



Synthesis and Characterization of Poly(methyl acrylate) + SiO₂ Hybrids

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Abstract: Poly(methyl acrylate) (PMA) + SiO₂ composites were synthesized via a sol-gel reaction. The base acrylic copolymers with a content of alkoxy silane groups were prepared by co-polymerization of methylacrylate (MA) with 3-(trimethoxysilyl) propylmethacrylate (3MPS) or vinyltrimethoxysilane (VTMS); the products were co-condensed with tetraethylorthosilicate (TEOS). The PMA + SiO₂ hybrids were characterized. Thermal stability of PMA is enhanced by copolymerization with 3-MPS or VTMS and the presence of SiO₂; significant weight loss occurs only above 400 °C. Decomposition temperatures are higher by 20 - 25 K as compared to the initial PMA. During the sol-gel process the trimethoxysilyl groups in PMA/3MPS are transformed into a strong silica network. Two different methods of creation of hybrids were used; ESEM shows that only one of them leads to uniform distribution of silica in polymeric matrices.

Keywords: hybrid material, methyl acrylate, sol-gel, hybrids, silica

Introduction

The need for making materials stronger is anything but new [1, 2]. For the past decade, organic + inorganic composites prepared by the sol-gel process have attracted much attention, especially in the fields of ceramics, polymer chemistry, organic and inorganic chemistry, and physics. The preparation, characterization, and applications of organic-inorganic hybrid materials have become a fast expanding area of research in materials science [3 - 17]. The major driving forces behind the intense activities in this area are the new and different properties of the composites which the earlier materials do not have [18 - 24].

Through combinations of different inorganic and organic components in conjunction with appropriate processing methods, various types of primary and secondary bonding can be developed - leading to materials with new properties for electrical, optical, structural or other applications.

Organic + inorganic materials prepared by the sol-gel process can be generated using different synthetic techniques by incorporating inorganic and organic components with varied molecular structures [4, 25 - 31].

Creation of inorganic + organic polymer-containing hybrid materials makes it possible to optimize selected properties independently [32 - 49]. One of the ways to create hybrids is the use of the sol-gel process for introduction of organic groups into an inorganic network leading to new structure – property variations.

The objective of this work is synthesis and characterization of poly(methyl acrylate) (PMA) + SiO₂ hybrid composites via a sol-gel reaction. Earlier work on positively charged PMA + SiO₂ nanohybrids by Wu and coworkers [50] needs to be noted. We have prepared acrylic based copolymers with a content of alkoxy silane groups by copolymerization of methylacrylate (MA) with 3-(trimethoxysilyl)-propylmethacrylate (3MPS) and vinyltrimethoxysilane (VTMS). The products were co-condensed with tetraethylorthosilicate (TEOS).

Two different methods have been used for obtaining various compositions of PMA with SiO₂. The first one was the formation of covalently connected composites by functionalization of organic polymer backbones with trialkoxysilyl groups – which results in hydrolysis and condensation processes providing an inorganic SiO₂ network.

The second method is based on grafting polymeric molecules through covalent bonding to the existing hydroxyl groups; this includes silica surface treatment with a silane coupling agent followed by radical grafting polymerization in aqueous or non-aqueous systems [51].

We have used a variety of techniques to characterize our PMA + SiO₂ hybrid materials, including Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and environmental scanning electron microscopy (ESEM). Results of study of tribology of the hybrids (friction, wear) and also their behavior in a simulated body fluid (SBF) will be reported in later papers.

Thermal properties

The thermal properties of the PMA copolymers and PMA copolymer + SiO₂ composite materials have been investigated by TGA and DSC.

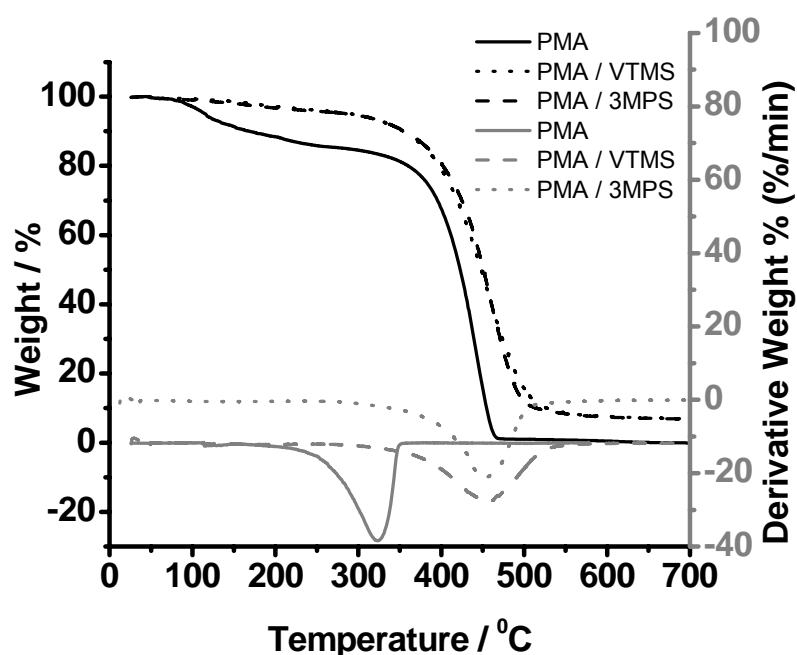


Fig. 1. TGA scans and derivative curves for the PMA and copolymers.

TGA diagrams of the samples are shown in Figure 1. The thermograms show a single stage weight loss in all the copolymer samples. We see thermal stability up to 350°C. Decomposition temperatures T_d have been evaluated from TGA derivative curves and are listed below in Table 1.

TGA results show us also that above 400 °C the weight loss increases noticeably; thermal degradation is completed around 500 - 550°C. We find clearly that the thermal stability of the copolymers is enhanced by the 3-MPS and VTMS presence - as compared to the pure PMA. Our two copolymer systems have a comparable thermal stability.

TGA spectra of PMA/3MPS + SiO₂ hybrids were also determined and are shown in Figure 2. Here thermal degradation occurs in the range 300 – 550°C (Figure 3), at temperatures higher than those for PMA. Again pertinent numerical values are listed in Table 1.

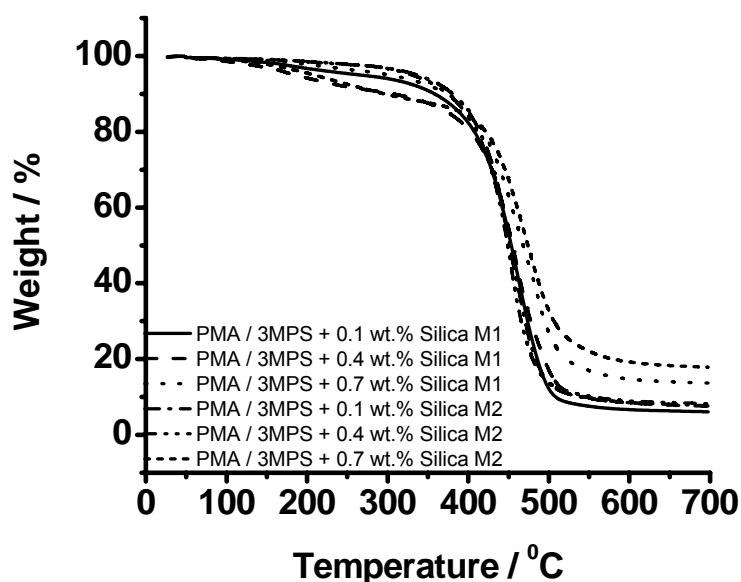


Fig. 2. The TGA curves for the PMA /3MPS + SiO₂ composite materials.

Two methods have been used to obtain the hybrids (see the Experimental section). We find that thermal degradation temperatures are relatively higher for PMA/3MPS + SiO₂ from Method 2. Apparently during the sol-gel process the trimethoxysilyl groups in PMA/3MPS are transformed into a strong silica network. Formation of the network occurs through co-polymerization.

Thermal degradation curves for all the compositions are shown in Figure 3. We see in the thermograms single characteristic weight loss peaks for all samples - presumably due to decomposition of organic parts of the samples. The peaks appear all in the same temperature range.

We also see in Figures 2 and 3 consequences of the two routes. Silica networks in the PMA/3MPS+ SiO₂ hybrids obtained by Method 1 are unstable - which results in beginning of the hybrids degradation already around 200°C. By contrast, for the samples obtained by Method 2 we see higher degradation temperatures. Thus, thermal stability of the hybrids is improved.

Moreover, in Method 2 we can vary properties of the resulting materials through a proper selection of the grafting monomers and the grafting conditions.

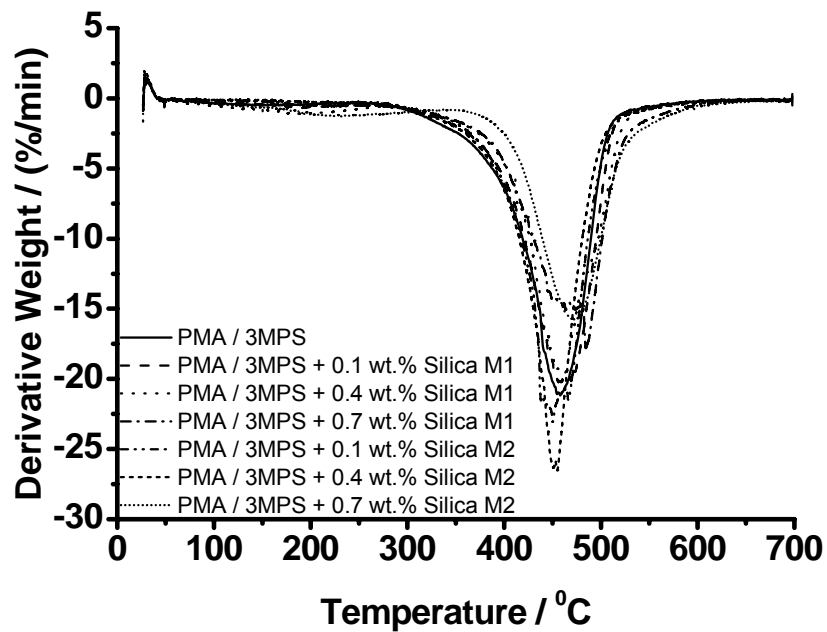


Fig. 3. The derivative of the TGA scan for PMA / 3MPS + SiO₂ composites.

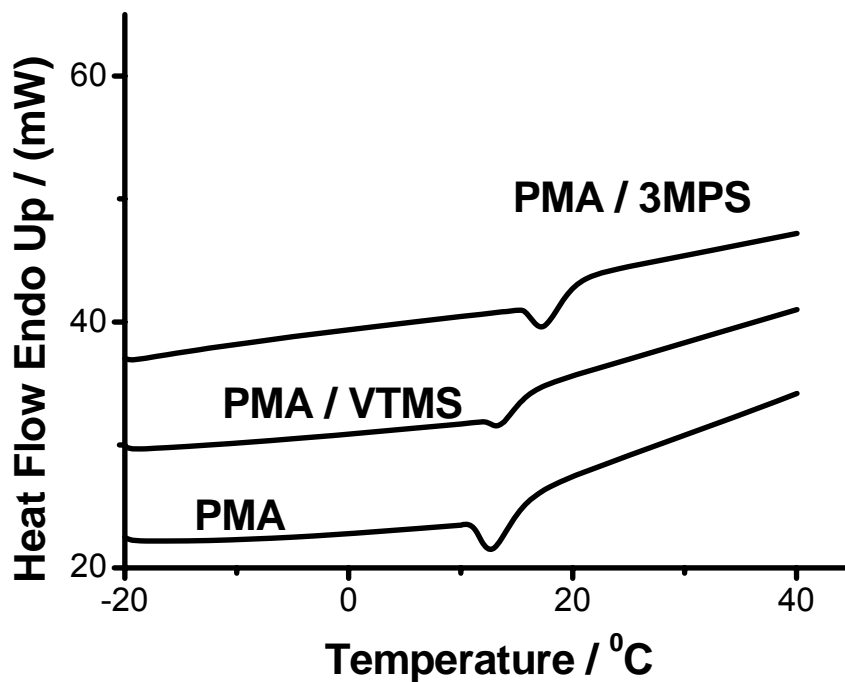


Fig. 4. DSC thermograms of the PMA and copolymers.

DSC thermograms of the PMA and copolymer systems are shown in Figure 4. We see in Figure 4 that the glass transition temperatures T_g vary, namely they increase in cases of PMA copolymers compared to pure PMA; this effect of copolymerization

can be explained in terms of the ratio of trimethoxysilane groups to copolymerization products. The thermal properties of obtained products are listed in Table 1.

Tab. 1. Thermal properties of the PMA /3MPS + SiO₂ composites.

Name	T _d /°C	ΔY/ (wt.%)	T _g /°C
PMA	444	99.9	15.5
PMA / 3MPS	459	93.0	17.7
PMA / VTMS	456	92.8	16.4
PMA / 3MPS + 0.1 wt. % silica M1	451	92.1	17.6
PMA / 3MPS + 0.4 wt. % silica M1	457	91.5	18.1
PMA / 3MPS + 0.7 wt. % silica M1	461	81.9	18.7
PMA / 3MPS + 0.1 wt. % silica M2	464	93.6	17.9
PMA / 3MPS + 0.4 wt. % silica M2	464	92.2	18.6
PMA / 3MPS + 0.7 wt. % silica M2	469	86.1	19.2

As seen in Table 1, the decomposition temperatures T_d are up to 25 K higher than that of the neat PMA. ΔY in Table 1 represents the percentage weight lost by thermal decomposition. We thus see that only 0.1 % of PMA remains – in contrast with the composition at the bottom of the Table in which 13.9 % of the original material ‘survives’. Glass transition temperatures of the PMA/3MPS + SiO₂ and PMA/VTMS + SiO₂ hybrids are somewhat higher than those of the initial copolymer.

FTIR and Raman results

FTIR analysis is known as a suitable method to determine the presence of specific interactions between various groups in polymer compositions; it is sensitive to both inter- and intermolecular interactions. Figure 5 shows the FTIR and Raman spectra for PMA, PMA/3MPS and PMA/VTMS copolymer systems. Since the differences between hybrids obtained by M1 and M2 are not significant, nor are they much different from those for PMA, PMA/3MPS and PMA/VTMS copolymers, they are omitted here for brevity.

The peak in the range 3000 – 3600 cm⁻¹ is characteristic for the – OH stretching of the water molecules. The vibrations seem to appear in the case of PMA/3MPS and PMA/VTMS copolymer samples as small peaks; the peaks are evidence of partial hydrolysis and condensation of unstable -Si(OCH₃)₃ groups by traces of water in the sample preparation system.

The peaks in the region ~2800 – 3000 cm⁻¹ are associated with the methylene (- CH₂ -) and dimethylene (- CH₂ - CH₂ -) stretching of the samples.

The absence of the peaks at ~1600 cm⁻¹ in each case proves the absence of monomer impurities. The bands due to the carbonyl group –C=O of MA and acrylic comonomer apparently overlap around ~1700 cm⁻¹.

Functional group changes in the PMA and copolymer materials are seen in Figure 6 FTIR spectra in the 650 – 1500 cm⁻¹ region.

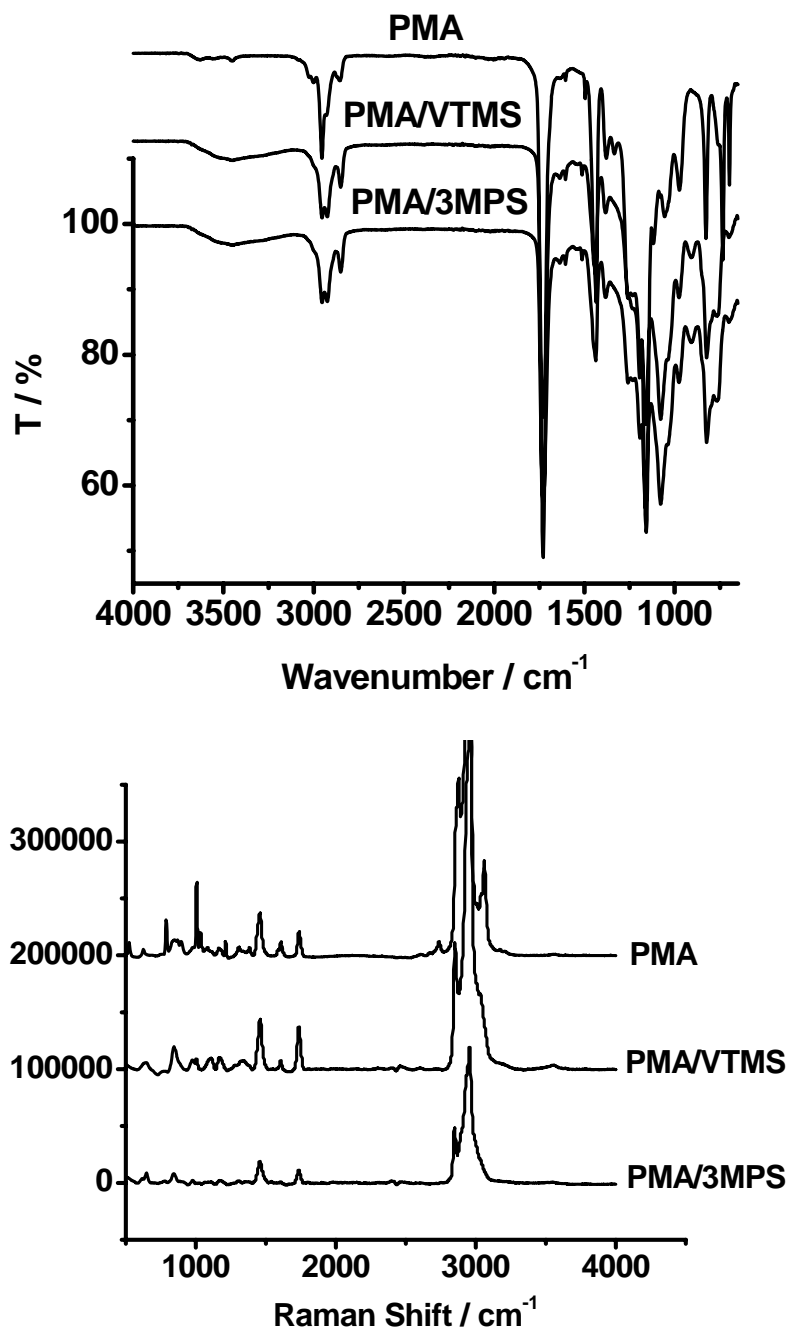


Fig. 5. FTIR and Raman spectra for PMA and copolymers.

We see in Figure 6 that $\sim 1200\text{ cm}^{-1}$ $-\text{C}-\text{O}-\text{C}-$ absorption peaks gradually weaken, while peaks at $650 - 1100\text{ cm}^{-1}$ region increase in size; formation of newly formed groups is observed in the $650 - 1500\text{ cm}^{-1}$ region. These signals are characteristic for the $-\text{Si}-\text{O}-\text{C}$, $-\text{Si}-\text{OH}$ and $\text{Si}-\text{O}-\text{Si}$ groups of the partial hydrolyzation and condensation of the unstable $-\text{Si}(\text{OCH}_3)_3$ groups, producing such groups as $-\text{Si}(\text{OH})(\text{OCH}_3)_2$, $-\text{Si}-\text{O}-\text{Si}(\text{OH})(\text{OCH}_3)_2$, a fact confirmed by Raman spectroscopy.

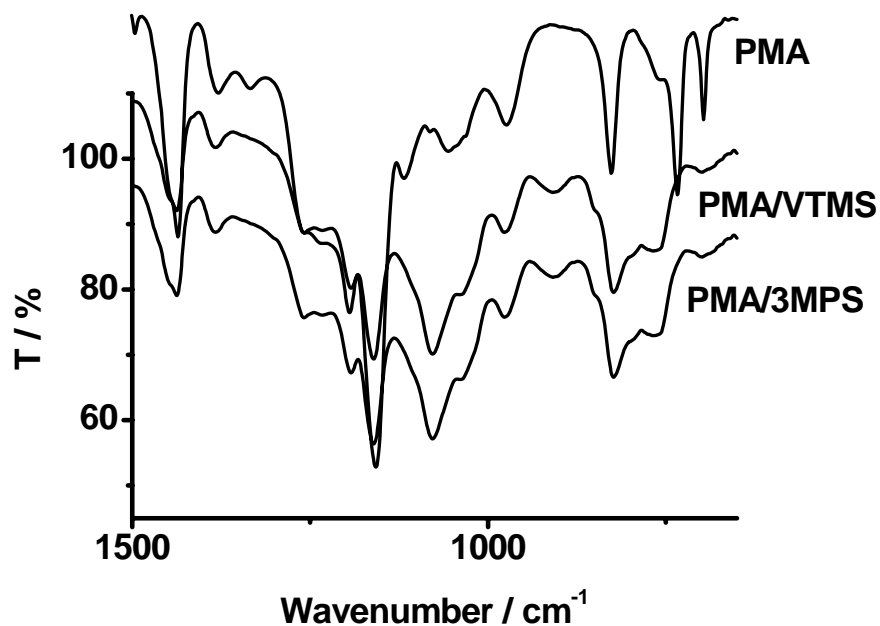


Fig. 6. FTIR spectra for of the PMA and copolymers.

Blends morphology

Morphology of our samples and also silica particle shapes were studied with ESEM. Figure 7 is an ESEM image of silica particles obtained according to Step 1 in Method 2. We recall that better thermophysical properties have been obtained with that method than with Method 1; see again Table 1.

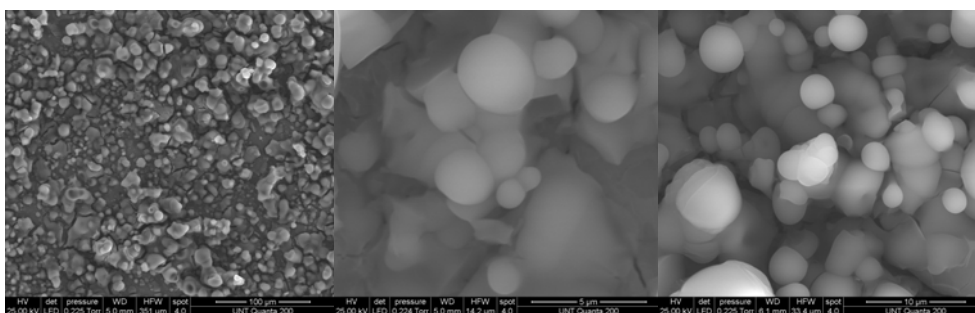


Fig. 7. ESEM micrographs of silica particles Method 2 – Step 1.

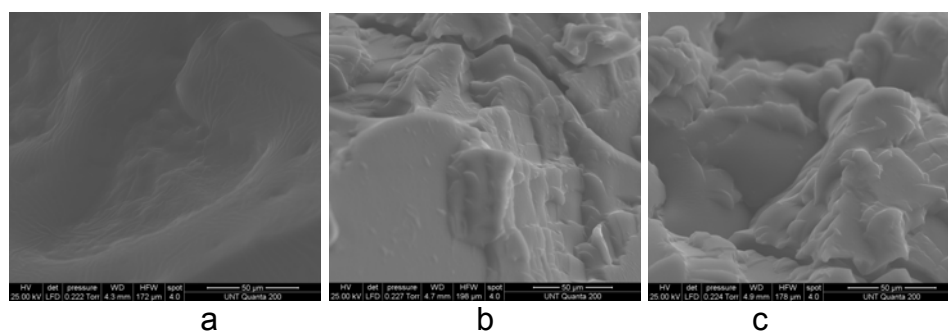


Fig. 8. (a, b, c). Scanning electron micrographs of cryogenically fractured surfaces of the PMA, PMA/3MPS and PMA/VTMS, respectively.

This is while the molar ratio, time, temperature etc. have been the same as in Step 2 of Method 1. The outer diameter of the particles varies from 1 to 3 μm , with the majority around 2.5 μm . From high magnification images of silica particles, we see that they have fairly uniform spherical shapes.

Morphologies of the PMA and copolymer materials are shown in Figure 8. The images show a brittle network, as compared to the homogeneous appearance of a pure PMA. This can also be explained by formation of silica networks. We recall that the definition of brittleness [52] involves elongation at break. The elongation is as a rule higher for polymers than for silica networks.

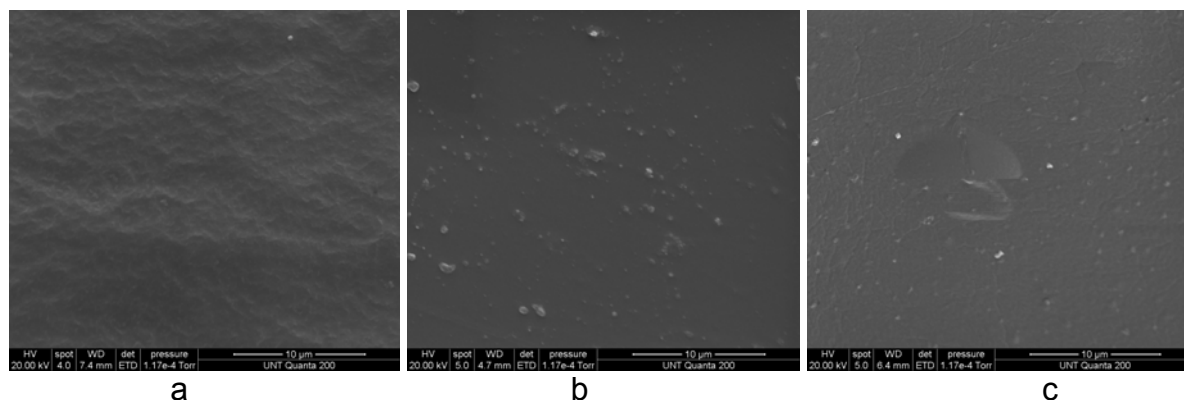


Fig. 9. (a, b, c) ESEM images of PMA and PMA/3MPS+ SiO_2 samples containing 0.7 wt. % SiO_2 (b and c correspond to Method # 1 and 2 respectively).

ESEM was conducted to investigate the distribution of silica in the hybrid material. ESEM images obtained for the PMA/3MPS samples containing 0.7 wt. % SiO_2 (Method 1 and 2) show similar morphologies. From Figure 9 (b, c) we also see a rather nonuniform distribution of silica particles. A better particle distribution results in samples from Method 2 (Figure 9 c). The major effect comes from used methodology Method 2 – Step 2. Formation of covalent bonding between PMA macromolecular chains and silica particles enhances the particle dispersion and their adhesion to the chains. This is achieved by grafting of polymerizable groups onto the oxide surfaces via hydroxyl groups followed by copolymerization with organic monomers.

By contrast, apparently in Method 1 the reaction does not proceed quite uniformly, hence there is coagulation and formation of larger SiO_2 particles after the sol-gel process. As discussed by Rabello [53], fillers are widely used to improve polymer properties. While for instance uniform distribution of the metal filler phase has been achieved in low density polyethylene [13], the uniformity is by no means assured in general. Interphase energies are decisive here [54].

Experimental part

Materials

Methyl acrylate (**MA**, $\text{CH}_2=\text{CHCOOCH}_3$), vinyltrimethoxysilane (**VTMS**, $\text{H}_2\text{C}=\text{CHSi}(\text{OCH}_3)_3$), benzoyl peroxide (BPO), toluene and tetrahydrofuran (THF) were supplied by Aldrich Chemicals Co. Tetraethylorthosilicate, hexane and 3-methacryloxypropyl trimethoxysilane (**3MPS**, $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CO}_2(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$) were obtained from Fluka and Sigma Chemicals Co., respectively.

Tetrahydrofuran (THF) and toluene were used as the solvents for the polymerization. Hexane was used as a purification solvent. All reagents were of analytical grade and were used as received.

Materials and Sample Preparation

-Method 1

- Step 1. Co-polymerization: (a) MA
 (b) MA + 3MPS
 (c) MA + VTMS

According to the blending ratios displayed in Table 2, two different functionalized poly(methacrylate) were prepared with different organic ligands. We have performed a free radical polymerization of vinyltrimethoxysilane (VTMS) or 3-methacryloxypropyl trimethoxysilane (3-MPS) with methyl acrylate (MA) using benzoyl peroxide (BPO) 1 mol. % as an initiator and dry toluene as solvent. The polymerization was carried out in a reaction flask equipped with a condenser at 95 °C with constant stirring under nitrogen. The system was then subjected to mixing at a medium speed for 8 h.

Tab. 2. Initial Composition of Copolymers.

Name	Experimental Samples	MA (mol)	Co-monomer (mol)	Initiator 1 mol. %	Solvent (mol)
a	MA	0.2	MA	1	0.25
b	MA + 3MPS	0.2	3-MPS 0.05	1	0.25
c	MA + VTMS	0.2	VTMS 0.05	1	0.25

Polymerization conditions: monomer = methyl acrylate, comonomer = vinyltrimethoxysilane or 3-methacryloxypropyltrimethoxysilane; temperature 95 °C, solvent toluene, nonsolvent hexane.

The resulting products were purified by repeated precipitation from dry hexane to remove unreacted comonomers and initiator species. The purified copolymers were dried in vacuum at 40 °C for several hours.

Pure PMA was made for comparison via the same free radical polymerization method.

Step 2. Hydrolization and co-condensation of co-polymers with TEOS, that is:

- a (MA) + TEOS; b (MA / 3MPS) + TEOS; c (MA / VTMS) + TEOS

Hydrolization and co-condensation of co-polymers with TEOS were achieved via a sol-gel process. The co-polymers were directly hydrolyzed and condensed with tetraethylorthosilicate in THF solution with HCl aq. solution to yield a hybrid sol-gel material. A silica precursor in the presence of tetrahydrofuran was mixed with deionized water and hydrochloric acid.

The PMA and copolymers were dissolved in THF at the concentration of 20 wt. % and after 30 min mixing the solution was combined with varying amounts of the first system.

Two mixing procedures were used - as represented in Figure 10.

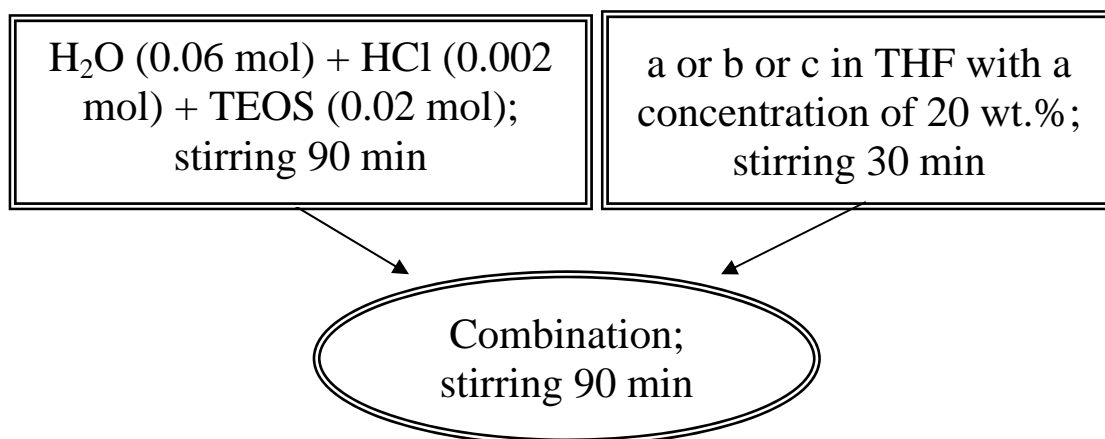


Fig. 10. Schematic Diagram of Sample Preparation.

The resulting systems were dried at room temperature for one week in a Teflon mold. The compositions so obtained contained in turn 0.1, 0.4 and 0.7 wt. % SiO₂.

-Method 2

Step 1. Preparation of silica

The sol-gel silica solution was prepared by acid catalysis of 0.02 mol TEOS and 0.06 mol deionized water. 0.06 mol THF was used as a solvent and 0.002 mol aq. HCl as the catalyst. Tetraethylorthosilicate (TEOS) was placed in a beaker and an intimate mixture of water, solvent and aq. HCl (37 mass. %) added under constant stirring at room temperature for 2 hours.

Particle shapes and sizes were determined using environmental scanning electron microscopy (ESEM).

Step 2. Introduction of reactive groups onto the silica surfaces

The resulting mixture was then subjected to treatment using 3MPS or VTMS in order to modify the surface and maximize the introduction of reactive groups. The resulting sol from step 1 was combined with 2.9 ml 3MPS or VTMS and 2.8 ml THF at room temperature. The system so obtained was then heated at 10 K·min⁻¹ to the maximum temperature of 70 °C. The mixture was held under constant stirring at 70 °C for 5 h.

Step 3. Polymerization

Composites of silica with PMA, PMA + 3MPS and PMA + VTMS were prepared by free radical polymerization. The molar ratio between used components was the same as in Method 1. Namely, the system obtained after Step 1 and 2 was put into a flask and then monomer MA was added; after 1 h mixing 1 mol. % initiator was added and the temperature was increased. The polymerization was carried out in a reaction flask equipped with a condenser at 70 °C with constant stirring under nitrogen. The system was then subjected to mixing at a medium speed for 5 h.

The resulting products were purified by repeated precipitation from dry hexane to remove unreacted comonomers and initiator species. The purified samples were dried in vacuum at 40 °C for several hours.

Differential scanning calorimetry (DSC)

DSC measurements were performed on a Perkin Elmer DSC-7 instrument. The conditions were the temperature range from -20 to 250 °C; the heating rate 10 K/min under a nitrogen atmosphere; a sealed liquid type aluminum capsule pan was used. Glass transition temperatures T_g were evaluated on the basis of thermograms.

Thermogravimetric analysis (TGA)

All the samples were analyzed by TGA in nitrogen atmosphere at the heating rate of 20 K/min.

Isothermal thermogravimetry (TG) was applied to determine a temperature profile. A Perkin Elmer TG-7 instrument was used. Several milligrams of each dried sample were placed on a balance located in the furnace which was heated over the temperature range from + 50 to 700 °C temperature. Thermophysical characterization techniques including DSC and TGA have been described for instance by Menard and his colleagues [55, 56] or by Lucas and her colleagues [57].

FTIR spectroscopy

The spectra were recorded on a Nexus 470 FTIR ESP Series spectrometer equipped with an attenuated total reflectance (ATR) objective. FTIR spectra were collected over the range from 4000 to 650 cm^{-1} with the resolution of 4 cm^{-1} . To enhance the signal to noise ratio, each of the reference and sample spectra presented constitutes the average of 40 scans recorded.

Raman spectroscopy

The Raman spectra of the samples were obtained at 12.1-19.9 cm^{-1} estimated resolution in 4247 to 84 cm^{-1} spectra range with a Nicolet Almega XR Dispersive Raman spectrometer. The 532 nm line laser was used as an excitation source for the Raman spectra. The collect exposure time, preview exposure time and sample exposure were 5.0, 0.5 and 4 s, respectively.

Environmental scanning electro microscopy

Micrographs of all samples and particle shape and size of silica were taken and determined using a FEI Quanta Environmental Scanning Electronic Microscope (ESEM). A small portion of the samples were fractured in liquid nitrogen, mounted on a copper stub and coated with a thin layer of gold to avoid electrostatic charging during examination.

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