# Effect of the Incorporation of Modified Silicas on the Final Properties of Wood Adhesives

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The effect of the incorporation of three different surface modified silicas on the final properties of poly(vinyl acetate) (PVAc) latex based wood adhesives is assessed. It is shown that the compatibility and reactivity of the silica with the polymer determines its state of dispersion throughout the polymer matrix. While silicas revealing the best compatibility with the monomer are located inside or close to the polymer particles surface, the silica that presents the lowest compatibility with the monomer is located exclusively on the surface of the polymer particles. This is found to affect the properties of the adhesives as higher tensile strengths are measured in the presence of silicas with good compatibility with the monomer. The reactivity between one of the silica modifiers and the polymer is the key to substantially improve the hydrophobicity and the adhesion of hybrid PVAc based adhesives.
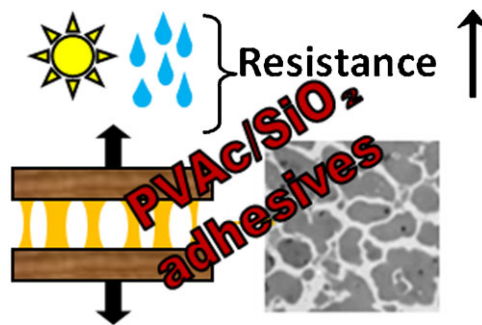
1. Introduction

The interest and development of organic-inorganic hybrids (so-called nanocomposites) has grown enormously in the last two decades. In recent years, it has been shown that the stress transfer occurring from the polymer matrix to the inorganic particles allowed obtaining substantial improvements of the hybrid material properties, such as higher tensile strength, higher thermal degradation, better scratch resistance and better resistance to fire, among others.[1–6] Besides decreasing the production costs, the addition of an inorganic material to a polymer allows widening its application range. This consequence has been of great interest for many industries such as the wood industry, which has tried for many years to lower the costs while keeping the same quality of the product, mainly for the development of good wood adhesives for outdoor applications.

The most important properties of a wood adhesive are strong adhesion to wood and strong cohesive force within the adhesive. This can be achieved by the formation of a network in the polymer (to get a good cohesion) and by good chemical interactions between the polymer and the timber (for a good adhesion). Among the different polymers employed for the synthesis of wood adhesives, poly(vinyl acetate) (PVAc) gets the major interest mainly because of its low cost, ease of use and least negative impact on the environment. However, the PVAc based adhesives are only

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able to pass the dry test during the standard performance evaluations because they lose their bonding resistance capacity at high temperatures or in a high moisture content environment.

Therefore, to increase the performance of PVAc in wood joints, different strategies have been employed such as the copolymerization of PVAc with more hydrophobic monomers (to impart steric hindrance to the chains)[7,8] or with functional monomers able to increase the crosslinking density of the adhesive (to provide water and creep resistance).[7,9] These copolymerizations have shown to present some stability problems and surfactants have to be added in order to stabilize the system, increasing the water absorption of the adhesive or acting as plasticizer, thus reducing the stiffness and tensile modulus.[7] Hence, some authors produced an adhesive with a hardener such as melanine-urea-formaldehyde (MUF)[7,10] or with inorganic materials such as clays,[11,12] metal oxides[13,14] or silica.[13,15,16] Due to the high cost of MUF, particular attention has been paid to the study and development of the polymerization of vinyl acetate in the presence of inorganic materials.

Among the different inorganic materials available, silica has shown the major researchers interest owing to its easy processability, high chemical inertness and good colloidal stability.[17] Depending on the size of the silica, on the modifier employed for the surface coverage of the silica and on its compatibility with the monomer/polymer, a broad range of morphologies has been reported.[18–30] Ding et al.[18] managed to encapsulate silica in polystyrene particles by in-situ polymerization of styrene on the surface of silica particles modified with oleic acid. They showed that the hydrogen bonds formed between the oleic acid and the silanol groups present at the silica surface allowed using it as a functionalized monomer for silica since its double bond can react during the polymerization. Following this approach, Forcada and co-workers[22] synthesized hybrid silica/polystyrene nanoparticles by miniemulsion polymerization by modifying silica with 3-(trimethoxysilyl) propyl methacrylate (TPM) and/or oleic acid. They showed that while the use of both components allowed obtaining a high degree of encapsulation, the use of only TPM or oleic acid decreased the encapsulation. Armes and co-workers prepared polystyrene/silica colloidal nanocomposite particles by emulsion polymerization using a glycerol functionalized silica sol.[24] They showed that the surface coverage of silica was essential in order to get the silica particles at the surface of the polymer particles as the use of unmodified silica led to polystyrene latex coexisting with the silica nanoparticles.

Other modifiers were also employed to increase the compatibility of the silica with the polymer. Bailly et al.[20] grafted an alkoxyamine initiator at the surface of the silica. They employed the modified silica in a nitroxide mediated polymerization of styrene in order to get polystyrene grafted silicas that were further employed in the mini-emulsion polymerization of styrene. By this way, they managed to obtain silica particles encapsulated inside the polymer particles. However, this process had to be optimized since many empty particles were obtained. Zhang and co-workers[19] synthesized SiO$_2$/polystyrene nanocomposite particles with core-shell or raspberry-like morphologies by varying the size of the silica and the surfactant concentration. In this case, the modifier employed was methacryloxy(propyl)trimethoxysilane (MPS), which was also employed by other researchers with the same purpose.[26,28,29] The good interactions obtained between the polymer and silica allowed obtaining hybrid materials with better mechanical and thermal properties than the neat polymer.[26,27,29,30]

As it can be seen, among all the works carried out with silica, very few involved vinyl acetate as monomer[15,16] and in none of them silica has been used together with PVAc and poly(vinyl alcohol) (PVA). Therefore, the present work was carried out in an attempt to further widen the knowledge on hybrids based on vinyl acetate and silica, stabilized by PVA. In this study, three different commercial silicas were employed in the semi-continuous (mini)emulsion polymerization of vinyl acetate using a mixture of PVAs as particle stabilizers. The aim was to produce PVAc based hybrid adhesives by in-situ incorporating silica to the complex process of the emulsion polymerization of vinyl acetate stabilized by PVA. The conventional emulsion polymerization process used to produce this wood adhesive was modified to enhance the incorporation of hydrophobic silica to the polymer particles. It has been demonstrated that the correct modification of the silica nanoparticles can lead to substantial improvements of the mechanical properties of the latexes in the more demanding conditions of humidity and high temperature.

2. Experimental Section

2.1. Materials

The monomer vinyl acetate (VAc) from Quimidroga was used as received. A mixture of PVAs, comprising Mowiol 23-88/Mowiol 28-99 (kindly supplied by Kuraray) at 3/1 weight ratio was used in the polymerizations. Potassium persulfate, KPS, and sodium bicarbonate, NaHCO$_3$, both from Sigma-Aldrich, were used as received.

Three silicas were employed in this work. The surface treatment and the average diameter of particles determined by transmission electron microscopy (TEM) analysis of the silicas is given in Table 1 The silicas (kindly supplied by ALTANA) dispersed in a mineral spirit were dried in an oven at 60 °C for one day and grinded before mixing with the monomer.

Table 1. Characteristics of the silicas used in this work (D_n = diameter).

Sample	Surface treatment	D_n (nm) (TEM)
SiA	Silicone treated silica	78
SiD	None	62
SiE	Silica coated with vinyl groups	85

2.2. Preparation of the Miniemulsion

The recipe of the formulation is given in Table 2. For the preparation of the organic phase, the silica was first dispersed in the monomer by 5 min of ultrasonication (80% Amplitude, 320 W) and magnetic stirring overnight. The PVA aqueous solution (prepared by dissolving the PVA at 85 °C for 2 h) and the buffer solution were mixed with the organic phase by magnetic stirring for 15 min. The mixture was used to prepare a miniemulsion using sonication (Branson Sonifier 450, operating at 8-output control and 80% duty cycle for 5 min) together with magnetic stirring. Then, the miniemulsion was loaded in the 500 mL glass reactor using mechanical stirring under nitrogen atmosphere. Once the system reached the desired temperature, the KPS initiator solution (at 1.6 wt%) corresponding to the first step was fed for 5 min.

For the synthesis of the latexes, the first step was carried out at 65 °C, and the miniemulsion was left to react for 1 h. Once the seed prepared by batch miniemulsion polymerization was obtained, the temperature was increased to 70 °C and the monomer and initiator solution corresponding to step 2 were fed during 3 h. After the feed period had finished, a shot of initiator solution was added and the latex was left at 70 °C for one hour before cooling it down. The final solids content was around 50% for all latexes.

2.3. Characterization

The wettability of the silica powder with water and with vinyl acetate was measured using a KSV Sigma 700 tensiometer. The monomer conversions were measured gravimetrically.

The morphology of the latexes and the films were studied by means of TEM using a Tecnai™ G^2 20 Twin device at 200 kV (FEI Electron Microscopes). The latexes were diluted to 0.5% of solids content and a drop was left to dry at 5 °C on the TEM grid. For the preparation of the film, a sample of the latex was applied onto a silicone mould and dried at 23 °C and 55% of humidity for one week.

The dried films were cryo-sectioned with a Reichert-Jung Ultracut E cryo-ultramicrotome at −70 °C with a Diatome 45° diamond knife, with the aid of a Philips CM10 transmission electron microscope operated at 80 kV. No staining was used in any of the samples.

For the scanning electron microscope (SEM) analysis, a Hitachi S-2700 SEM working at an accelerating voltage of 15 kV was employed. The latexes were diluted to 0.5%SC and some drops were deposited onto the sample stub and dried in controlled conditions (55% of humidity and 23 °C) for one day for the subsequent analysis.

The polymer particle size distributions were determined by two different ways: from the TEM micrographs of the films and from SEM analysis of the dispersions. In both cases, the diameter of polymer particles was measured using the software ImagePro (Media Cybernetics) and the reported average particle size was obtained from the measurement of the diameter of an average of 500 particles.

Different properties were measured for the wood adhesives. First, the tensile strength evaluation of hybrid wood adhesives was performed according to EN204-D1, EN204-D2 and EN14257 (WATT'91) standard. Pressing was performed at room temperature for 1–2 h. The tensile shear strength was measured with an Alwetron TCT50. The samples were glued without any addition of BDGA or hardener.

In order to measure the amount of water absorbed by the films, the films were casted onto silicone molds and were dried under controlled environment (23 °C and 55% humidity) for one week. The obtained films were weighted (m_0) and were placed into different flasks full of distilled water. Then, they were removed from the flask at given times; they were dried with filter paper and weighted (m_t). After weighing the films, they were placed again in their respective flasks. The amount of absorbed water was defined as:

$$Water\ uptake(\%) = \frac{m_t - m_0}{m_0} \times 100.$$

Table 2. Formulation used in the synthesis of the hybrid polymer particles.

Ingredient	Step 1 (g)	Step 2 (g)	Post-polymerization (g)
VAc	56.45	131.05–141.05	–
Silica	0–10	–	–
Buffer (NaHCO$_3$) solution at 2.44 wt%	0.35	–	–
Initiator (KPS) solution at 1.6 wt%	28.55	13.8	2.25
PVA solution at 7.3 wt%	157.5	–	–

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3. Results and Discussion

3.1. Compatibility of Silica with the Aqueous and with the Monomer Phase

It is well-known that the compatibility (relative interfacial tensions between phases) of the inorganic particle with monomer/polymer and water phases determines the final morphology of the hybrid waterborne polymeric dispersions.[4,5,25,31] Thus, in an attempt to explain the morphologies obtained in this work, the compatibility of the silicas with water and the monomer was assessed.

First, the hydrophilicity of the silicas was determined by mixing 1 wt% of silica in water, stirring overnight, then putting the vials in an ultrasonic bath for 5 min and leaving at rest. Figure 1 shows the state of the dispersions after leaving at rest for 5 h and 3 d. The pictures show that silicone treated silica (SiA) was more hydrophilic and was still well dispersed in water after 5 h. On the other hand, it could be observed that the silica coated with vinyl groups (SiE) and untreated silica (SiD) settled down fast. After 5 h the water dispersion was almost transparent and after 3 d all the silica had settled down.

In order to confirm these results, the contact angles of the silicas with water were determined. The results were: $\theta_{\text{SiE-water}} = 89°$, $\theta_{\text{SiD-water}} = 87.5°$ and $\theta_{\text{SiA-water}} = 53.5°$. Thus, it could be concluded that SiE was the most hydrophobic one, followed by SiD and SiA which was the most hydrophilic. It is important to note that the untreated silica was dispersed in a mineral spirit when received and therefore some stabilizers were needed to obtain a stable dispersion of silica. Those stabilizers might be present even after drying the silica and might explain the hydrophobic character of the untreated silica.

Also, the compatibility of the silicas with the monomer was first determined by mixing 3 wt% of silica in the monomer, vinyl acetate, for one day, then placing the mixture in an ultrasonic bath for one hour and leaving at rest.

It was observed that the sedimentation of SiA was faster than for the non-treated silica (SiD) and SiE (see Figure 2). Also, the silica treated with vinyl groups settled down
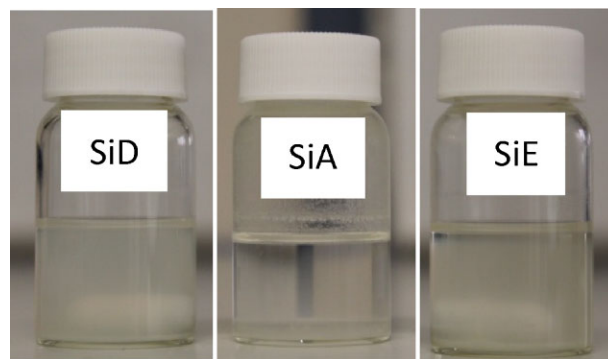

Figure 2. State of dispersion of silicas in vinyl acetate after 1 d at rest.

slightly faster than the non-treated silica. In order to confirm those results, the wettability of the silicas with the monomers was determined using the tensiometer. The contact angles obtained were: $\theta_{\text{SiE-VAc}} = 76°$, $\theta_{\text{SiD-VAc}} = 58.5°$ and $\theta_{\text{SiA-VAc}} = 82°$. Thus, it can be concluded that the non-treated silica (SiD) was the most compatible one with the monomer, followed by SiE and SiA which was the least compatible one.

3.2. Polymerization Experiments

In this study, six latexes containing 2.5 wt% and 5 wt% of each silica were synthesized in order to study the influence of the modifier onto the morphology and final properties of the material. Also, for the sake of comparison, an additional latex was synthesized without silica. The results of the synthesis are given in Table 3.

It can be observed that all the final latexes presented high or full final conversions. Table 3 presents the average particle diameters obtained by TEM analysis of the films and by SEM analysis of the dispersions for each run. Both techniques were in good agreement since similar particle diameters were measured. In addition, Table 3 shows that the presence of 2.5 wt% of SiD and SiE did not affect the diameter of particle and similar particle sizes were obtained for run 0 and for run 1D and run 1E. However, the increase of SiE concentrations up to 5 wt% led to a slight decrease of the measured diameter of particle. This shows that the silica affected the polymer particles aggregation during the polymerization. On the other hand, in the presence of 2.5 wt% of SiA, a larger diameter of particle was obtained no matter what the silica concentration was. This last observation could be explained by the observation of the TEM micrographs of the films casted from the different latexes.
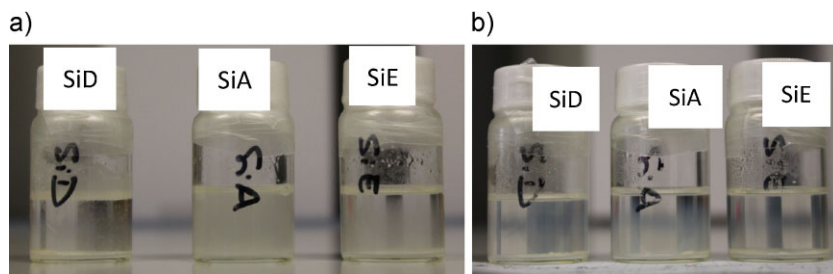

Figure 1. State of the dispersion of silicas in water after a) 5 h and b) 3 d at rest.

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Table 3. Final conversion of the latexes (X_{final}), diameter of particles (D_n) obtained by TEM of the films and by SEM of the dispersions and polydispersity index (Đ) for the experiments obtained with and without the different silicas.

Run	X_{final} (%)	D_n (nm) (TEM)	D_n (nm) (SEM)	Đ[a] (SEM)
run 0 (no silica)	100	745	789	1.1
run 1A (2.5 wt% SiA)	100	909	1015	1.2
run 1D (2.5 wt% SiD)	100	755	663	1.2
run 1E (2.5 wt% SiE)	100	734	727	1.4
run 2A (5 wt% SiA)	97	821	878	1.2
run 2D (5 wt% SiD)	98	631	702	1.2
run 2E (5 wt% SiE)	96	577	546	1.3

[a] $Đ = \frac{Dw}{Dn}$

Figure 3 and Figure 4 display the TEM micrographs of the films casted from run 1A (2.5 wt% SiA) and run 2A (5 wt% SiA) and the SEM micrographs of run 2A, respectively.

First, it can be observed that the particle size was in the micron size and the particle size distribution was rather broad, which is commonly observed when PVA is employed as protective colloid instead of standard surfactants.[7,32,33] Next, from Figure 3 it was clear that the silica particles (in black) were located outside the polymer particles and the SEM micrographs demonstrated that the silica particles were located at the aqueous phase-polymer particles interface (Figure 4). In addition, Figure 3 shows that the silica particles were mostly aggregated and that as the concentration of silica increased, the amount of aggregated silica increased too. SiA was treated with silicone and presented the lowest compatibility with the monomer and the best compatibility with water. Thus, the morphology of the hybrid latex agrees reasonably well with the theoretical predictions.[25] The larger average particle diameter measured for the hybrid latexes can be due to the reduced amount of PVA available to stabilize the polymer particles, that has been competitively adsorbed on the silica particle aggregates.

Figure 5 and Figure 6 present the TEM micrographs of the dispersion of run 2D and of the films obtained from the latexes containing 2.5 wt% SiD (run 1D) and 5 wt% SiD (run 2D), respectively. Figure 7 displays the SEM micrographs of run 2D.

It can be observed that the silica particles were located within the polymer particles (Figure 5) and no silica was observed at the surface or outside of the polymer particles (Figure 6 and Figure 7). The SEM micrographs also displayed a more spherical or smoother surfaces
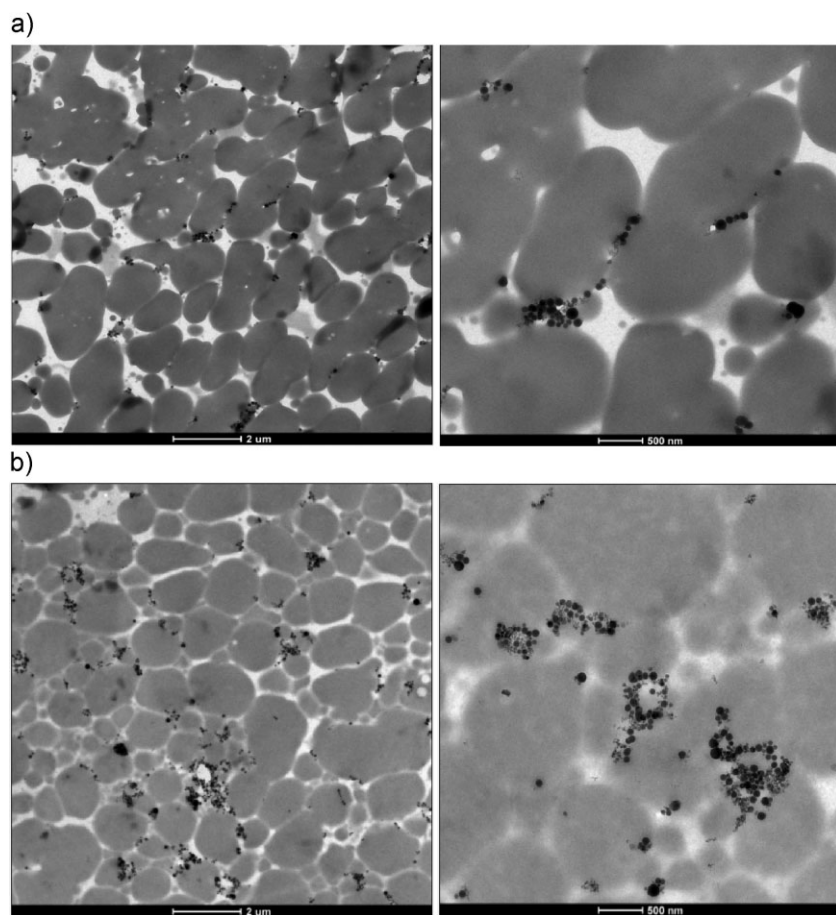

Figure 3. TEM micrographs of the films casted from the PVAc/silica hybrid latexes containing a) 2.5 wt% SiA (run 1A) and b) 5 wt% SiA (run 2A).
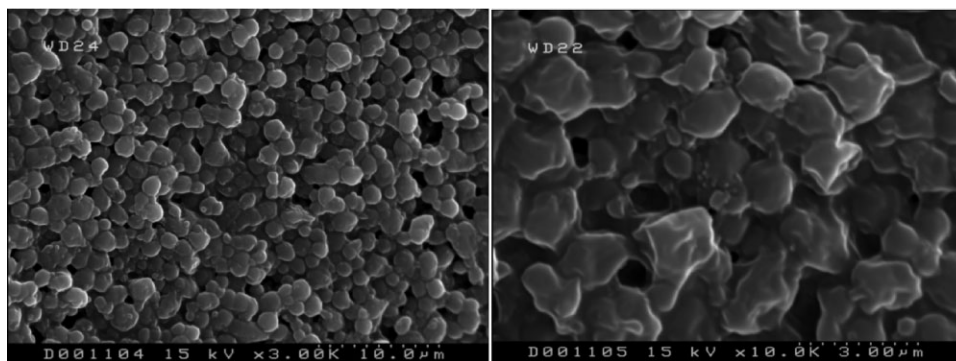
Figure 4. SEM micrographs of the film casted from the PVAc/silica hybrid latex containing 5 wt% SiA (run 2A).
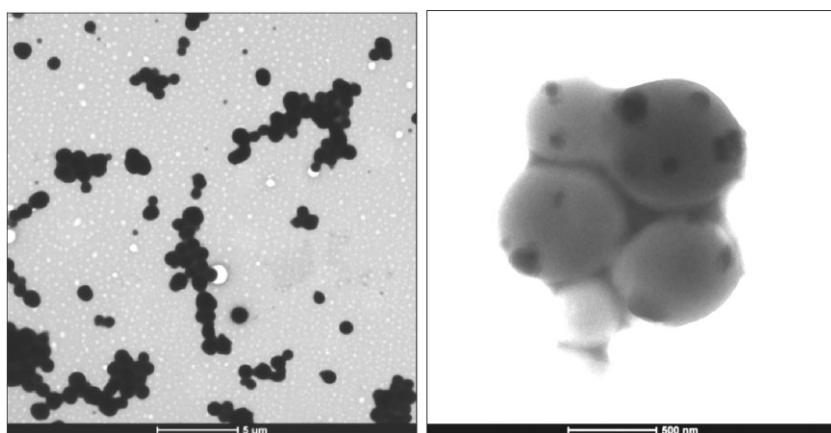

Figure 5. TEM micrographs of the final PVAc/silica hybrid latex containing 5 wt% of SiD (run 2D).

Figure 8 presents the TEM micrographs of the seed (Figure 8-a) and the final latex (Figure 8-b) obtained from run 2E and Figure 9 displays the TEM micrographs from the films obtained from the latexes containing 2.5 wt% SiE (run 1E) and 5 wt% SiE (run 2E). The TEM analysis of the seed dispersion (see Figure 8-a) shows the initial silica/polymer hybrid particles formed during the first step of the polymerization. At the end of the first step, hybrid particles of submicron size, where the silica particles were intimately associated with the polymer particles, were produced, as displayed in Figure 8-a. During the second step, the growing and aggregation, typically produced in the polymerization of PVAc/PVA, would take place, producing some hybrid particles containing silica and pure PVAc/PVA, as shown in Figure 8-b.

Figure 9 shows that the particle size distribution was pretty broad, showing particles above and below the micron size. Also, most of the silicas were aggregated and little silica was observed alone. Moreover, the silica was located inside or close to the polymer particles surface. This was confirmed by the SEM micrographs of run 2E (Figure 10) where no silica particles were observed at the surface of the polymer particles. Furthermore, the higher the amount of silica, the higher the amount of aggregates and empty particles (Figure 9-b). This was due to the poorer quality of the dispersion of such amount of silica in the monomer. The presence of the vinyl groups at the surface of the silica allowed it to react with the monomer during the polymerization and thus to embed the silica particles in the polymer particles.

Figure 11 displays the time evolution of water uptake measured for all hybrid latexes and the reference latex without silica (run 0). First, it has to be noticed that the
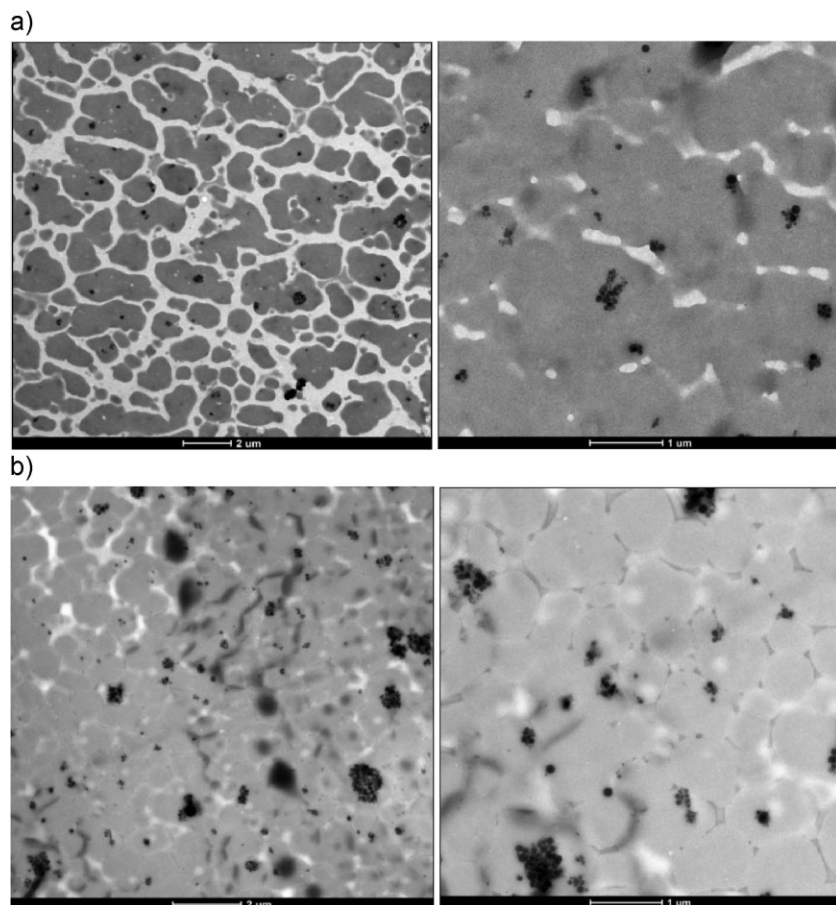
than for the particles produced with SiA. The silica dispersion in the film obtained from run 1D (Figure 6-a) was good and only small aggregates were observed. Nonetheless, as the silica content increased, more aggregates of silica were observed (see Figure 6-b) and some polymer particles were without silica. This is in agreement with the work carried out by McKenna and co-workers[27] who carried out the encapsulation of silicone treated silica in poly(methyl methacrylate) (PMMA) and poly(MMA-*co*-n-butyl acrylate) polymer particles. They observed by cryoTEM analysis that the silica nanoparticles were located inside the polymer particles and none were found outside the polymer particles. In addition, they showed that the distribution of the silica particles was heterogeneous and some polymer particles were also empty. As discussed above, SiD was the modified silica having the best compatibility with the monomer. This is consistent with the good dispersion of the silica in the polymer matrix as well as with the location of the silica inside the polymer particles.[25]

a)

b)

It was observed that the water uptake of the films containing the silicone treated silica was independent of the amount of silica present in the film and the water absorption of both runs 1A and 2A were very similar. The amount of water absorbed was higher than the one obtained for run 0 because of the hydrophilic character of the silicone treated silica that renders the film more hydrophilic. Then, Figure 11 shows that the film obtained from run 1D absorbed the same amount of water than the film without silica. However at higher concentration of silica, the film absorbed more water than the reference. This was surprising because this silica presented a high contact angle with water, which meant that it was not hydrophilic, and a good compatibility with the polymer since it was located inside the polymer particles. The presence of large silica aggregates might account for the higher water absorption. For the samples containing silica A and silica D, the water absorption decreased after some time. This might be due to desorption of salts and PVA due to the fast water absorption. The same behavior was observed in the presence of hydrophilic clay in acrylic films.[34] This also explained the fact that the films were very brittle after some time in water. Finally, it was observed that the films containing the silica coated with vinyl groups presented the lowest water uptake at the beginning of the experiment. After 5 h the sample obtained from run 2E absorbed more water than the other samples due to the salts desorption of these ones. The presence of vinyl groups at the surface of the silica allowed forming
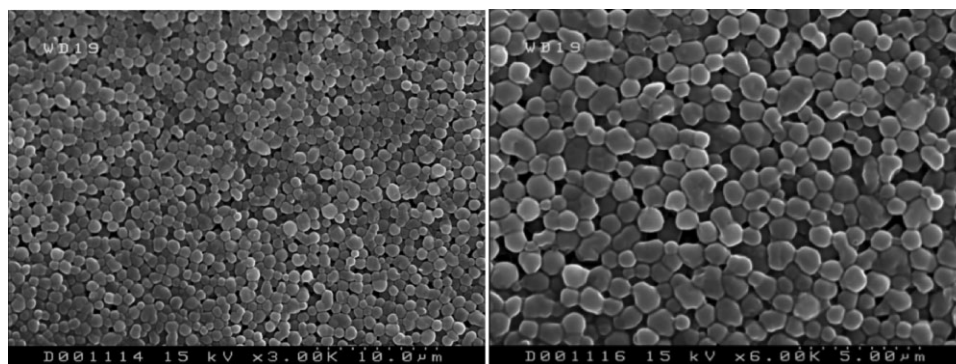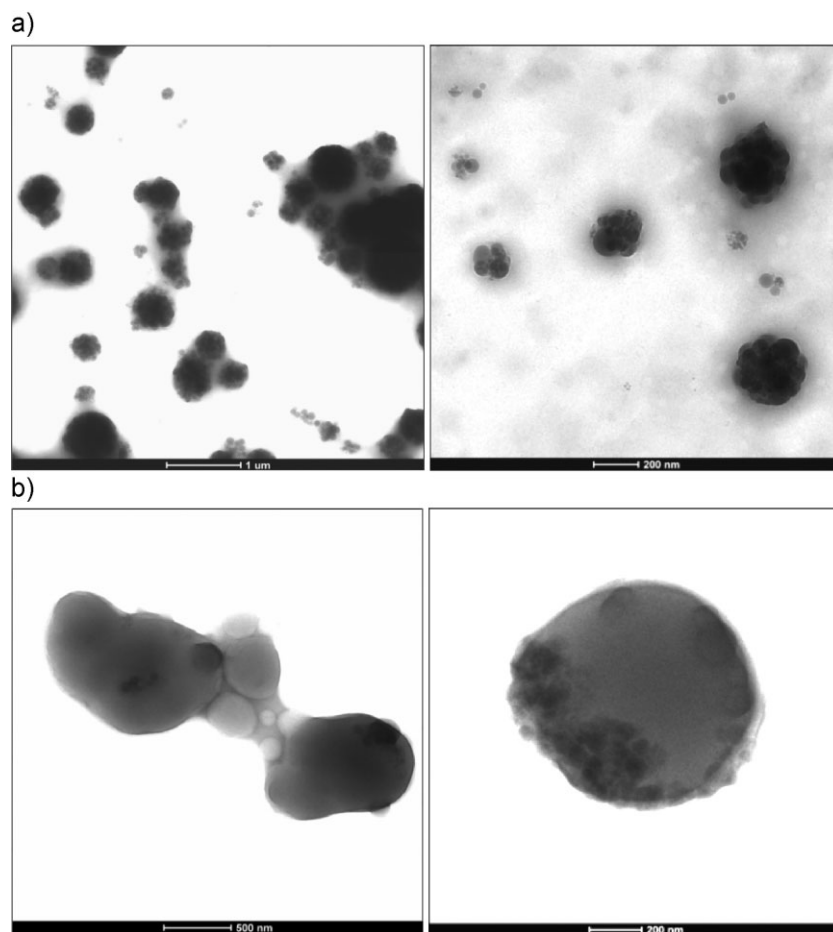
Figure 6. TEM micrographs of the films casted from the PVAc/silica hybrid latexes containing a) 2.5 wt% SiD (run 1D) and b) 5 wt% SiD (run 2D).

sample without clay completely decomposed after 5 h in water (approximately at values above 12 in the X-axis of Figure 11). Also, the samples obtained from run 1D, 1A, 2D and 2A were difficult to handle after the same time, whereas the samples obtained from run 1E and 2E were still hard.

Figure 7. SEM micrographs of the film obtained from the PVAc/silica hybrid latex containing 5 wt% SiD (run 2D).

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a)

b)

■ *Figure 8*. TEM micrographs of a) the seed and b) the final PVAc/silica hybrid latex containing 5 wt% SiE (run 2E).

chemical links between the polymer and the silica which provide high strength and a better resistance to water absorption, even at higher silica concentration.

Table 4 presents the results of the bond strength measurements of the adhesives corresponding to the EN204-D1 standard test. It can be mentioned that the failure was cohesive in all the cases. It can be observed that the presence of silica allowed improving the toughness of the adhesive and higher bond strengths were measured for the silica containing films compared to the blank one. Actually, all the samples containing silica presented bond strengths of around 10 MPa (for the film containing 5 wt% SiE) or higher than this value.

Figure 12 displays the results of the tensile strength measurements of the adhesive films corresponding to the EN204-D2 (Figure 12-a) and EN14257 (WATT'91) (Figure 12-b) standard tests carried out for run 1A, run 2A, run 2D and run 2E. The results were compared to the reference latex (run 0). It can be mentioned that the failure was cohesive in all these cases too.

The results of the EN204-D2 test show that, depending on the modifier and the amount of silica, the results vary notably. The addition of 2.5 wt% of silicone treated silica (SiA) did not noticeably increase the tensile strength. However when a higher amount of this silica was employed (5 wt% SiA), the tensile strength increased remarkably from 7 to 10 MPa. This result was not expected because the amount of aggregated silica was higher in this case. Possibly, the arrangement of the silicas around the polymer particles forms percolated networks that allow resisting to the stretching even after the storage in water. The presence of the non-treated silica (SiD) worsened the tensile strength obtained after storing the adhesive in water and re-drying it. This result was supported by the results of water uptake where it was observed that the water absorption was larger in the presence of this silica. In this case, the tensile strength achieved was even lower than the blank one due to the higher water absorption of the film; the water molecules adsorbed by the OH groups at the surface of the silica could act as plasticizer and decrease the stiffness of the film.
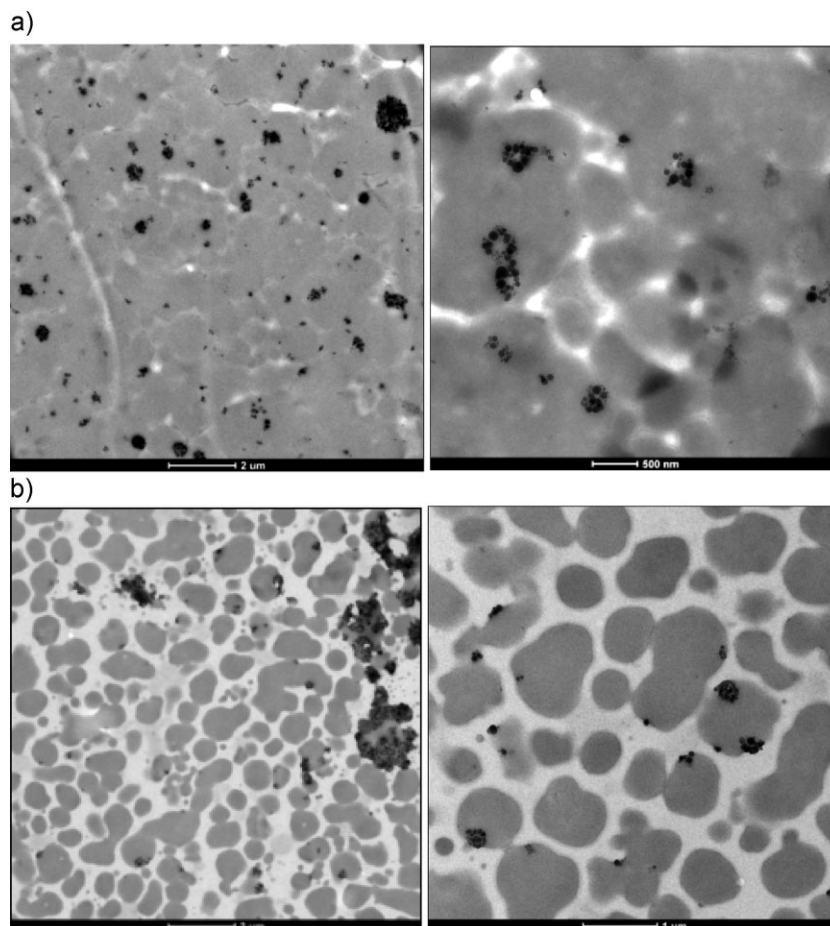
■ *Figure 9*. TEM micrographs of the films casted from the PVAc/silica hybrid latexes containing a) 2.5 wt% SiE (run 1E) and b) 5 wt% SiE (run 2E).

Finally, the addition of the silica coated with vinyl groups increased the tensile strength of the adhesive. This was due to the chemical bonds between the silica and the polymer matrix that render the material more resistant to the stretching.

The WATT'91 results reveal that the presence of silica increased the tensile strength in all cases. In the presence of SiA the results were independent on the amount of silica employed, and the increase was relatively small. This is explained by the fact that this silica did not present good interactions with the polymer and was clearly located outside the polymer particles. However, in the presence of SiD, the tensile strength increase was more pronounced, due to the better compatibility and the better dispersion of
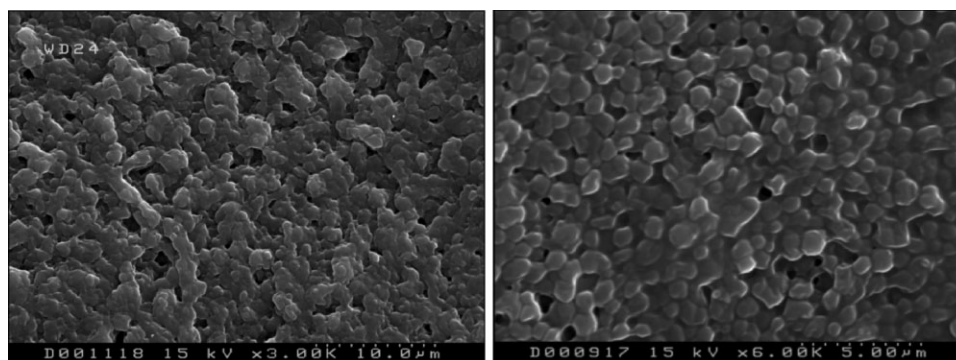

■ *Figure 10*. SEM micrographs of the film casted from the PVAc/silica hybrid latex containing 5 wt% SiE (run 2E).
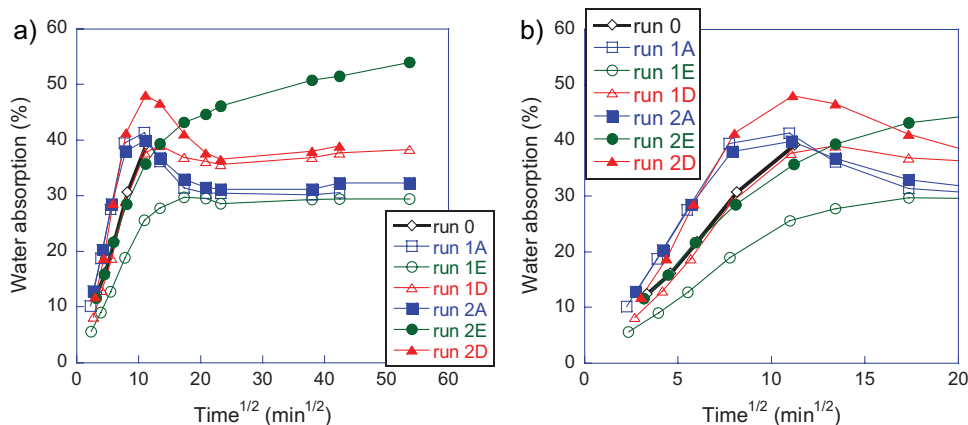
Figure 11. Results of the water uptake measurements obtained for all runs a) full analysis and b) initial part.

Table 4. Results of the bond strength measurements of the films casted from the latexes without silica (run 0), with 2.5 wt% and 5 wt% SiA (run 1A and run 2A, respectively), with 5 wt% SiD (run 2D) and 5 wt% SiE (run 2E) corresponding to the EN204-D1 standard test.

Run	Bond strength (N·mm^{-2})
run 0	8.2 +/− 0.6
run 1A	13 +/− 0.7
run 2A	12 +/− 1.2
run 2D	11.5 +/− 1
run 2E	9.7 +/− 0.9

the silica in the polymer matrix. Finally, the silica coated with vinyl groups presented again the best results, owed to the chemical bonds between the silica and the polymer matrix, allowing a better transfer of the stress from the polymer matrix to the inorganic particle.

It has to be highlighted that an adhesive with water resistance of class D2 according to PN-EN204 must have a minimum tensile strength of 8 MPa[35] and when fabricating window frame squares the minimum requirement regarding heat resistance is 7 MPa according to DIN EN14257 (WATT'91).[36] The latex that fulfilled this condition was run 2E. This result shows that forming covalent bonds between the polymer and the silica is the best way to improve the adhesive properties of the PVAc latexes. This is in accordance with one of our previous works on clays where better properties were obtained by using a reactive modifier for the surface covering of the clay.[37]

The tensile strength results for runs 1D and run 1E are not presented because the viscosity of the latexes was too large and when the samples were spread on the wood, they started to film form before they had adhered to the wood.

The glass transition temperature and the decomposition temperature (calculated from the maximum of the derivative weight loss versus temperature curve) obtained from the thermal gravimetric analyses of all the films were
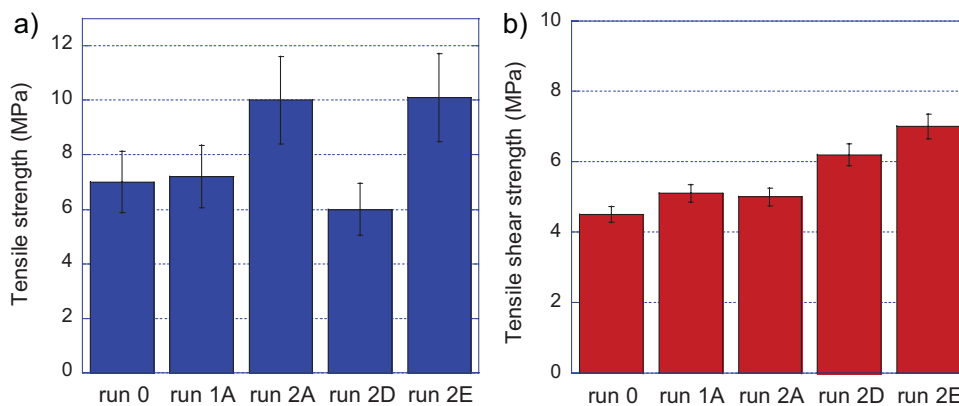

Figure 12. Results of the a) EN204-D2 and b) WATT'91 standard tests carried out for run 0 (0% silica), run 1A (2.5 wt% SiA), run 2A (5 wt% SiA), run 2D (5 wt% SiD) and run 2E (5 wt% SiE).

measured. It was observed that the presence of silica did affect neither the glass transition temperature nor the thermal stability of the adhesive.

4. Conclusion

In this work, the synthesis of hybrid PVAc/silica latexes stabilized by PVA was carried out using silica nanoparticles with different modifiers. Moreover, the morphology, mechanical properties, and water-uptake of the films were analyzed. The results show that the location of the silica particles with respect to the polymer particles varies according to their compatibility with the monomer and the aqueous phase. The most compatible silicas were located inside or close to the surface of the polymer particles while the least compatible one was localized at the polymer particles surface. Also, it was proven that the presence of vinyl groups at the silica surface, able to be covalently bonded with the polymer matrix, allowed increasing the tensile strength at the most demanding conditions of humidity and temperature. The results of water uptake showed that the silicone coated silica or the untreated silica increased the water absorption of the films while in the presence of the silica coated with vinyl groups, the water absorption was the lowest one and the film kept its hardness even after 48 h in water. This shows that the formation of covalent bonds between the silica and PVAc not only offers a general improvement of the strength of the polymer network at normal climate conditions, but is the key to substantially improve the adhesion of this PVAc based adhesive at increased moisture and temperature.

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