

Measurements of Size Distribution Nanoparticles in Ultraviolet-Curable Methacrylate-Based Boehmite Nanocomposites

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ABSTRACT: A deep study on the possibility to increase the quality of the dispersion of organically modified Boehmite nanoparticles into photo-polymerizable methacrylic-siloxane monomers, to be used as coatings, was conducted using unconventional indirect analyses. The nanocomposites were produced using two different procedures, starting from the conventional “solvent dispersion method.” The two procedures used differ for the technique used to obtain the dispersion of Boehmite, i.e., sonication or magnetic stirring and for the time used in each procedure. The efficiency of each method of preparation of nanostructured systems was analyzed, both in the liquid (uncured) and ultraviolet (UV) cured state. First, dynamic light scattering and rheological measurements were performed on the liquid suspensions, supplying experimental data used in proper theoretical models to estimate the dimensions and distribution of Boehmite particles. The suspensions obtained with the two different methods were, then, UV cured obtaining thin and thick films, on which scanning electron microscopy and transmittance measurements were performed. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 128: 4102–4109, 2013

KEYWORDS: nanostructured polymers; optical properties; photopolymerization

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INTRODUCTION

Many nanocomposites studies related to several different applications were published in the last decade. Thermoplastic polymers like polyolefins (PP and PE), polyurethanes, polyimides, and nylons are among the most studied matrices.¹ Improved scratch and impact resistance, Young's modulus, modulus of rupture are among the most researched properties for thermoplastic nanocomposites. Flame, fire, and moisture resistance seem to be also improved by clay introduction and exfoliation in thermoplastic polymers. Their unique phase morphology, derived by layer intercalation or exfoliation, is able, in fact, to maximize the interfacial area between the organic and inorganic phases and to enhance the bulk properties.¹

Thermosetting nanocomposite studies are fewer than those performed on thermoplastic matrices. Processes with the former are less common: even if the thermosets cover a wide range of industrial applications, their use as nanocomposites is lower than for thermoplastics. Adhesives and coatings, especially based on epoxies and acrylates, are two very widespread families of products which are both under continuous development. The use of reinforcing agents for such applications is quite important, and this is one of the reasons why nanocomposite studies are becoming popular. The most used nanofillers are: aluminum

oxide (Al_2O_3), clay, calcium carbonate (CaCO_3), silica (SiO_2), and titanium dioxide (TiO_2).^{1,2} Montmorillonite exfoliation in epoxy polymer was one of the most studied,^{3,4} due to the peculiar properties, such as increased Young's modulus⁵ and fracture toughness.⁶ Nanocomposites were also prepared with nanocarbon fibers,⁷ presenting higher temperature performance capability, better mechanical performance, an extreme environment corrosion resistance, and an improved dimensional control compared with neat epoxy. Epoxy-silica nanocomposites showed improvements in elastic modulus and glass transition temperature. In all the nanostructured systems analyzed, the procedure to obtain the nanocomposite is one of the key factors to tailor the final properties.

Only few examples related to the incorporation of Boehmite into polymers to prepare nanocomposite materials have been reported in the literature.^{8–11} The Boehmite particles are colloidal plate-like crystals with a high anisotropy. They consist of double layers of oxygen octahedra partially filled with Al cations.¹² Their aqueous dispersions exhibit flow birefringence and thixotropy.¹³ A valuable advantage of Boehmite nanoparticles is their availability on a large industrial scale coupled with a tailorable interface (either hydrophobic, hydrophilic, or silane treated) able to promote their dispersion in a large number of

resins. A proper surface modification is required, in particular, to obtain a good compatibility with different matrices still using the conventional preparation techniques for nanocomposites.¹⁴

Nanocomposites based on acrylic resins have started to be studied in the last 10 years.¹⁵ These studies are largely due to the growth of ultraviolet (UV) radiation curable acrylic-based coatings in many industries. UV coatings present important advances for the finishing technology, in terms of reducing curing times, absence of solvent emissions, good scratch and wear resistance, and final performance.^{16–22}

In this study, starting from a UV-curable Boehmite nanocomposite, previous developed and proposed as protective coating for wood elements,^{23–25} an intense research about the way to improve the dispersion of the same Boehmite nanoparticles in the photopolymerizable siloxane-modified acrylic formulation was performed. To this aim, the average dimensions and size distribution of the nanoparticles dispersed in the polymeric matrix, both liquid and UV cured, was measured by using different experimental analytical techniques. The wide analysis performed in this study gives clear and important information about the best procedure able to optimize the dimensions and dispersion of the Boehmite nanoparticles in the methacrylic-siloxane matrix and to maximize the final properties of the UV-cured protective coatings.

EXPERIMENTAL

Materials

Organically modified Boehmite (OMB), supplied by Sasol, Milan, Italy commercially available as Disperal-MEMO was used. It was used as received, i.e., organically modified with the surface modifier trimethoxypropyl silane metacrylate (MEMO). As reported in the technical data sheet, OMB nanoparticles have an average size dimension of about 100 nm and a crystallite size [1,2,0] of about 10 [nm].

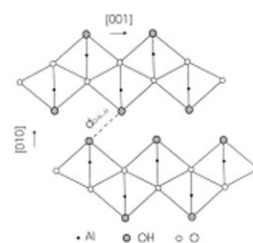
The projection of unmodified Boehmite (UB) crystalline structure is reported in Scheme 1. The chemical formula of the organic stabilizer for OMB nanoparticles, the trimethoxypropyl silane metacrylate (MEMO), is also reported in Scheme 1.

Trimethylolpropane trimethacrylate (TMPTMA) was chosen as the main polymeric component of the coating, due to its high reactivity. The product, whose formula is schematized in Scheme 1, was supplied by Cray Valley, Boretto, Reggio Emilia, Italy.

The trimethoxypropyl silane metacrylate monomer MEMO, commercially used to modify the Boehmite, was used as a coupling agent to enhance the dispersion of the nanofiller into the organic coatings. It was supplied by Dow Corning, Milan, Italy as Z6030 and shown in Scheme 1.

A vinyl terminated polydimethylsiloxane (VT PDMS), supplied by Aldrich, Milan Italy, was added to the acrylic mixture to enhance the water repellence of the coatings. The VT PDMS used has a number average molecular weight in the region of 25,000. Its chemical formula is again reported in Scheme 1.

A 3-Mercaptopropyltriethoxysilane (MPTS), supplied by Aldrich, was added to the siloxane modified methacrylic resin system to reduce the effect of inhibition of oxygen toward



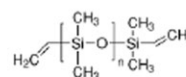
UB



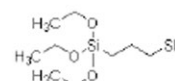
TMPTMA



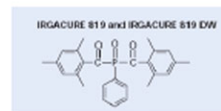
MEMO



VT PDMS



(MPTS)



Scheme 1. Chemical structure of: Boehmite (UM), Trimethylolpropane trimethacrylate (TMPTMA); alkoxy silane methacrylate functionalized (MEMO); vinyl terminated polydimethylsiloxane (VT PDMS); 3-Mercaptopropyltriethoxysilane (MPTS); Photoinitiator (Irgacure 819). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

radical photopolymerization.²⁴ MPTS has a number average molecular weight of about 238.42 g mol⁻¹. The functionalization of VT PDMS with MPTS was performed by mixing the two components at 100°C in 1 : 1 molar ratio in presence of 1 wt % of diethylamine (DTA), again supplied by Aldrich.

Preparation of Nanocomposite Mixtures

To improve the dispersion of the OMB in the each mixture and to obtain in turn a nanocomposite, two different modifications of the conventional “solvent dispersion method”²⁵ were proposed. Following these procedures, the OMB was first dispersed in MEMO silane, due to its high compatibility with modified Boehmite, and subsequently in the TMPTMA resin and VT PDMS, functionalized with MPTS (in the following named as PDMS_m).

The two procedures employed to add the nanosized OMB to the mixture TMPTMA/PDMS_m are reported as follows:

Table I. Details of Composition of All the Mixtures Produced

Sample	Weight composition
80T-10M-5 PDMS _{m819}	85% TMPTMA, 10% MEMO, 5% mPDMS, 1% IRGACURE 819
85T-10M-5PDMS _m - 3OMB _{819method1}	85% TMPTMA, 10% MEMO, 5% mPDMS, 1% IRGACURE 819, 3pph OMB
85T-10M-5PDMS _m - 3OMB _{819method2}	85% TMPTMA, 10% MEMO, 5% mPDMS, 1% IRGACURE 819, 3pph OMB

Method 1

- Mechanical mixing for 5 min and subsequent sonication for 2 h of modified Boehmite in MEMO at ambient temperature (about 23°C). This mixture was called MEMO/OMB_{method1};
- Addition of the modified Boehmite dispersion to the VT PDMS, functionalized with MPTS, as previous described, and magnetic stirring for 5 min at ambient temperature (about 23°C);
- Addition of the TMPTMA to the previous prepared mixture and mechanical mixing for 5 min at ambient temperature (about 23°C);
- Addition of the photoinitiator to the dispersion and mechanical mixing for 5 min at ambient temperature (about 23°C);
- Each mixture was, finally, kept for 2 h in an ultrasonic bath at ambient temperature (about 23°C).

The amounts of each component added are reported in Table I. The suspension obtained with this experimental preparation procedure was called 85T-10M-5PDMS_m-3OMB_{819method1}.

Method 2

For comparison purposes, a different method to prepare the suspension was also used in which the sonication used in the first and the fourth step was replaced by magnetic stirring for 24 h and mechanical mixing for 5 min, respectively, keeping in both cases the temperature at ~ 23°C. The suspension obtained with this second experimental preparation procedure was called 85T-10M-5PDMS_m-3OMB_{819method2} and its composition outlined in Table I.

Both suspensions were, then, photocured on a glass substrate by using a medium pressure Hg UV lamp (UV HG 200 ULTRA), with radiation intensity on the surface of the sample of 9.60 μWatt mm⁻², working in air atmosphere. The maximum time necessary for the complete curing of the films was 6 h, as previously demonstrated.²⁵ A cured film of about 100 μm thickness was obtained.

Experimental Techniques

Several experimental techniques were used to characterize the suspensions produced, both in the liquid and in the solid states.

The particles size and their distribution in the liquid mixtures were measured by dynamic light scattering (DLS Zetasizer). The measure was performed just after their preparation and after different time spans, up to 1 month. Moreover, the same measurements were also performed on OMB/MEMO suspensions, to check the effectiveness of the methods used to mix the two components.

The amount of organic modifier in the nanofiller OMB was determined by thermogravimetric analysis (TGA/DSC1 Star and System, METTLER Toledo). Samples were heated from room temperature up to 800°C at 10°C min⁻¹ in nitrogen atmosphere. The weight fraction of nanofiller was determined as the residual weight of sample, accounting for the transformation of Boehmite in alumina with a loss of half mole of H₂O.

The rheological characterization of all the suspensions produced was performed in a strain controlled Rheometer (Ares Rheometric Scientific). The tests were performed with a plate and plate flow geometry (radius = 12.5 mm) in the steady state mode, at room temperature (25°C) using a shear rate ranging from 0.05 to 100 s⁻¹. A first sweep experiment was always followed by a second one performed on the same sample and using the same conditions, to exclude aggregation effects. The rheological experiments were repeated at least three times to check the repeatability of results.

Wide-angle X-ray diffractions (WAXD) of Boehmite particles, obtained as solid residue from TGA analysis performed on liquid suspensions and calcinations of UV cured systems (burning out the cured films in an oven, as described in the “Results” section), were collected on a PW 1729 Philips, using Cu Kα radiation in reflection mode (λ = 0.154 nm). All the samples were step-scanned at room temperature from 2θ values of 10°–60°.

Transmittance spectra of UV cured films of 10 μm thickness were recorded at normal light incidence in the spectral range of wavelength 200–1500 nm with a Varian Cary 500 UV-Vis-NIR double-beam spectrophotometer.

The morphology and size of the Boehmite particles, dispersed in both UV cured films, were characterized by scanning electron microscopy (SEM) micrographs using a Jeol JSM-6550F.

Pencil hardness measurements were used to determine the hardness of 100 μm thickness films, according with the Standard Test Method for Film Hardness by Pencil Test, i.e., ASTM D 3633.²⁶

Hardness Shore D of 1-mm-thick specimens was measured using a digital durometer Sh D, Gibitre Instruments, according to ASTM D2240.²⁵ These thick specimens were prepared using the same conditions previously described (lamp intensity, temperature, and time). In this case, the liquid mixtures were poured in polycarbonate moulds and subsequently UV-cured. Five tests were performed for each system.

RESULTS AND DISCUSSION**Characterization of the Liquid Suspensions**

From a complete characterization performed on the OMB nanosized particles (comprising XRD, TGA), reported elsewhere,²⁵ it was obtained that the particles of Boehmite have an orthorhombic crystalline structure with an average crystalline

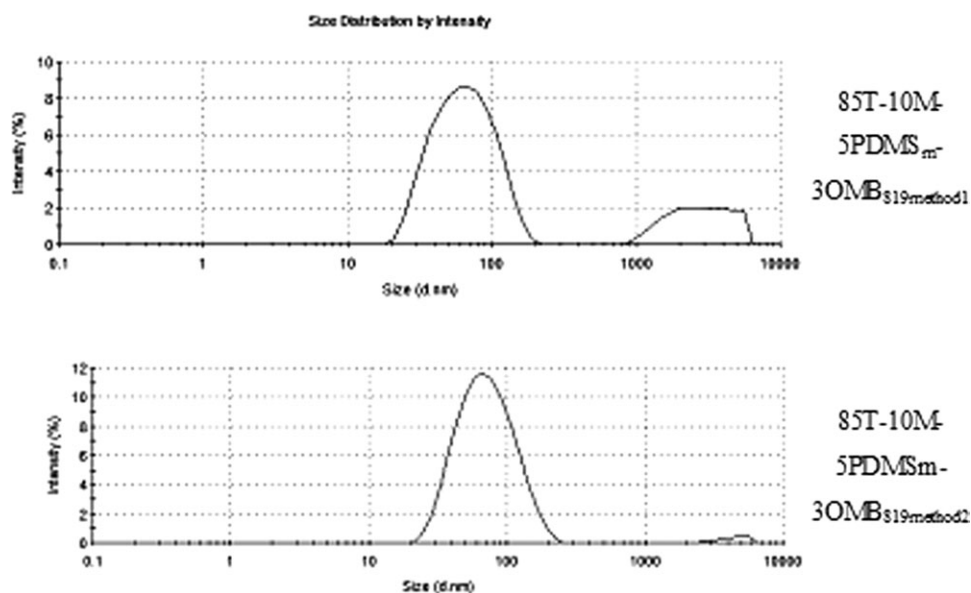


Figure 1. DLS patterns of (up) 85T-10M-5PDMS_m-3OMB_{819method1} and (down) 85T-10M-5PDMS_m-3OMB_{819method2} suspensions.

thickness, $L = 36.4 + 0.9$ nm and a content of organic modifier MEMO of about 16%.

In Figure 1 (up and down), the particle size and their distribution, measured by DLS, of the silane modified acrylic-based dispersions, containing OMB and obtained following procedures 1 and 2, respectively, are reported.

For both methods, a bimodal distribution of the particles was observed, with an average dimension of the highest percentage of particles lower than 100 nm. However, the suspension obtained with the first procedure displays a stronger bimodal feature, with about 20% particles of dimensions higher than 1 μm . On the other hand, with the second method, only 2% particles show micrometric dimensions. Both suspensions, finally, display a quite stable dimension of the particles, as can be seen from data of Table II, where the average diameter of the particles present in the highest percentage in both mixtures, 1 day and 1 month after their preparation, are reported. In the same Table II, the results of the DLS analysis performed on the initial OMB/MEMO suspensions, obtained with the same two procedures, are also reported. In these latter cases, a unimodal nanometric distribution of the particle size is always found. Moreover, the dimensions of the particles remained stable in time.

TGA analysis is allowed to determine the solid residue of the two liquid suspensions, that is, for both of about 5.8%. On the other hand, the solid residue obtained analyzing the unfilled organic mixture was about 3.5%. It is principally due to the presence of silane (organic stabilizer or components of the liquid mixture) that contribute to increase the solid residue, leaving pyrolyzed silica articles, after the burn out of the organic mixture. As a consequence, it is confirmed that the amount of OMB added was about 3 wt %. The volume fraction of OMB (ϕ) in the nanocomposites was, then, obtained starting from the solid residue from TGA experiments performed on both the suspensions, as follows:

$$\phi = \frac{\frac{\text{ewc}w_{\text{OMB}}}{\rho_B}}{\frac{\text{ewc}w_{\text{OMB}}}{\rho_B} + \frac{w_p + w_{\text{lom}} \times w_{\text{OMB}}}{\rho_{\text{or}}}} \quad (1)$$

where the weight fraction of modified Boehmite, w_{OMB} , is multiplied by the effective weight content of OMB (ewc) calculated by TGA, equal to 0.79. The organic weight fraction includes the weight fraction of siloxane modified acrylic-based mixture, w_p , plus the weight fraction of the organic modifier for Boehmite, calculated by multiplying the weight loss of the organic modifier (w_{lom}), equal to 0.16, to the weight fraction of OMB (w_{OMB}). In eq. (1), it is assumed that the densities of the resins and the organic modifier are very close, and their value, i.e., 1.1 g cm^{-3} , is reported as ρ_{or} . The density of Boehmite, ρ_B , is 3.07 g cm^{-3} . From eq. (1), a value of $\phi = 0.008$ for the volume fraction of OMB in both the nanostructured suspensions was calculated.

To analyze the morphological properties of the particles contained in the filled suspensions, the solid residues obtained starting from the TGA analysis performed on both liquid formulations (85T-10M-5PDMS_m-3OMB_{819method1}, 85T-10M-5PDMS_m-3OMB_{819method2}) were analyzed by WAXD analysis.

Table II. Results of DLS Analysis Performed on the Mixtures

Sample	Average particles dimensions (nm) at time 0 days	Average particles dimensions (nm) at time 30 days
OMB/MEMO _{method1}	81.42 ± 0.83	80.98 ± 0.59
OMB/MEMO _{method2}	76.64 ± 1.55	75.97 ± 0.97
85T-10M-5PDMS _m -3OMB _{819method1}	69.77 ± 1.42	60.56 ± 7.98
85T-10M-5PDMS _m -3OMB _{819method2}	86.07 ± 0.94	84.42 ± 1.77

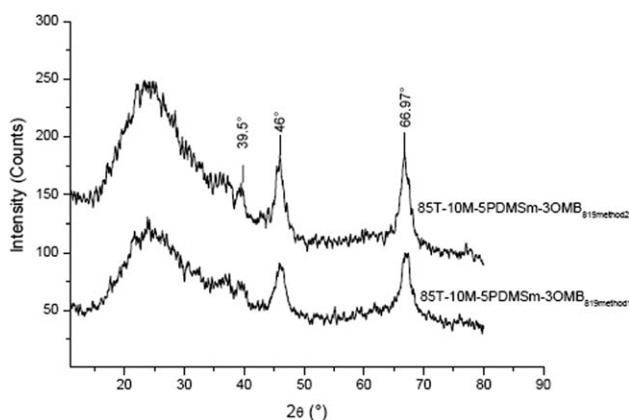
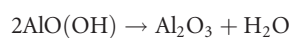


Figure 2. WAXD patterns of 85T-10M-5PDMS_m-3OMB_{819method1} and 85T-10M-5PDMS_m-3OMB_{819method2} suspensions.

This latter investigation is important to analyze the possible morphological changes, affecting the structure of the material that might occur to the Boehmite filler, after heating the liquid suspensions up to 800°C.

The WAXD patterns related to Boehmite particles obtained from the two kinds of suspensions, reported in Figure 2, are comparable. Both spectra, in fact, exhibit the presence of the characteristic peaks of alumina (Al₂O₃) particles (i.e. $2\theta = 39^\circ$, 46° and 67°), due to dehydroxylation of Boehmite and occurring between 300° and 600°C, according to the following reaction:^{26–28}



Both the WAXD patterns are very different from that obtained on as received modified Boehmite particles, reported in a previous work²⁵: due to heat treatment, necessary to allow the complete evaporation of the liquid polymeric components, all the Boehmite was transformed in alumina. These results were confirmed also by RAMAN spectra.

To have an indirect measure of the dimensions of the nanoparticles dispersed in both formulations, steady rheological measurements were performed. The results, reported in Figure 3, show that all the mixtures possess a pseudo-plastic behavior and that the viscosity of the unfilled suspension (80T-10M-5mP₈₁₉) increases in presence of 3 wt % of OMB, irrespective to the method used to prepare the suspension.

As the rheology of multiphase systems, and more specifically of solid–liquid suspensions, was the object of numerous investigations, both theoretical and experimental, starting from the work of Einstein,^{10,29–31} it was found that the viscosity of a suspension depends on the dimensions of the solid particles, i.e., by increasing of the dimension of the particles an increase of the viscosity of the suspension is obtained. The Einstein equation can be applied to very dilute suspensions (solid volume fraction $\Phi < 0.02$) of rigid spheres in a Newtonian field, i.e.:

$$\eta_r = 1 + k_1 * \Phi \quad (2)$$

where η_r is the relative viscosity of the suspension, calculated as the ratio between the viscosity of the filled suspensions, η , and

the viscosity of the suspending medium, η_s . The parameter k_1 takes into account the shape of the particles in suspension and equals 2.5 for spherical particles, as in Einstein equation. Guth found that, in the case of nonspherical particles, k_1 depends on the aspect ratio, p , i.e., the ratio between the highest and the lowest diameters of the ellipsoid particles, according to equation:³¹

$$k_1 = \frac{p}{2 \ln(2p) - 3} + 2 \quad (3)$$

By substituting in eq. (2) the eq. (3) and by calculating the relative viscosity of the two suspensions analyzed, starting from the experimental data of Figure 3, a value of $p = 2.3$ was calculated, for both the suspensions prepared with the first and the second method, irrespective to the shear rate investigated. Assuming an average value of the highest diameter equal to 80 nm in the case of the suspension prepared with the first procedure and equal to 86 nm for the suspension prepared with the second procedure, as obtained from DLS analysis (see Figure 1), a lowest diameter of the nanoparticle of about 35 and 37 nm was also determined for the two suspensions, respectively.

From the analyses performed on the liquid suspensions, it can be concluded that the average dimensions of the particles present in the suspensions slightly depends on the procedure used. The dimensions are more uniform using the second method, which allows to obtain a quasi-unimodal distribution of the particles. Moreover, the second method of preparation for the suspensions is even more effective to enhance the dispersion of the nanoparticles in the polymeric matrix.

Characterization of the UV Cured Systems

Optical transparency of the 10 μm cured films, coated on a glass substrate and UV cured, was determined by light transmittance measures and the results are reported in Figure 4.

The light transmittance of the nanocomposites prepared with both methods is greater (ranging between $\sim 75\%$ and 88% , for the first, and 79% and 99% , for the second method) than that

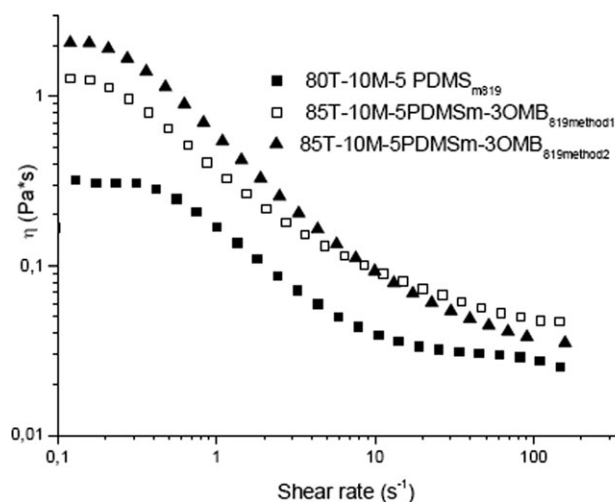


Figure 3. Rheological curves of 85T-10M-5PDMS_m-3OMB_{819method1} and 85T-10M-5PDMS_m-3OMB_{819method2} and 80T-10M-5 PDMS_{m819} suspensions.

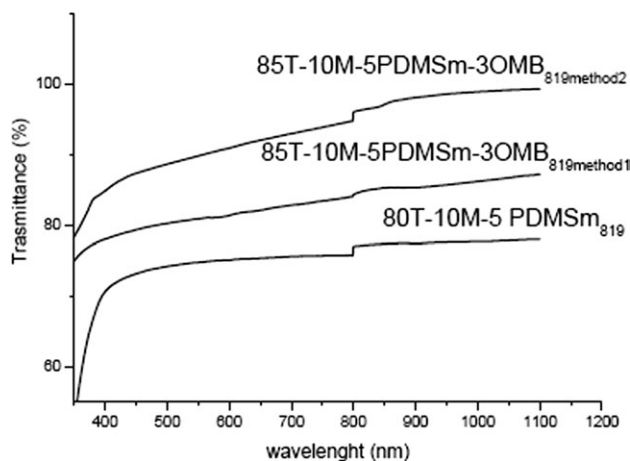


Figure 4. Light transmittance of the UV cured films realized with the mixtures 85T-10M-5PDMS_m-3OMB_{819method1} and 85T-10M-5PDMS_m-3OMB_{819method2} and 80T-10M-5 PDMS_{m819}.

of the unfilled coating, i.e., 80T-10M-5 PDMS_{m819}, ranging between 55% and 78%. The appreciable increase of the optical transparency of nanocomposite confirms again that the Boehmite nanoparticles have been homogeneously dispersed in the polymeric matrix, especially following the second procedure of preparation. Generally, the introduction of inorganic nanoparticles into transparent polymers, even at low contents, leads to opaque nanocomposites due to light scattering caused by the nanoparticles because of the refractive index mismatch between nanoparticles and polymer matrices.³² As observed in a previous work,³³ the light scattering of different amounts of modified Boehmite particles dispersed into an epoxy resin causes a decrease in the transmittance spectra. Clearly, this means an increase in absorbance which, in turn, results from the sum of scattering and absorption components. These latter effects can be principally attributed to the presence of higher-size particles, able to increase the light scattering process.

These results seem to suggest that the absence of the sonication during the preparation of the liquid suspensions allows to obtain after UV curing a smaller amount of micrometric aggre-

Table III. Results of Pencil and Surface Hardness Measurements Performed on Photo-Cured Films

Sample	Pencil hardness	Surface hardness (ShD)
80T-10M-5 PDMS _{m819}	7H	13.6 ± 0.2
85T-10M-5PDMS _m -3OMB _{819method1}	> 9H	21.3 ± 0.1
85T-10M-5PDMS _m -3OMB _{819method2}	> 9H	22.7 ± 0.3

gates of OMB; these, furthermore, are characterized by an average lower dimension. Figure 5(a) (1000×) shows, in fact, the presence of large aggregates with a rough spherical shape and dimensions up to 10 μm. On the other hand, Figure 5(b) (10,000×) shows the presence of a small amount of spherical micrometric aggregates. These are characterized by dimensions never higher than 0.7–0.8 μm. Both the SEM images, however, reveal the presence of Boehmite particles randomly dispersed in the polymeric matrix. As with this technique, only the micrometric aggregates are visible, the results obtained with this analysis suggest that in the film coating obtained from the UV cure of the 85T-10M-5PDMS_m-3OMB_{819method2} suspension a better dispersion of the OMB particles can be achieved, guarantying, in addition, a much lower dimension of the few aggregates of Boehmite that are still present in the polymeric matrix. This latter result is in accordance to that obtained from the transmittance measurements and the following calculations.

A statistical analysis was performed on 20 SEM images, with a scan size of 10 μm and acquired in different parts of the samples, using a dedicated program that allows to estimate the average dimension of the aggregated particles formed during the UV-curing process. Besides, the small particles having major axis ranging between 20 and 70 nm, a certain number of particles have dimensions in the order of hundreds of nanometer. The amount of larger particles is higher in the case of the nanocomposite films obtained starting from Method 1. These results are again in agreements with that obtained from the application of the Beer law to experimental data of transmittance of Figure 4.

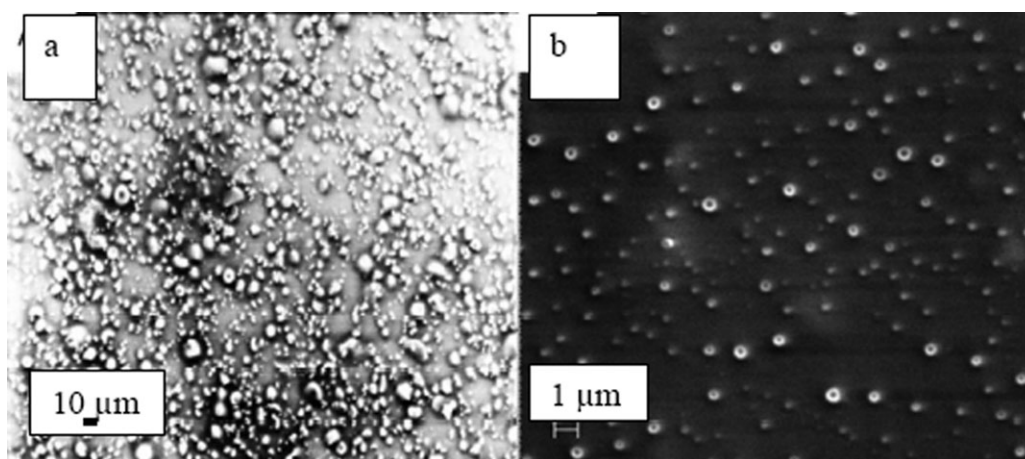


Figure 5. SEM images of the UV cured films realized with the mixtures 85T-10M-5PDMS_m-3OMB_{819method1} and 85T-10M-5PDMS_m-3OMB_{819method2}.

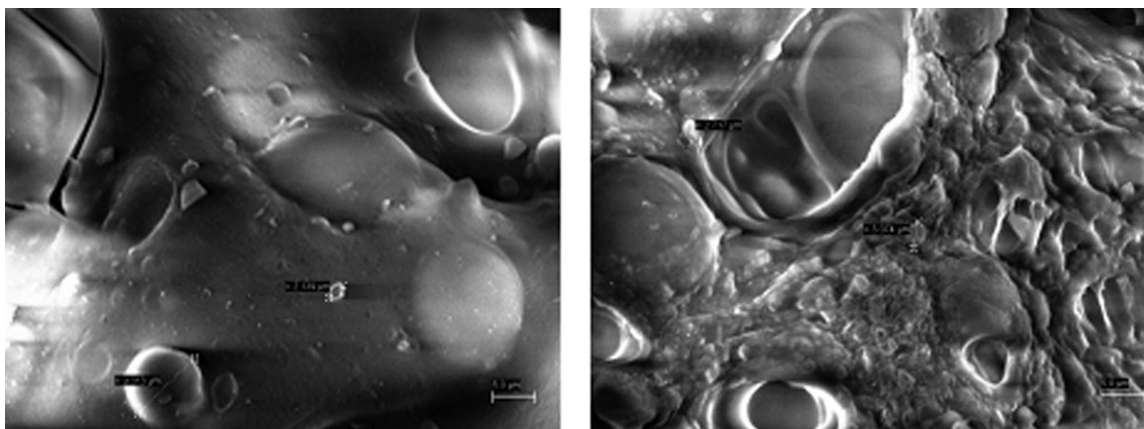


Figure 6. SEM images solid residue obtained after a 800°C treatment on coatings obtained starting from the first (a) and the second (b) methods, respectively.

Moreover, the statistical analysis of the volumetric distribution of particles reports a percent of 0.8 vol %. This value is the same calculated from TGA, i.e., $\phi = 0.008$.

The surface hardness Shore D and the pencil hardness measurements, performed on the UV-cured systems and reported in Table III, shows the presence of the Boehmite nanoparticles appreciably enhances also the surface resistance properties. These results are particularly interesting for coating applications. By adding a small amount of Boehmite nanoparticles, in fact, it is possible to increase the surface and scratch hardness of the coating, with an additional increase in the transparency of the coatings.

The morphological features of the solid nanoparticles present in the UV cured specimens (1-mm thick) were analyzed by SEM/WAXD analyses. To this aim, the UV cured samples were burn out in an oven at 800°C. In Figure 6(a,b), the SEM images of the solid residual of the two systems after the treatment at 800°C are reported. The images show that the burn out of the suspension prepared with the first method led to the presence of large aggregations of particles [Figure 6(a)]. On the other hand, more homogeneous and smaller aggregates are obtained with the burn out of the suspension prepared with the second procedure [Figure 6(b)]. This latter observation indirectly confirms the results of light transmittance measurements (Figure 4), i.e., the second procedure is more suitable to preserve smaller-size Boehmite nanoparticles, dispersed in the UV curable matrix.

WAXD patterns of the solid residue obtained from the calcination of the two coatings at 800°C correspond exactly to those determined for the alumina particles, obtained from the evaporation of the liquid polymeric matrix at the same temperature and reported in Figure 2.

CONCLUSIONS

In this article, two different modifications of the conventional “solvent dispersion method” were proposed to prepare polymeric nanocomposite systems based on modified Boehmite. In the two procedures used, the dispersion of Boehmite step was performed using two different techniques: sonication or magnetic stirring,

using also different times for each procedure. The efficiency of each method of preparation of nanostructured systems was analyzed, both in the liquid (uncured) and UV cured state. All the analyses performed are concurrent in demonstrate that the second method, i.e., using the magnetic stirring, is more efficient than the first. In particular, the second procedure is able to obtain a more homogeneously and more stable dispersed nanofilled suspension in liquid state, as shown by DLS measurements. Through rheological analysis, it was possible to estimate that the average dimension of the Boehmite particles in suspensions is of about 100 nm in both cases. In addition, the transmittance and SEM measurements performed on the UV cured coatings confirm that the second method is able to improve the dispersion of the nanofiller and prove that it allows to produce a system containing nanometric aggregates of particles even after UV curing. Finally, for both methods, it was possible to achieve an appreciable increase in transparency and surface hardness.

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