the POSS compounds into a variety of conventional polymers, first it was performed an advanced characterization to get information about their chemical structure, degree of crystallinity, thermal behavior, etc. This step was compulsory because in the case of POSS compounds, with a very recent history, such information that can be found in the literature are incomplete, missing or controversial.

Experimental part

Materials

All materials used in this study are commercially available and were used as received. Three different POSS compounds were selected: two types of monofunctional-POSS, **HISO-POSS** (POSS-(1-Propylmethacrylate)-Heptaisobutyl substituted, and **CPENTYL-POSS** (POSS-3-[(3, 5, 7, 9, 11, 13, 15-Heptacyclopentylpentacyclo [9.5.1.1^{3,9}.1^{5,15}.1^{7,13}] octasiloxan-1-yloxy)dimethylsilyl] propyl methacrylate) and one octafunctional **MA-POSS** (Methacryl substituted POSS, cage mixture, n=8, 10, 12) and **UDMA** (urethane dimethacrylate) monomer (fig. 1). The POSS compounds and UDMA monomer were purchased from Sigma-Aldrich Chemicals.

Characterization

X-Ray Photoelectron Spectroscopy (XPS)

The XPS Spectra were recorded on a Thermo Scientific K-Alpha equipment, fully integrated, with an aluminum anode monochromatic source. Survey scans (0-1200 eV) were performed to identify constitutive elements.

X-Ray Diffraction (XRD)

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

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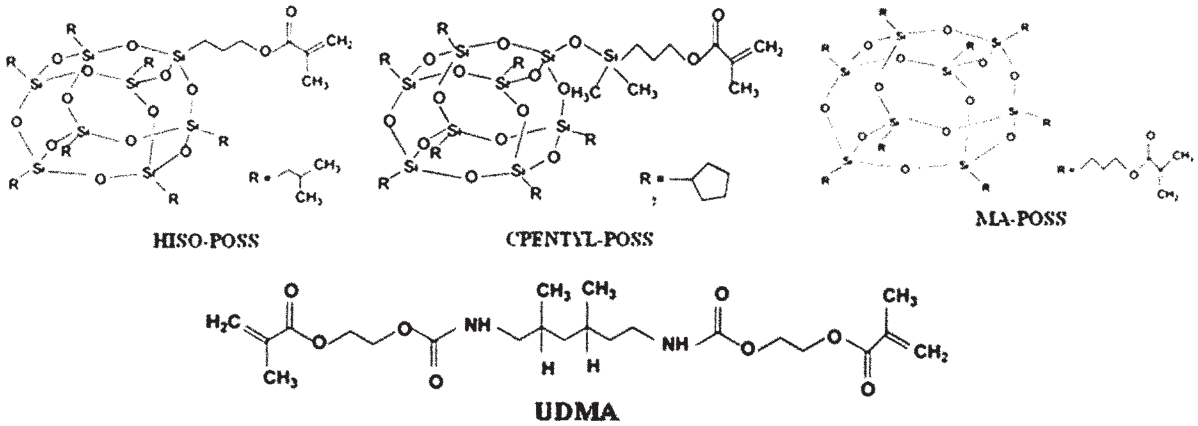

Fig.. 1. The chemical structure of POSS nanostructured compounds and UDMA monomer

Differential Scanning Calorimetry (DSC)

The DSC curves were isothermally recorded on a Netzch equipment at 10K/min heating rate in 30°C - 400°C temperature range.

Thermogravimetric Analysis (TGA)

The TGA curves were registered on a Q500 TA instrument at 10°C/min heating rate, from 25°C to 550°C under nitrogen atmosphere.

Synthesis of POSS-based nanocomposite

Three types of nanocomposites based on UDMA monomer and MA-POSS (octafunctional-POSS), HISO-POSS and CPENTYL-POSS (monofunctional POSS) were synthesized using a certain POSS concentration (25%). The nanocomposites were prepared by bulk polymerization using as initiator benzoyl peroxide (BP) at 80°C [13].

To prove the influence of the POSS type on the nanocomposites thermostability thermogravimetric analyses were performed between 25°C and 550°C under nitrogen atmosphere.

Results and discussion

Previously, the chemical composition of the nanostructured POSS compounds was studied by FTIR and dispersive RAMAN spectroscopy [14-17]. These techniques provided valuable information about the structure of the selected POSS compounds.

In this study, complementary information about the chemical structure is obtained by XPS. XPS is an elemental analysis technique that is unique in providing chemical state information of the detected elements [13].

XPS analysis

XPS survey spectra

The XPS survey spectra were registered in order to identify the surface elements and showed distinct carbon, silicone and oxygen peaks which are the major constituents of the investigated monofunctional HISO-POSS and CPENTYL-POSS. No other major elements were detected. Octafunctional POSS (MA-POSS) can not be studied by XPS because it is viscous and therefore it is not compatible with the equipment.

The XPS survey spectra are shown in figure 2 and the relative atomic concentrations (At%) for carbon, oxygen and silicone are listed in table 1.

There are no significant differences in elements concentration for the two studied monofunctional POSS.

C (1s) high resolution XPS spectra

The high resolution XPS spectra for the nanostructurated compounds, in the region of C 1s are shown in figure 3.

The C 1s peak from the HISO-POSS was deconvoluted into three peaks (fig. 3a). The low energy peak, denoted as C, noticed at 284.2 eV was attributed to the Si-C bonds. A second peak appears at a higher binding energy, denoted as B, observed at approximatively 285.8 eV. This peak can be assigned to the C-C /C-H bonds and to C=C bonds. The third peak, A, at 287 eV was assigned to the O=C-O group.

Also, the observed C 1s peak of CPENTYL-POSS was deconvoluted into three similar peaks (fig. 3b). The peak, denoted as C, noticed at 284.7 eV corresponds to Si-C bonds. The second peak, denoted as B from 287.6 eV was assigned to C-C/C-H bonds and to C=C bonds. The last peak, denoted as A, at 288.2 eV was attributed to O=C-O group.

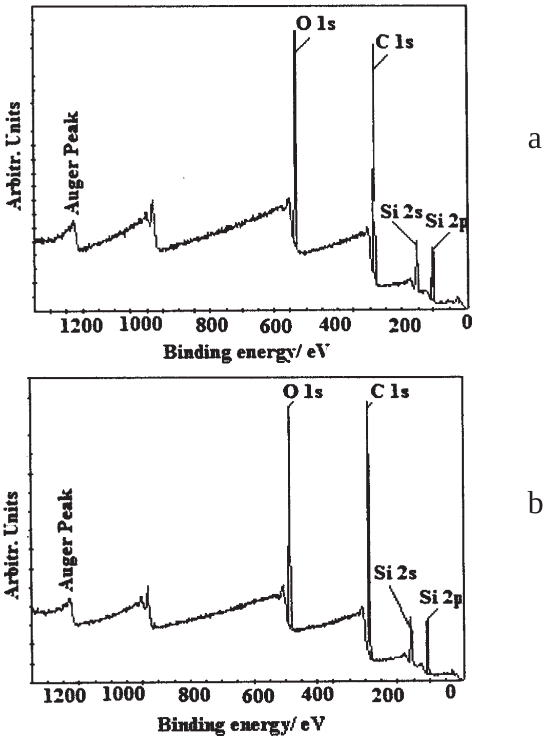

Fig. 2. XPS survey spectra for a) HISO-POSS and b) CPENTYL-POSS

Table 1
RELATIVE ATOMIC CONCENTRATIONS (AT%)
OF THE ELEMENTS FROM THE XPS SURVEY SPECTRA

POSS / At%	C	O	Si
HISO-POSS	60.7	22.7	16.6
CPENTYL-POSS	62.9	20.8	16.3

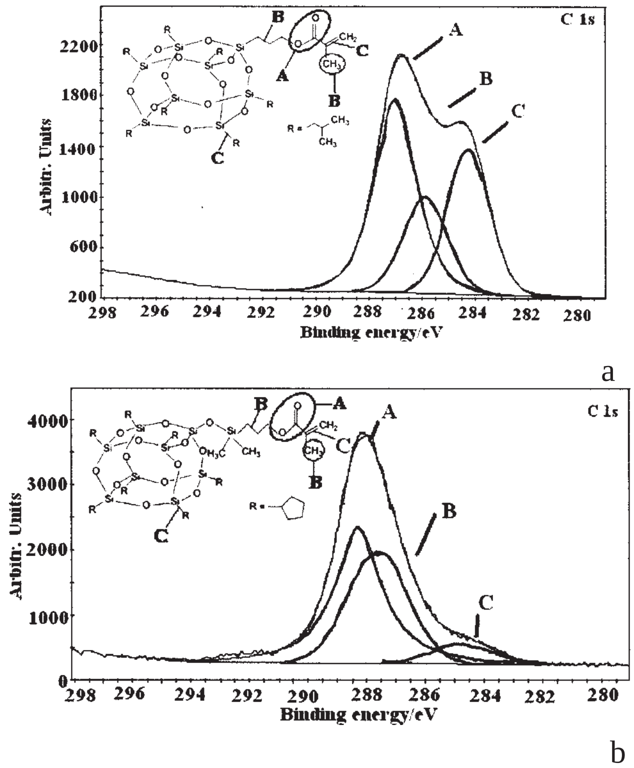

Fig. 3. C (1s) high resolution XPS spectra for HISO-POSS (a) and CPENTYL-POSS (b)

Si (2p) high resolution XPS spectra

The high resolution XPS spectra for the nanostructurated compounds, in the region of Si 2p, are shown in figure 4. The observed peaks for HISO-POSS and for CPENTYL-POSS were deconvoluted in two distinct peaks. For both compounds, the low energy peak, denoted as B, at 102-103 eV was attributed to the Si-C bond formed between the cage and the substituents. The high energy peak, denoted as A, observed at 104-105 eV, is assigned to Si-O bond from the cage.

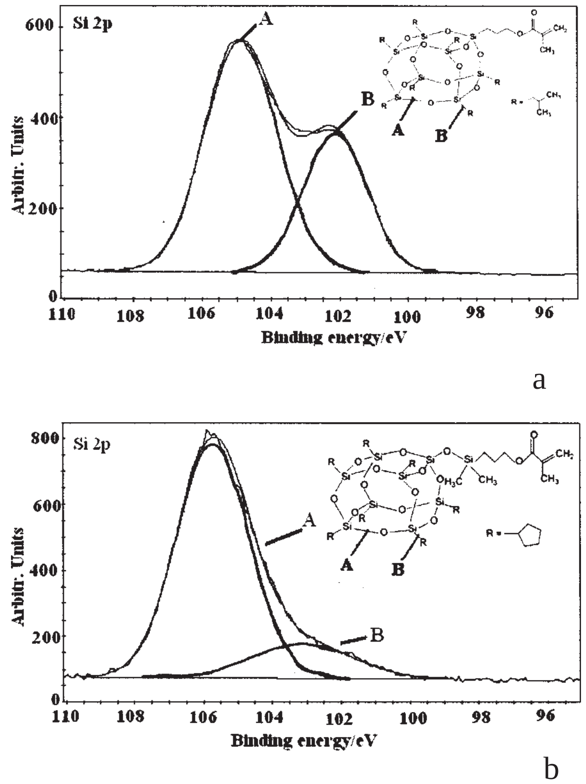

Fig. 4. Si (2p) high resolution XPS spectra for HISO-POSS (a) and CPENTYL-POSS (b)

XRD analysis

XRD is used to identify the inorganic elements and crystalline phases occuring in POSS compounds. XRD analyses complete the chemical data obtained by FTIR, dispersive RAMAN and XPS.

XRD patterns were recorded only for HISO-POSS (fig. 5a) and CPENTYL-POSS (fig. 5b), which are provided as powders, while the MA-POSS exhibits a viscous-fluid consistency and can not be placed in the equipment. The X-ray diffraction peaks for commercial POSS compounds are sharp and well defined indicating a high purity. Their perfectly defined architecture and isotropic character facilitate the crystalline structure.

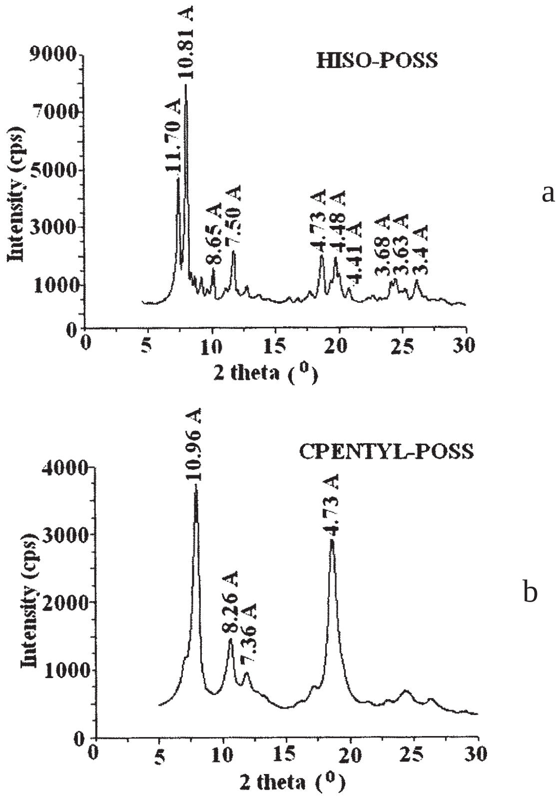

Fig. 5. XRD profiles for POSS compounds a) HISO-POSS and b) CPENTYL-POSS

Thus, HISO-POSS exhibits more distinct peaks at 2θ= 7.54°, 8.17°, 10.21°, 11.78°, 18.71°, 19.79°, 20.08° and 24.13°, which correspond to Bragg distances of 11.70 Å, 10.81Å, 8.65Å, 7.50Å, 4.73Å, 4.48Å, 4.41 Å and 3.68 Å. XRD profile for HISO-POSS shows that the main diffraction peaks correspond to Miller index h k l = (1 0 0), (0 1/-1 0), (1 -1 0), (1 1 0), (1 2 0), (2 1 1), (2 1 -1) (-1 3 3).

For CPENTYL-POSS, on the XRD pattern one may distinguish 5 distinct peaks at 2θ = 8.05°, 10.69°, 12.00°, 18.73° and 24.43°, which correspond to Bragg distances of 10.96Å, 8.26Å, 7.36Å, 4.73Å and 3.64Å. 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 maximum XRD diffraction corresponds to the Bragg distance d = 10.21Å (in HISO-POSS) and respectively d = 10.96Å (in CPENTYL-POSS) being due to the size of the POSS molecule. The other peaks are caused by the crystalline structure of POSS molecules.

DSC analysis

Previously, we demonstrated by TGA studies [14] that MA-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

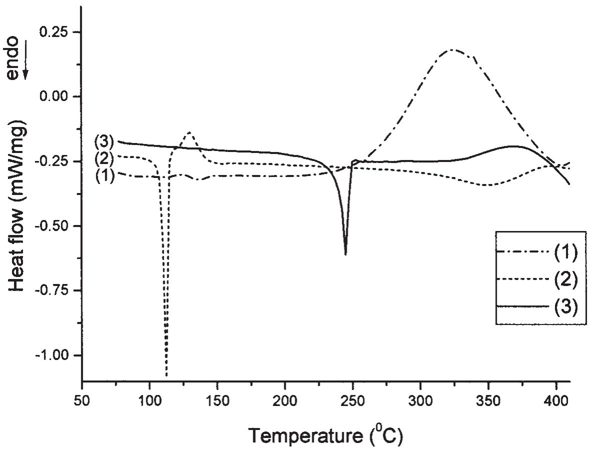

Fig. 6. DSC curves for POSS compounds (1) MA-POSS; (2) HISO-POSS; (3) CPENTYL-POSS

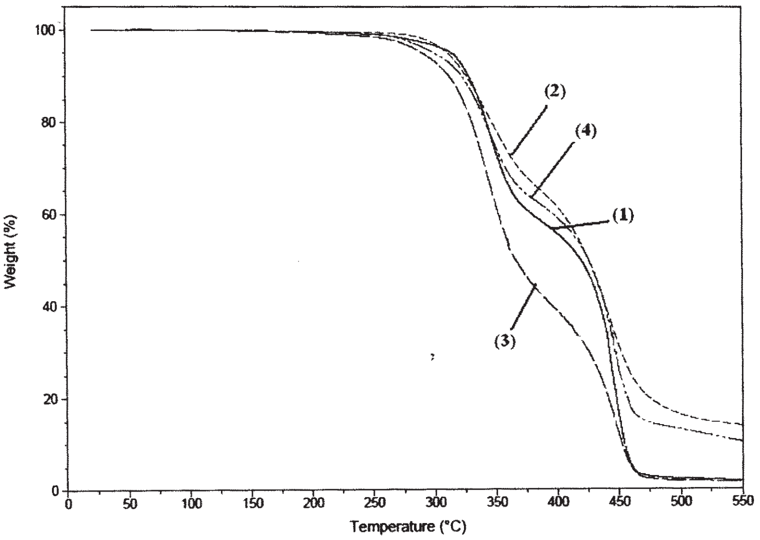

Fig. 7.Thermal decomposition of the nanocomposites based on various types of POSS (1) UDMA homopolymer, (2) 25%MA-POSS_75%UDMA, (3) 25%HISO-POSS_75%UDMA, (4) 25%CPENTYL-POSS_75%UDMA

Table 2
THE THERMOSTABILITY FOR THE NANOCOMPOSITES

Nanocomposites	T_{onset} (°C)	T_{max} (°C)	Weight loss (%)
UDMA	281	346	98
25%MA-POSS_75%UDMA	293	347	86
25%HISO-POSS_75%UDMA	263	343	98
25%CPENTYL-POSS_75%UDMA	275	345	89

due to the structure of MA-POSS which includes eight methacrylic groups.

DSC is an analytical tool which helps to understand the thermal behaviour of POSS compounds. In this work we have monitored the phase transitions for POSS compounds by DSC.

The DSC analysis of HISO-POSS reveals the presence of an endothermic peak suggesting that HISO-POSS powder is melting (112.5°C). The melting transition for HISO-POSS is probably caused by the lower molecular weight. As soon as the POSS is melted, the homopolymerization of the C=C bonds starts, which is indicated by an exothermic peak that corresponds to radical polymerization process (130°C).

During the heating, CPENTYL-POSS exhibits two phase transitions that involves: melting (endothermic peak at 245°C) and polymerization (exothermic peak at 370°C).

Both endo- and exo- peaks from CPENTYL-POSS are higher than in HISO-POSS. This can be due to the higher steric hindrance of the multiple cyclopentil groups on a POSS cage.

In contrast with mono-POSS compounds, MA-POSS with eight methacrylic groups doesn't melt. The only process that occurs is the homopolymerization of methacrylic groups at 325°C, higher than HISO-POSS, and lower than CPENTYL-POSS. The reason of this has to be found in the less reactivity of the methacrylic groups of the CPENTYL-POSS with respect to the MA-POSS [18].

Nanocomposites characterization

From the figure 7 and table 2 one may observe that MA-POSS increases the T_{onset} value in comparison with UDMA homopolymer. The value of T_{max} is not significantly modified by POSS type.

The nanocomposite based on HISO-POSS exhibits the same weight loss as UDMA homopolymer (98% weight loss), while nanocomposites based on MA-POSS and CPENTYL-POSS increase the thermostability.

Conclusions

The XPS survey spectra showed distinct carbon, silicone and oxygen peaks representing the major constituents of the investigated monofunctional HISO-POSS and CPENTYL-POSS. As expected, no other major elements were detected. On the C 1s high resolution spectra a single peak was observed which was deconvoluted into three peaks corresponding to the bonds from POSS structure. Also, the Si 2p high resolution spectra exhibits only one peak, which was deconvoluted into two peaks that correspond to the Si-C and Si-O bonds.

The X-ray diffraction peaks for commercial POSS compounds are sharp and well defined indicating a high purity. Their perfectly defined architecture and isotropism facilitate the crystalline structure.

The DSC analysis for monofunctional POSS compounds (HISO-POSS and CPENTYL-POSS) reveals the presence of an endothermic peak, which suggests the POSS melting, and an exothermic peak caused by the polymerization process. In contrast, MA-POSS exhibits only one process - the homopolymerization of methacrylic groups.

The thermostability of the POSS-based nanocomposites is strongly influenced by the POSS type. If HISO-POSS exhibits no effect, the MA-POSS and CPENTYL-POSS increase the thermostability.

Further, the nanostructured POSS compounds will be used as nanofillers in order to improve the flammability, thermal or polymer mechanical properties. The final properties of polymer–POSS nanocomposites systems could be highly related to the obtained microstructure, which in turn depends on the type of interaction between the nanocages and the matrix.

References

[1] IYER, S., SCHIRALDI, D.A., Macromolecules, **40**, 2007, p. 4942

[2] LIU, H., ZHENG, S., NIE, K., Macromolecules, **38**, 2005, p. 5088

[3] M. Sánchez-Soto , David A. Schiraldi , S. Illescas, European Journal Polymer, **45**, 2009, p. 341

[4] LIU, H., ZHENG, S., Macromol Rapid Commun, **26**, 2005, p. 196

[5] ZHU, Y., ZHAO, J., WANG, XI, and LI, Q., Chem. Res. Chinese Universities, **24**, 2008, p. 570

[6] SEURER, B., COUGHLIN, E.B., Macromol Chem Phy, **209**, 2008, p. 1198

[7] XU, H., YANG, B., WANG, J., GUANG, S., LI, C., J Polym Sci Part A: Polym Chem, **45,** 2007, p. 5308

[8] YOON, K.B., LEE, D.H., Polym Sci Tech (Korea), **16**, 2005, p. 833

[9] LIU, H., ZHENG, S., Macromol Rapid Commun, **26,** 2005, p. 196

[10] CARNIATO, F., BOCCALERI, E., MARCHESE, L., FINA, A., TABUANI, D., CAMINO, G., Eur J Inorg Chem, **4**, 2007, p. 585

[11] ZHANG, H., SHIN, Y., YOON, K., LEE, D., European Journal Polymer, **45**, 2009, p. 40

[12] ZHANG, Y., LEE, S., YOONESSI, M., LIANG, K., PITTMAN, C.U., Polymer, **47,** 2006, p. 2984

[13] SULCA, N.M., LUNGU, A., GAREA, S.A., IOVU, H., Journal of Raman Spectroscopy, accepted 2009

[14] SULCA, N.M., LUNGU, A., POPESCU, R., GAREA, S.A., IOVU, H., Mat. Plast. **46**, nr. 1, 2009, p. 1

[15] PETREA, C., ANDRONESCU, C., PANDELE, A.M., GÂREA, S.A., IOVU, H., Mat. Plast., **45**, nr. 4, 2008, p. 320

[16] GAREA, S.A., CONSTANTIN, F., VOICU, G:, IOVU, H., Mat. Plast., **45**, nr. 4, 2008, p. 414

[173] PETREA, C., GÂREA, S.A., IOVU, H., Mat. Plast., **45**, nr. 1, 2008, p. 34

[18] AMICI, M., PhD Thesis, L'Institut National des Sciences Appliquees de Lyon, 2006, p. 60

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