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Surface energies of linear and cross-linked polymers based on isobornyl methacrylate and methacryl-heptaisobutyl POSS

Ileana A. Zucchi, María J. Galante, Roberto J.J. Williams *

Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICET), J.B. Justo 4302, 7600 Mar del Plata, Argentina

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ABSTRACT

The use of monofunctional polyhedral oligomeric silsesquioxanes (POSS) as polymer modifiers requires controlling the phase separation process producing POSS-rich and polymer-rich domains that occurs in most systems due to the thermodynamic incompatibility between both components. One significant result of this study is the finding that isobornyl methacrylate (IBoMA) is an excellent reactive solvent of a commercial methacryl-heptaisobutyl POSS (MA-POSS). Formulations containing up to 30 wt% MA-POSS in IBoMA or in IBoMA (95 parts by weight)-diethylene glycol dimethacrylate (DEGDMA, 5 parts by weight), were polymerized using benzoyl peroxide as initiator up to complete conversion of C=C bonds (determined by FTIR). Transparent POSS-modified materials were obtained without any evidence of a macroscopic phase separation. POSS addition produced a decrease of the glass transition temperature and the glassy and rubbery elastic modulus. A significant decrease in surface energy for both linear and cross-linked polymers was observed. This effect was particularly important for cross-linked polymers where the addition of 30 wt% POSS decreased the surface energy from about 29 mN m^{-1} to 16 mN m^{-1}, a very low value for hydrocarbon materials. This study opens a way to obtain hydrophobic methacrylic coatings without the use of fluorinated monomers.

1. Introduction

Organic–inorganic hybrid nanocomposites based on the incorporation of polyhedral oligomeric silsesquioxanes (POSS) in linear or cross-linked polymers have been intensively studied in the last decade [1–46]. POSS are nanosized cage structures with formula $(RSiO_{1.5})_n$ ($n = 6, 8, 10, \ldots$), where R is an organic group and the octahedron ($n = 8$) is the most typical species. Covalent bonding of POSS to the polymer may be performed when one or more of the R groups have appropriate functional groups.

The present study is focused on the effect of POSS addition on the surface energy of poly(methacrylate) coatings. POSS containing non-polar or fluorinated R groups have been used to decrease the surface energy of polymer coatings [47–50]. This requires managing the miscibility of POSS in the polymer formulation to avoid a macroscopic phase separation. This can be achieved by matching chemical structures of the R groups with those of the polymer (e.g., a fluoroPOSS compound blended with a fluoropolymer).

Another possibility to control the size of segregated POSS-rich domains is to employ a block copolymer containing POSS units as one of the blocks with the other block being miscible with the polymer to be modified. This approach was recently discussed by Ni and Zheng [49], who used a POSS-capped polycaprolactone to modify an epoxy network. This led to a nanostructured thermoset with nanodomains of POSS stabilized by the miscible polycaprolactone blocks. The surface free energy decreased from about 30 mN m^{-1} for the neat epoxy to about 20 mN m^{-1} for POSS-modified epoxies containing 20–40 wt% of block

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* Corresponding author. Tel.: +54 223 481 6600; fax: +54 223 481 0046.
E-mail address: williams@fi.mdp.edu.ar (R.J.J. Williams).

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copolymer. The decrease of surface energy was ascribed to the enrichment of POSS domains on the surface, which was evidenced by X-ray photoelectron spectroscopy.

A different concept for the use of POSS in the generation of hydrophobic surfaces was analyzed by Chen et al. [48]. They performed a surface-initiated atom radical polymerization of a monofunctional methacryl-heptaisobutyl POSS from a flat silicon wafer. A polymer layer of about 40 nm thickness could be grown on the surface that presented hydrophobic characteristics (advancing water contact angle: 102.7°, receding angle: 92.5°).

The use of commercial monofunctional POSS to increase the hydrophobicity of polymer coatings limits the selection to formulations exhibiting a high miscibility with the typical organic groups present in these products: isobutyl, isooctyl, cyclopentyl, cyclohexyl, ethyl, etc. In most cases where miscibility in the initial formulation could be achieved, phase separation was observed in the course of co-polymerization of the monofunctional POSS with the selected co-monomers [8,19,20,26,29,33]. Therefore, the problem must be stated in the inverse form and asked for suitable co-monomers that can keep the miscibility of the selected commercial POSS up to the end of polymerization.

With the aim of developing a hydrophobic methacrylate coating we selected a commercial methacryl-heptaisobutyl POSS and searched an adequate methacrylate co-monomer that could keep the POSS miscible up to the end of polymerization. Besides, the selected co-monomer must lead to a cured product with a low surface energy and with a glass transition temperature appropriate for the application envisaged (in our case the aim was to obtain a glassy coating at room temperature). As shown by Okouchi et al. [51], the contact angle of water on the surface of amorphous poly(alkyl methacrylates) increases with the size of the alkyl group. However, the glass transition temperature decreases in the same direction except when the linear alkyl chain is replaced by a cyclic hydrocarbon. Based on these general concepts, the co-monomer selected in this study was isobornyl methacrylate (IBoMA) that *a priori* fulfilled the required conditions. IBoMA is a low-vapor-pressure liquid that can be polymerized in bulk giving a linear polymer with a glass transition temperature of 125 °C [52,53], it can be easily cross-linked with small amounts of diethylene glycol dimethacrylate (DEGDMA) [54], and it is a good solvent of non-polar compounds such as polyethylene waxes [55]. It could therefore be a good solvent for POSS cages containing seven isobutyl groups in the structure.

We will show that IBoMA is in fact an excellent reactive solvent to prepare POSS-modified methacrylic coatings exhibiting low values of surface energies.

2. Experimental

2.1. Materials

Chemical structures of the different reactants are shown in Fig. 1. Methacryl-heptaisobutyl POSS (MA-POSS, MA 0702 Hybrid Plastics) was a crystalline powder with melting temperature $T_m = 110$ °C and a molar mass of 943.6 g/mol. Isobornyl methacrylate (IBoMA, Aldrich) was used as received. It contained 150 ppm of *p*-methoxyphenol (MEHQ, methyl ether hydroquinone) as inhibitor. The crosslinking agent used was diethylene glycol dimethacrylate (DEGDMA, Aldrich). It contained 300 ppm MEHQ. Benzoyl peroxide (BPO, Akzo-Nobel) was used as initiator. Ethylene glycol (Aldrich, 99.1%) and bi-distilled ultra pure water were used for contact angle measurements.

2.2. Synthesis of POSS-modified polymers

The desired amount of MA-POSS (up to 30 wt%) was dissolved in IBoMA (to synthesize linear polymers) or in an IBoMA-DEGDMA mixture (95:5 by weight) (to generate cross-linked networks). Dispersions were stirred at room temperature until complete dissolution of MA-POSS took place and BPO was added in an amount of 0.01835 mol per mol of C═C groups (including those of MA-POSS). Solutions were transferred either to 3-mm tubes or cast as 1-mm thick films in aluminum molds. Tubes were introduced into an oven and polymerization was performed at 80 °C for 45 min followed by 2 h at 110 °C. Films were polymerized under a continuous flow of nitrogen using the same temperature vs. time schedule. For materials devoid of MA-POSS higher temperatures were necessary in order to attain complete conversion of C═C groups. For these materials polymerization was carried out at 80 °C for 1 h, followed by 30 min at 140 °C.

2.3. Characterization techniques

Fourier Transform Infrared Spectroscopy (FTIR) was used to determine the degree of reaction of C═C groups at the end of polymerization, monitoring the stretching vibration at 1640 cm^{-1}. A Genesis II-Mattson device was used in the absorbance mode with a resolution of 2 cm^{-1}. Spectra were obtained using pellets of the materials with KBr.

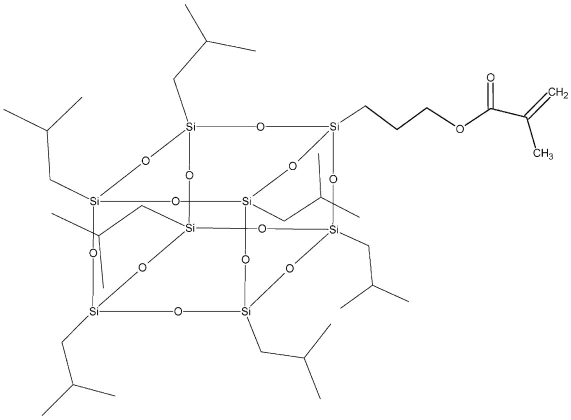
Wide-angle X-ray diffraction (WAXD) was used to determine the dispersion of MA-POSS in the hybrid materials. A Philips PW 1830/40 device was employed with Co Kα radiation ($\lambda = 1.790$ Å) and a scanning rate of 1 °/min.

Fracture surfaces were coated with a fine gold layer and observed by scanning electron microscopy (SEM, Jeol JXA-8600).

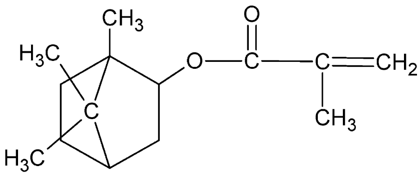
Differential scanning calorimetry (DSC, Pyris 1, Perkin-Elmer), was used to determine glass transition temperatures (T_g), defined as the onset value of the transition during a heating scan at 10 °C/min.

Dynamic-mechanical thermal analysis was performed with an Anton Paar rheometer (Physica MCR-301), provided with a CTD 600 thermo-chamber. Cylindrical specimens of 4.5-cm length and 4-mm diameter were subjected to small-amplitude oscillatory shear flow tests (amplitude = 0.01%), at a frequency of 1 Hz and a heating rate of 5 °C/min in the −50 °C to 240 °C range.

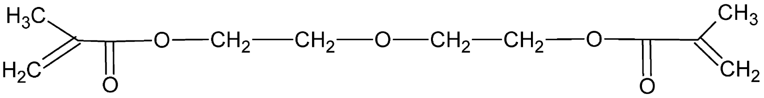
Contact angle determinations were made by the static sessile drop method using ethylene glycol and water. Drops were placed on the 1-mm thick films and contact angles were measured at room temperature using an MV-50 camera (zoom 6×) and an image NIH software. At least five drops of each one of the liquids were measured.



MA-POSS



IBoMA



DEGDMA

Fig. 1. Chemical structures of MA-POSS, IBoMA and DEGDMA.

The surface free energies were calculated according to the geometric mean model [49,56]:

$$\gamma_L(1+\cos\theta)/2 = (\gamma_S^d\gamma_L^d)^{1/2} + (\gamma_S^p\gamma_L^p)^{1/2} \quad (1)$$

where S and L refers to the solid and liquid, respectively; γ^d is the dispersive component, and γ^p is the polar component of the surface energy; and θ is the contact angle. Measuring contact angles of drops of two different liquids with known values of γ_L^d and γ_L^p (for water, $\gamma_L = 72.8\ \mathrm{mN\,m^{-1}}$, $\gamma_L^d = 21.8\ \mathrm{mN\,m^{-1}}$ and $\gamma_L^p = 51.0\ \mathrm{mN\,m^{-1}}$; for ethylene glycol, $\gamma_L = 48.3\ \mathrm{mN\,m^{-1}}$, $\gamma_L^d = 29.3\ \mathrm{mN\,m^{-1}}$ and $\gamma_L^p = 19.0\ \mathrm{mN\,m^{-1}}$) [49,57], enables to estimate the dispersive and polar components of the solid. The surface energy of the solid is calculated as:

$$\gamma_S = \gamma_S^d + \gamma_S^p \quad (2)$$

3. Results and discussion

3.1. Conversion of C=C groups

FTIR spectra of products obtained at the end of polymerization showed the complete disappearance of the band at 1640 $\mathrm{cm^{-1}}$ for both linear and cross-linked polymers containing different POSS amounts (Fig. 2). This means that the selected thermal cycles produced the covalent bonding of MA-POSS to both the linear and cross-linked polymers. The presence of POSS is revealed by several bands, in particular the strong band at about 1110 $\mathrm{cm^{-1}}$ arising from the antisymmetric stretching vibration of Si–O–Si bonds.

3.2. Dispersion of POSS cages

The first evidence of the good dispersion of POSS cages was the complete transparency of the whole set of hybrid materials at the end of polymerization. SEM micrographs of fracture surfaces did not evidence the presence of a separated phase at the highest possible resolution of the instrument (about 50 nm).

WAXD spectra of MA-POSS and the different reaction products are shown in Fig. 3. The unmodified linear and cross-linked polymers show broad scattering peaks centered at $2\theta \approx 17°$ and at $2\theta \approx 8°$. Scattering peaks in these regions have been observed for other methacrylic polymers and ascribed to characteristic distances in the

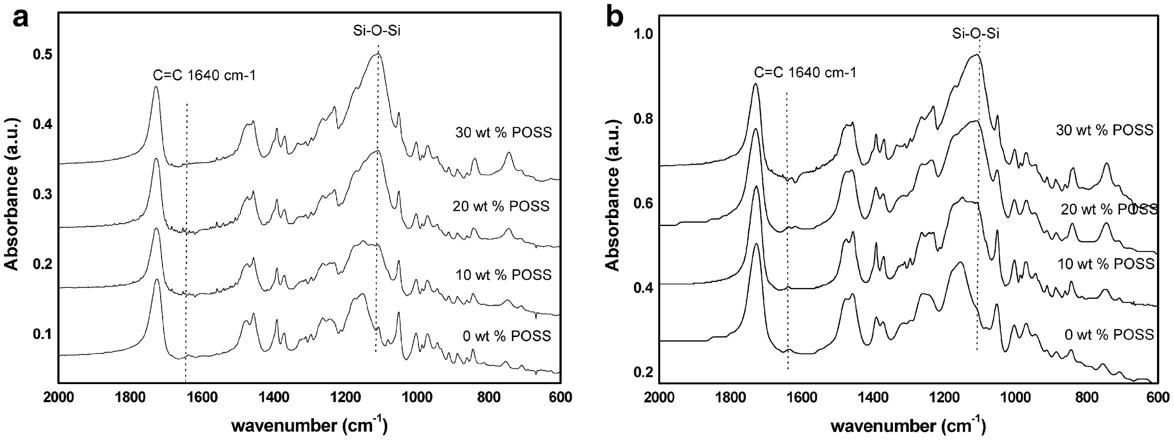


Fig. 2. FTIR spectra in the region 600–2000 cm^{-1}; (a) Linear polymer containing 0, 10, 20 and 30 wt% MA-POSS, (b) Cross-linked polymer containing 0, 10, 20 and 30 wt% MA-POSS.

amorphous packing of polymer chains [29,58]. Although MA-POSS is a crystalline compound with a rhombohedral unit cell [4,59], its covalent bonding in either the linear or the cross-linked polymer destroyed crystallinity, as reported by several authors for different systems [33,49, 59–63].

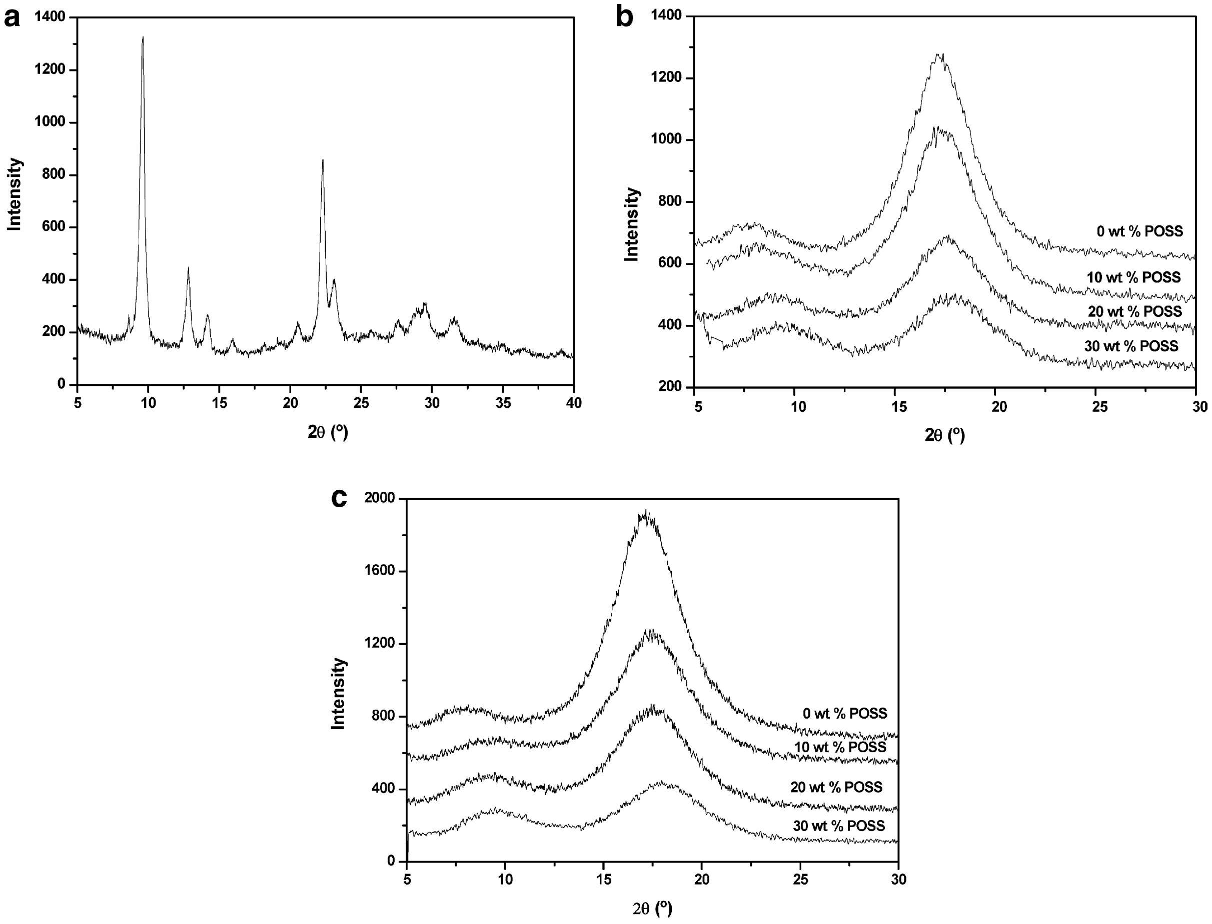


Fig. 3. X-ray diffraction spectra of: (a) MA-POSS; (b) Linear polymer containing 0, 10, 20 and 30 wt% MA-POSS; (c) Cross-linked polymer containing 0, 10, 20 and 30 wt% MA-POSS.

In both linear and cross-linked polymers the incorporation of increasing amounts of POSS produced a decrease in the intensity of the scattering peak at $2\theta \approx 17°$ and a shift of the maximum of the small peak from $2\theta \approx 8°$ to $2\theta \approx 9.7°$. This angle corresponds to the strongest reflection of crystalline MA-POSS (101 hkl reflection associated to a characteristic distance of 1.12 nm) [63]. Similar observations have been reported in the literature for other monofunctional POSS-modified polymers [15,20,49,59].

It is interesting to compare our results with those reported for a polymer network obtained using dicyclopentadiene and NB-POSS (a monofunctional POSS with seven isobutyl groups and one norbornenyl group) [15]. The cross-linked material was transparent without any evidence of a macroscopic phase separation. WAXD spectra revealed the existence of a broad peak located at the same position of the most intense peak of the crystalline structure, a fact that was assigned to the presence of aggregates containing three or four POSS molecules per cluster [15]. A similar situation is possibly present in our case, with POSS molecules dispersed as single units or forming small aggregates containing a few cages per cluster.

3.3. Glass transition of POSS-modified polymers

DSC thermograms of the POSS-modified cross-linked polymers are shown in Fig. 4. A single glass transition temperature (T_g) that decreases with the amount of POSS in the hybrid material, is observed. Similar results were obtained for the POSS-modified linear polymers.

Fig. 5 shows the glass transition temperatures for both linear and cross-linked polymers as a function of the wt% POSS. Cross-linking with 5 wt% DEGDMA increased the glass transition temperature of the neat polymer from 128 °C to 138 °C. The continuous decrease of T_g with the amount of POSS in the hybrid material reflects the presence of a single phase constituted by the dispersion of POSS cages that are covalently bonded to the polymer structure.

The experimental points could be satisfactory fitted for both systems employing the Gordon–Taylor equation [64]:

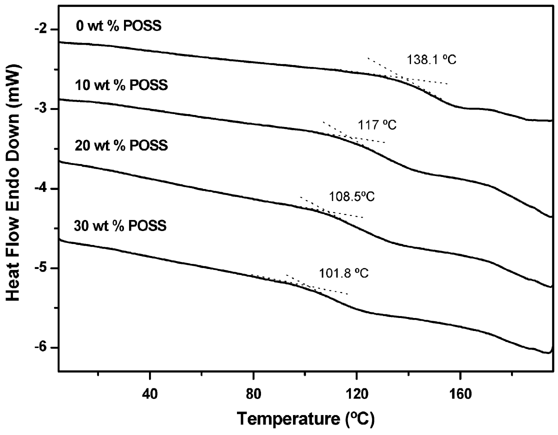


Fig. 4. DSC scans of cross-linked polymers containing 0, 10, 20 and 30 wt% MA-POSS.

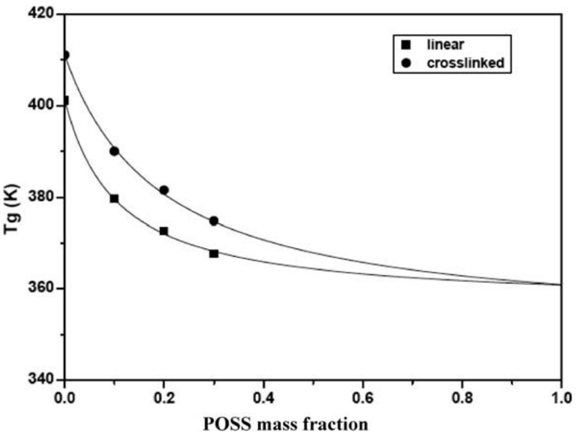


Fig. 5. Glass transition temperatures as a function of the mass fraction of POSS for linear and cross-linked polymers. Solid lines represent the fit obtained using the Gordon–Taylor equation.

$$Tg = [w_{POSS}T_{gPOSS} + k(1 - w_{POSS})T_{gPol}]/[w_{POSS} + k(1 - w_{POSS})] \quad (3)$$

where $k = \Delta\alpha_{Pol}/\Delta\alpha_{POSS}$ is the ratio of the difference of thermal expansion coefficients between glassy and liquid states for both components, and T_{gPOSS} and T_{gPol} are the glass transition temperatures of the pure homopolymers (T_{gPol} = 401 K for the linear polymer and 411 K for the cross-linked polymer). A very good fit of the experimental values was obtained with T_{gPOSS} = 360.8 K, $k_{crosslinked}$ = 0.162 and k_{linear} = 0.096 (Fig. 5; note that the fitting requires a single value of T_{gPOSS} for both curves).

The low values of k are associated with the large plasticizing effect of POSS (when $k \rightarrow 0$, $T_g \rightarrow T_{gPOSS}$ for any value of w_{POSS}). The fitted value for T_{gPOSS} (about 88 °C) is comparable to values reported in the literature for poly(metacryl-heptaisobutyl POSS) [59]. For a triblock copolymer containing a central block of poly(n-butyl acrylate) and terminal blocks of poly(metacryl-heptaisobutyl POSS) with a number average degree of polymerization close to 10, the T_g value of the block of POSS was 75 °C [59], slightly lower than the value arising from the Gordon–Taylor equation.

3.4. Dynamic mechanical thermal analysis of POSS-modified cross-linked polymers

The variation of the storage modulus (G') and tan δ with temperature for the series of cross-linked polymers is shown in Fig. 6. Apart from the decrease of the glass transition temperature already observed using DSC, the addition of POSS produced a decrease in the elastic modulus both in glassy and rubbery states.

The elastic modulus in the glassy state depends essentially on two main factors: the cohesive energy density and the existence of sub-glass relaxations that are active at the test temperature [65]. In our systems no secondary sub-vitreous relaxations were detected above −50 °C (the limiting temperature of our tests). We therefore ascribed the decrease in elastic modulus to a decrease in the cohesive energy density produced by POSS addition. This can be

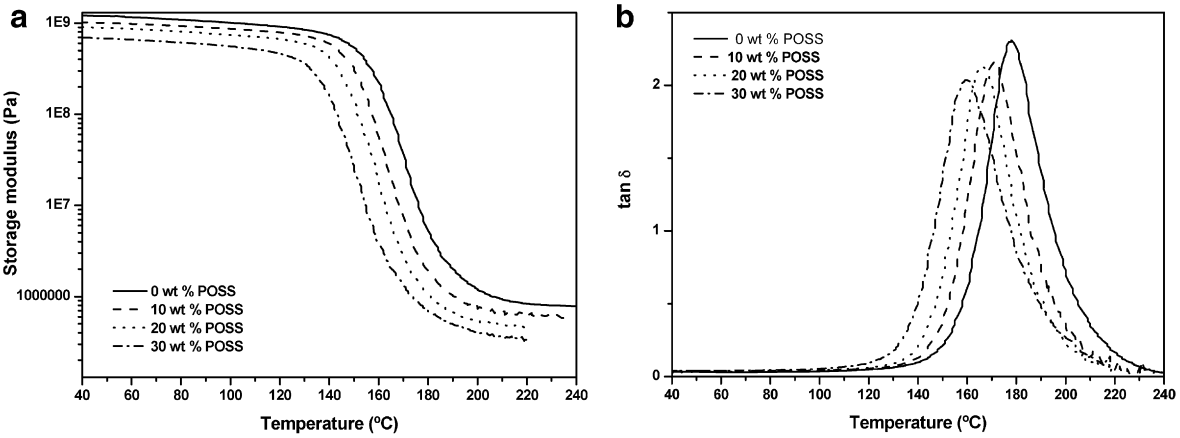


Fig. 6. (a) Storage modulus (G'), and (b) Loss factor (tan δ), of cross-linked polymers containing 0, 10, 20 and 30 wt% POSS, as a function of temperature.

easily accepted because the relative large size of POSS cages imposes a physical restriction to the packing of organic chains. A decrease in the cohesive strength by POSS addition has also been postulated in the literature to explain the decrease in fracture toughness and yield strength of the POSS-modified polymers [15].

The decrease of the rubbery modulus when adding POSS can be simply explained by the dilution effect produced by the mass of the bulky POSS cage on the concentration of cross-linking units (DEGDMA). Increasing the amount of POSS leads to a decrease in the concentration of DEGDMA units per unit volume and, consequently, to a decrease of the rubbery modulus.

3.5. Surface energy of POSS-modified polymers

Dispersive and polar components of the surface energy were estimated measuring contact angles of water and ethylene glycol. The resulting values are summarized in Table 1.

The addition of POSS produced a significant decrease in surface energy for both linear and cross-linked polymers. The effect was particularly important for cross-linked polymers where the addition of 30 wt% POSS decreased the surface energy from about 29 mN m^{-1} to 16 mN m^{-1}, a very low value for hydrocarbon materials. The main effect of POSS addition was the decrease of the dispersive component of surface energy; the polar component was practically not modified within experimental error. Presumably there is an enrichment of non-polar POSS units on the surface of the hybrid material, a fact that was recently confirmed by Ni and Zheng for a POSS-modified epoxy using X-ray photoelectron spectroscopy (XPS) [49].

4. Conclusions

The use of monofunctional POSS as polymer modifiers requires controlling the phase separation process producing POSS-rich and polymer-rich domains that occurs in most systems due to the thermodynamic incompatibility between both components. One significant result of this study is the finding that isobornyl methacrylate (IBoMA) is an excellent reactive solvent of a commercial methacryl-heptaisobutyl POSS (MA-POSS). This formulation might be the basis of POSS-modified methacrylic coatings. MA-POSS was co-polymerized with IBoMA and with IBoMA-DEGDMA (95:5 by weight) without exhibiting any detectable polymerization-induced phase separation (at least up to 30 wt% MA-POSS that was the maximum amount used due to processing restrictions). The resulting coatings were completely transparent although the presence of small agglomerates of POSS cages was inferred from WAXS results.

The use of POSS could not be justified based on thermal or mechanical properties impaired to the hybrid materials. POSS addition produced a decrease of the glass transition temperature and the elastic moduli in both glassy and rubbery states. However, the effect of POSS addition was

Table 1
Static contact angles and surface energy of POSS-modified linear and cross-linked polymers.

Polymer	POSS wt (%)	θ_{H_2O} (degrees)	$\theta_{ethyleneglycol}$ (degrees)	γ_S^d (mN/m)	γ_S^p (mN/m)	γ_S (mN/m)
Linear	0	93.6 ± 1.3	68.9 ± 1.5	22.0	2.9	24.9
	10	95.1 ± 1.8	73.6 ± 2.4	17.5	3.6	21.1
	20	98.0 ± 1.9	78.1 ± 1.7	15.2	3.4	18.6
	30	96.4 ± 2.4	77.9 ± 0.9	13.4	4.5	17.9
Cross-linked	0	89.1 ± 1.3	61.8 ± 4.8	25.7	3.5	29.2
	10	93.8 ± 2.2	74.4 ± 4.7	14.9	5.0	19.9
	20	100.3 ± 0.8	79.4 ± 0.5	16.3	2.4	18.7
	30	98.2 ± 2.3	81.1 ± 3.6	11.9	4.5	16.4

significant on the reduction of surface energy, opening the way to obtain hydrophobic methacrylic coatings without the use of fluorinated monomers.

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