Influence of Stone Particles on the Rheological Behavior of a Novel Photopolymerizable Siloxane-Modified Acrylic Resin

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ABSTRACT: A study was made of the effects of calcarenitic stone particles, known as *pietra gentile*, inclusions on the rheological behavior of photopolymerizable siloxane-modified acrylic formulations, intended as protective for the calcarenitic stone structures. Different amounts of stone particles (ranging from 15% wt to 35% wt) were added to the modified acrylic mixture to achieve a natural color matching for calcarenitic stone substrates. The presence of stone particles was expected to modify the rheological behavior of the protective formulation. Therefore, the viscosity of the mixtures was studied at ambient temperature as function of the shear rate and the solid volume fraction. A relationship was obtained to predict the modification of viscosity of each formulation as a consequence of inclusions of different amounts of stone. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 942–947, 2011

Key words: UV-photopolymerizable acrylic resins; rheology

INTRODUCTION

Polymers based on acrylic and metacrylic monomers are widely used for the protection and conservation of stone buildings, due to their ability to form water repellent and optically clear coatings.[1–17] There are, however, durability issues on the outdoor use of acrylic systems for the long term protection of historical buildings.[18–20] Acrylic coatings exert a poor adhesion to porous substrates and provide a sufficient drainage of the water from the coated surface.

To overcome these deficiencies, water-borne silane modified acrylic resins and partially fluorinated acrylic copolymers have recently been proposed.[3–17] The free radicals for the initiation of the polymerization reactions of such systems are generally produced by the decomposition of a peroxide initiated by the heat generated through IR lamps. However, this technique is not suitable for the coating of large area substrates.

In a first stage of research, methacrylate resin based mixtures were proposed for the protection of stone using as curing method the exposure to ultraviolet (UV) and visible radiations.[21] This procedure was proposed, in fact, to overcome the intrinsic deficiencies of acrylic coatings and to explore an alternative high energy radiation curing. UV sources are widely used for the curing of coatings, inks, and even adhesives; little use has been made so far of this method in the applications of coatings for the protection of stones.[22,23] The selected methacrylate monomer (trimethylolpropane trimethacrylate, TMPTMA) was modified with a methacrylate silane coupling agent (trimethoxypropyl silane metacrylate, MEMO) to enhance the adhesion to the inorganic substrate.[3] In addition, a high molecular weight polysiloxane unsaturated oligomer was employed to increase the hydrophobicity and the viscosity of the acrlylic-silane mixture. The increase of the hydrophobicity is required to enhance the water repellency of the coatings, while the increase of the viscosity is useful to control the penetration of the monomer characterized by a low viscosity.[3]

In the present work a further increase in viscosity of the acrylic based formulations was obtained by adding an inorganic filler, consisting of a finely ground calcarenitic stone known as *pietra gentile*. The primary reason for choosing this filler was to provide a color matched pigmentation for similar calcarenitic stone substrates. In addition, the presence of stone particles in the organic mixtures is expected to provide a decrease of interfacial tension between the unreacted liquid coating and the stone substrate that could, in turn, enhance the wetting of the mixtures during their application. Although from a technological point of view the use of commercial calcium

Sample	Weight composition	Volumetric composition
T_{819}	TMPTMA + 1.5 pph IRGACURE 819	
90T-10M$_{819}$	90% TMPTMA + 10% MEMO + 1.5 pph IRGACURE 819	
87T-10M-3PDMS$_{819}$	87% TMPTMA + 10% MEMO + 3% VT PDMS + 1.5 pph IRGACURE 819	
T_{784}	TMPTMA + 1.5 pph IRGACURE 784	
90T-10M$_{784}$	90% TMPTMA + 10% MEMO + 1.5 pph IRGACURE 784	
97T-3PDMS$_{784}$	97% TMPTMA + 3% VT PDMS + 1.5 pph IRGACURE 784	
97T-3PDMS$_{819}$ /0S	97% TMPTMA + 3% VT PDMS + 1.5 pph IRGACURE 819 +0 pph stone particles	100% vol. (97T-3PDMS$_{819}$) +0% vol. Stone particles
97T-3PDMS$_{819}$ /15S	97% TMPTMA + 3% VT PDMS + 1.5 pph IRGACURE 819 + 15 pph stone particles	99.94% vol. (97T-3PDMS$_{819}$) +0.064% vol. stone particles
97T-3PDMS$_{819}$ /25S	97% TMPTMA + 3% VT PDMS + 1.5 pph IRGACURE 819 + 25 pph stone particles	99.9% vol. (97T-3PDMS$_{819}$) + 0.1% vol. stone particles
97T-3PDMS$_{819}$ /35S	97% TMPTMA + 3% VT PDMS + 1.5 pph IRGACURE 819+ 35 pph stone particles	99.86 % vol. (97T-3PDMS$_{819}$) + 0.14% vol. stone particles

carbonate filler would be a more realistic chose for a future industrial transferability, our initial purpose was more focused on a scientific interest, i.e., to select a ground stone belonging to the same mineralogical family of the stone elements on which the protective will be applied.

The purpose of this work is to study the viscosity of the formulations at ambient temperature as a function of the solid volume fraction and to predict the modification of viscosity of each formulation as a consequence of the inclusion of different amounts of stone. Rheological characteristics, in fact, strongly depend on several process parameters, such as temperature, time, composition. For any specific process, an appropriate viscosity range for the resin can be identified.[24] The possibility to predict how each parameter can affect the viscosity of the product would make it possible to select coating systems for any specific application avoiding the experimental rheological characterization of any proposed formulation.

EXPERIMENTAL

Materials

Trimethylolpropane trimethacrylate (TMPTMA) was chosen as the main component of the coating, due to its high reactivity. The product used was supplied by Cray Valley.

A trimethoxypropyl silane metacrylate monomer, supplied by Dow Corning as Z6030, known as MEMO, was used as a coupling agent to enhance the adhesion of the organic coatings to the stone substrate.

A vinyl terminated polydimethylsiloxane (VT PDMS), supplied by Aldrich, 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.

Two differed types of photoinitiator, Irgacure 819 (Bis (2,4,6-trimethylbenzoyl)-phenylphosphineoxide) and Irgacure 784 (Bis (eta 5-2,4-cyclopentadien-1-yl) Bis [2,6-difluoro-3-(1H-pyrrol-1yl)phenyl]titanium) were supplied by Ciba. These were chosen for their broad absorption characteristics and being capable to catalyze the reaction under UV (Irgacure 819) and visible radiations (Irgacure 784). All mixtures contained 1.5 wt parts per hundred (pph) of one of each photoinitiotor. In this paper the rheological behavior of the un-cured mixtures, containing each photoinitiator, has been only analyzed. The kinetics analysis on the same formulations is still in process.

A calcarenitic ground stone, known as *pietra gentile* was used as filler. Its mineralogical composition is that of calcite, natural calcium carbonate ($CaCO_3$). *Pietra gentile* stone has a density of 2.7 g/cm^3 and an open porosity of 23%.[25] The stone was finely crushed in a mortar grinder; the dimensions of the obtained particles were measured as described following. The particles were, then, added to the liquid acrylic mixture in different compositions.

The compositions of all the mixtures produced are outlined in Table I. Starting from the densities of the monomers, about 1 g/cm^3 as reported in their technical data sheet, and that of the stone, the volumetric compositions of the formulations containing the stone particles were calculated and again reported in Table I.

Experimental techniques

The morphology and size of the solid filler were characterized by Scanning Electron Microscopy (SEM) using a Jeol JSM-6550F.

The rheological characterization of the formulations produced with both photoiniziators, with or without the stone solid filler, was carried out in a strain controlled Rheometer (Ares Rheometric
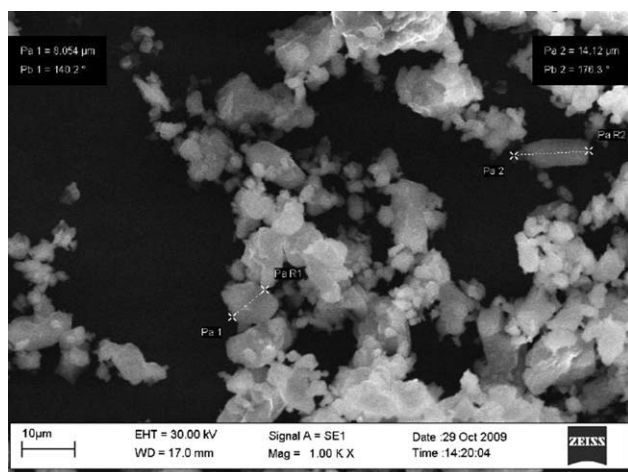
Figure 1 SEM image of ground *pietra gentile*.

Scientific). The tests were performed with a plate and plate flow geometry (radius = 12.5 mm) in the steady state mode, at room temperature (30°C) using a shear rate ranging from 0.05 to 200 s^{-1}. A first sweep experiment was always followed by a second one performed on the same sample and using the same conditions. The rheological experiments were repeated at least three times to check the repeatability of results.

RESULTS AND DISCUSSION

Characterization of stone particles

A SEM image of the ground *pietra gentile* stone is reported in Figure 1. The particles show micrometric dimensions of different size with an elongated shape. Starting from the SEM image in Figure 1, the distribution of the aspect ratio of the particles (p)
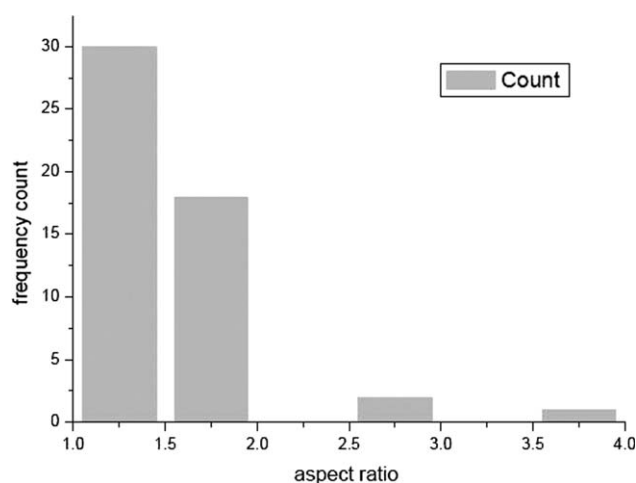
was obtained using a dedicated program. The results are reported in Figure 2. The average value of the aspect ratio for elliptic shaped particles, obtained as the major axis/minor axis equal to 1.52 ($\pm$0.46).

Rheological characterization of the unfilled acrylic mixtures

The rheological behavior of all the acrylic based formulations, activated with Irgacure 819 and Irgacure 784, respectively, as well as of the pure components, was measured as function of the shear rate at room temperature. A Newtonian behavior was observed irrespective to the composition and no difference was detected between the two consecutive measurements on the same sample. The average viscosity values of all the mixtures analyzed are reported in Table II. The viscosity values for MEMO and VT PDMS are those reported on the relative data sheets.

The results indicate that the addition of MEMO to the acrylic resin halved the viscosity of the pure TMPTMA resin. Conversely, when a small amount of VT PDMS is also present, a smaller reduction of viscosity was registered, in the region of 16–18% with respect of the viscosity of TMPTMA resin.

Rheological analysis of the acrylic/stone mixtures

Starting from the results of the rheological analysis performed on the mixtures containing the silane coupling agent MEMO and the siloxane VT PDMS, it was suggested to replace MEMO with finely ground particles of *pietra gentile* stone. This to increase the viscosity of the acrylic formulations containing MEMO, still assuring a good compatibility between the polymeric photopolymerizable protective and the inorganic stone surface.

Figure 2 Frequency count distribution of the aspect ratio, p, of the ground *pietra gentile*.

TABLE II
Measured Newtonian Viscosity Values for All the Mixtures Produced

Sample	Measured average viscosity (mPa s)
MEMO	2.8[a]
VT PDMS	145[a]
T_{819}	45.27 $\pm$ 0.37
90T-10M$_{819}$	21.95 $\pm$ 0.19
87T-10M-3PDMS$_{819}$	37.10$\pm$0.29
T_{784}	50.75 $\pm$ 0.59
90T-10M$_{784}$	33.22 $\pm$ 0.25
87 T-10M-3PDMS$_{784}$	43.12 $\pm$ 0.19
97T-3PDMS$_{819}$ /0S	52.76 $\pm$ 0.2
97T-3PDMS$_{819}$ /15S	56.32$\pm$ 0.7
97T-3PDMS$_{819}$ /25S	63.70 $\pm$ 0.6
97T-3PDMS$_{819}$ /35S	87.16$\pm$ 0.15[b]

[a] From data sheet.
[b] Average Newtonian viscosity measured in shear rate range 10 s^{-1} to 100 s^{-1}.
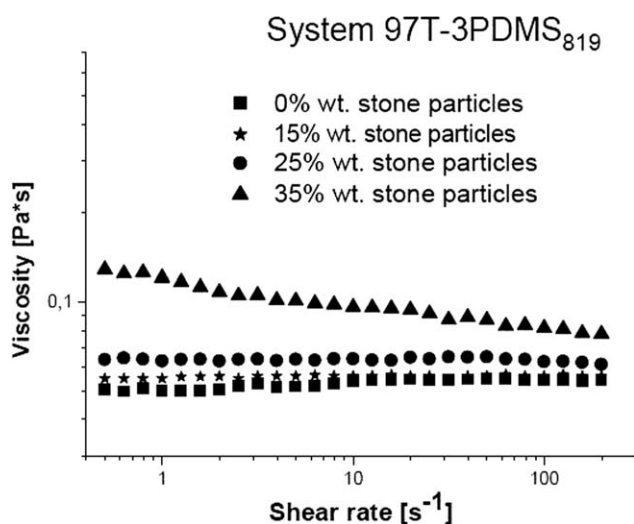
Figure 3 Viscosity versus shear rate curves for acrylic formulations, with or without ground *pietra gentile*, measured at 30°C.

The change of rheological behavior of the formulations based on the acrylic-PDMS resin with the addition of stone particles was, then, examined.

The viscosity of the acrylic-stone suspensions measured in two subsequent sweep experiments did not display differences between the two rheological curves, indicating the absence of any possible strong effect of aggregation of the stone particles. It has to be borne in mind, however, that a preshear step was always performed on the mixtures before the actual rheological measurements.

In Figure 3, the viscosity of the unfilled acrylic mixture as a function of the shear rate is compared with those of acrylic formulations filled with 15, 25, and 35 pph of stone particles, respectively. A general increase in viscosity is observed with increasing the content of stone particles. Furthermore, the system containing 35 pph of stone particles shows a slight pseudoplastic rheological behavior. The very small deviation from the Newtonian behavior observed at the highest level of stone content cannot be attributed to aggregation phenomena, since the preshear step would have eliminated this effect. It was attributed to the resin enrichment at the interface. This effect was, in fact, previously observed in the case of polymer melts containing solid fillers. This effect is probably also present at the lowest content of stone particles but it is likely to be not measurable with the instrumentation used. However, in the following calculations, the rheological behavior of the latter mixture was considered only in the Newtonian region, corresponding to a shear rate range characteristic of the typical application methods (for instance: spraying).

The average viscosity for the mixtures analyzed are reported in Table II. In the same Table, the average viscosity for the mixture containing 35 pph of stone particles calculated in the Newtonian region, shear rate from 10 s^{-1} to 100 s^{-1}, is also showed.

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.[26–28] The Einstein equation can be applied to very dilute suspensions (solid volume fraction Φ < 0.02) of rigid spheres in a Newtonian field, i.e.:

$$\eta_r = 1 + 2.5^*\Phi \qquad (1)$$

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. However, to the best of our knowledge, the dependency of the relative viscosity on the volume fraction of solid porous particles possessing micrometric dimensions and not necessarily spherical has not yet been considered in depth. There are only few studies in literature dealing with this topic.[29] As reported in this latter paper, when the suspensions are based on porous particles the equation that better describes the dependence of relative viscosity on solid volume fraction should be completed with a factor representing the influence of size and structure of porous particles. In this case, apart from the concentration variable Φ, a different variable in the description has to be considered. In particular, a variable characteristic of the pore volume fraction in a suspension, Φ_p, was chosen. The relative viscosity can be, then, determined as function of Φ and Φ_p, as following:

$$\eta_r = f(\Phi)g(\Phi_p) \qquad (2)$$

The function $g(\Phi_p)$ was slightly modified respect to that reported in literature, as following:

$$g(\Phi_p) = K\exp(\Phi_p^{0.5}) \qquad (3)$$

where K is a parameter of description. The value Φ_p, expressed in cm^3 of pores/cm^3 of suspension, was defined as equal to:

$$\Phi_p = V_p\rho\Phi \qquad (4)$$

where V_p is the pore volume, in cm^3/g; ρ is the particles density (2.7g/cm^3); Φ is the volume fraction of dispersed phase, in cm^3/cm^3 of the suspension.[29]

Referring to the function $f(\Phi)$, the Einstein equation cannot be used to fit the experimental data of the formulations analyzed in the present study, since the amount of the solid filler contained in them is too high (Φ > 0.02) and the shape of the particles does not appear like rigid spheres.
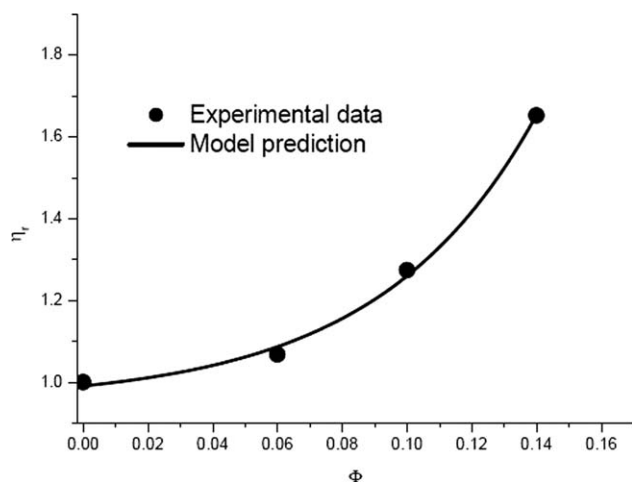
Figure 4 Prediction of eq. (2) compared with experimental rheological data for acrylic formulations containing stone particles.

Starting from Einstein equation, a large number of correlations between the relative viscosity, η_r, and the volume fraction of the solid particles, Φ, were published in literature.[27–29] Mooney equation was found to provide a good fit for the experimental data[28]:

$$\eta_r = \exp\left(\frac{K_1 \Phi}{1 - \frac{\Phi}{\Phi_{max}}}\right) \qquad (5)$$

Equation (5) is obtained from the classical Einstein model, operating a correction that takes into account the effect of a more concentrated suspension of particles. Referring to the physical significance of the parameters introduced in eq. (5), Φ_{max} is the maximum solid volume fraction at which the suspension behaves as a solid.[28] It is assumed that, when the solid volume fraction is equal to Φ_{max}, the viscosity of the suspension becomes ∞.

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. Jeffery found that, in the case of non spherical particles, k_1 depends on the aspect ratio,[28] p, according to:

$$k_1 = 2.5 + 0.4075(p - 1)^{1.508} \qquad (6)$$

where the value of p is between 1 and 15.

By substituting in eq. (6) the average value of p obtained from SEM images (i.e., 1.52), a value of 2.68 ± 0.28 was calculated for k_1.

The relative viscosity of each mixture, η as well as that of the pure acrylic mixture (calculated varying the shear rate values, from 10 s^{-1} to 100 s^{-1}) were, therefore, reported as a function of the volume fraction of the stone particles (Φ). The data were fitted

employing eq. (1), where $f(\Phi)$ is assumed equal to Mooney eq. (5) and $g(\Phi)$ is assumed equal to eq. (3). The volume fractions, calculated starting from the weight composition, are reported in Table I.

The comparison between experimental data and theoretical prevision from eq. (5) is presented in Figure 4. The values of parameters Φ_{max} and K are respectively, 0.25 and 0.82. As reported in the literature,[30] the relatively low value of the maximum solid loading of the suspensions confirmed the influence of the porous structures of the stone particles on the viscosity of the suspensions. The results of the fitting also confirmed that the maximum packing fraction is a physical parameter depending only on the type and size distribution of the solids.

CONCLUSIONS

In this work the rheological behavior of a photopolymerizable siloxane-modified methacrylate monomer added with stone particles of *pietra gentile* was analyzed at room temperature, to assess the viscosity of the mixtures to be used as protective for stone surfaces made of the same calcarenitic stone.

The relative viscosity of the formulations containing different amounts of particles stone was found to depend on their content, i.e., the volume fraction of mixtures, micrometric dimensions and on their porosity. In particular, the viscosity increased by increasing the filler content, maintaining a Newtonian behavior up to 15% wt. When a larger amount of stone particles was added, a slight pseudoplastic trend was observed for this mixture, according to the common rheological behavior displayed by polymeric suspensions. For each of the observed dependences an accurate relationship was found able to fit the experimental rheological data.

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