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Research Note

The effect of silica/zeolite-A nanocomposite on the polyvinyl acetate wood adhesive

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Abstract. The silica/zeolite-A nanocomposite additive was loaded at different amounts (1–4% wt) into the polyvinyl acetate matrix to improve its wood adhesive properties. The silica nanoparticles were prepared by calcination method using rice husk as the source material. X-ray diffraction analysis, Fourier Transform Infrared (FTIR) spectroscopy, and Scanning Electron Microscopy (SEM) techniques were used for the characterization of the nanocomposite. The thermal stability and adhesion properties of the modified polyvinyl acetate were evaluated by Thermo-Gravimetric Analysis (TGA) method and shear strength measurement of wood joints, respectively. According to the results, addition of silica/zeolite-A nanocomposite to the polyvinyl acetate in dry conditions and elevated temperatures enhanced the shear strength of wood joints. However, in wet conditions, improvement in shear strength resulting from adding silica/zeolite-A nanocomposite was lower than that in dry conditions. In addition, the thermal stability of polyvinyl acetate was affected by silica/zeolite-A nanocomposite. Polyvinyl acetate containing silica/zeolite-A nanocomposite additive exhibited better stability in water than the pristine polyvinyl acetate.

1. Introduction

Adhesives, especially wood adhesives, play a key role in manufacturing different products and essentials in a variety of applications in packaging, furniture production, and building decoration [1–3]. Wood adhesives are prepared by different polymers such as polyurethane, chitosan, lignin, starch, epoxy, phenol-formaldehyde, and Polyvinyl Acetate (PVAc) [4–9].

PVAc is a linear amorphous non-crystalline thermoplastic polymer which is widely used for bonding many porous materials such as woods [10,11]. Compared to other wood adhesives, PVAc enjoys several advantages including low cost, non-toxicity, and environmentally-friendly nature. Despite these advantages, PVAc has some drawbacks as well such as its low resistance against water, humidity, and elevated temperatures as well as its high tendency to creep [12,13]. These drawbacks are referred to as the weak polar interactions between PVAc chains and their partial hydrolysis during the polymerization. Formation of hydroxy and carboxy groups contributes to the poor performance of PVAc polymer as an adhesive [14]. Different modifications are applied to improve the performance of PVAc as the adhesive. Two modification approaches are conventional:

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Table 1. Typical properties of Polyvinyl acetate (PVAc).

Appearance	Semitransparent milky emulsion
pH	3–4
Dry matter (%)	$50 \pm 1\%$
Minimum film formation temperature	16–18°C
Solubility in water	Soluble in any proportion
Density	1.02–1.13 g/cm^3
Ionic nature	Non ionic
Viscosity	500–700 poise
Film appearance	Transparent and flexible

1. Copolymerization of vinyl acetate with more hydrophobic monomers;
2. Blending of PVAc with other adhesives or hardeners.

Nowadays, following the development of nanotechnology and production of nanoparticles, water and heat resistance of PVAc can be improved using low percentage of nanoparticles, thus facilitating the production of high-performance polymeric adhesives [15]. Nanoparticles such as TiO_2, SiO_2, Fe_2O_3, and Al_2O_3 are widely used as additives in polymer matrices to improve their properties. Silica nanoparticles are one of the most important nanoparticulate additives in the polymer industry. Application of silica nanoparticles in polymer matrices improves their physical, mechanical, and adhesion properties. Interactions among the functional groups of polymer and silica form the physical crosslinks between polymer chains, thus increasing the mechanical strength of the polymer [16–19]. Silica nanoparticles with high purity, high surface area, and low production cost can be obtained from rice husk [20]. Aluminosilicates as other inorganic rigid materials are widely used in polymer matrices to improve their properties [21]. Zeolites are hydrated aluminosilicates with a three-dimensional crystalline and porous structure consisting of AlO_4 and SiO_4 tetrahedral units [22,23]. The pores and channels of zeolites function as hosts for polymer chains and they cause strong interactions between the zeolite structure and polymer chains; therefore, the mechanical strength of the zeolite-contained polymer can be improved [24,25]. Zeolite-A is the most used aluminosilicate with the silicon-to-aluminum ratio of 1:1. Incorporation of zeolite-A into the polymer matrix improves the thermal, optical, electrical, mechanical, and catalytic properties of polymer composites [11].

The main objective of this study was to study the effect of silica nanoparticles and zeolite-A on the thermal, mechanical, and adhesion properties of PVAc. Silica nanoparticles can be obtained from rice husk through a simple calcination method which is used for the preparation of silica/zeolite-A nanocomposite additive.

2. Experimental

2.1. Reagents and materials

PVAc was purchased from Pars Polymer Company (Iran) in emulsion form. The rice husk and zeolite-A were purchased from a supplier in Rasht (Iran) and Kimia Khatam Company (Iran), respectively. HCl and H_2SO_4 were obtained from Merck Company (Germany). All reactants were of analytical grade and all solutions were prepared by distilled water. Typical properties of PVAc are presented in Table 1.

2.2. Preparation of silica nanoparticles

Rice husk was washed with distilled water to remove adhered soil and dust. The process of acid leaching was carried out by reflux boiling of rice husk in 3% (v/v) HCl aqueous solution at a ratio of 50 g rice husk in 1 L acid solution under stirring in a glass round-bottom flask at 100°C for 2 h to remove metal impurities. The mixture was filtered and the obtained husk was washed with distilled water and dried in a vacuum oven at 100°C overnight. Acid leaching of the dried rice husks was again performed by reflux boiling in 10% (v/v) H_2SO_4 aqueous solution in the abovementioned condition. Then, the washed and dried husk was calcinated in a furnace at 900°C for 5 h. Finally, the white ash containing 90–97% silica nanoparticles was obtained [26].

2.3. Modification of PVAc adhesive with silica/zeolite-A nanocomposite additive

The prepared silica nanoparticles were mixed with zeolite-A (weight ratio of 1:1) and dispersed in distilled water by sonication for 3 min at 30 W power followed by mixing on magnetic stirrer for 8 h. The mixture was filtered and dried at 50°C for 10 h. Different percentages of the obtained powder (1%, 2%, and 4% w/w) were dispersed in the distilled water by sonication for 2 min at 30 W power and were added to the PVAc emulsion; then, the blends were stirred for 30 min. After mixing, the materials were cast on a Teflon film and allowed to dry at room temperature for two weeks.

2.4. Structural and morphological characterization

2.4.1. X-Ray Diffraction (XRD) analysis

XRD patterns were used to characterize the structure of silica nanoparticles, zeolite-A and silica/zeolite-A nanocomposite. The patterns were recorded using a Siemens D500 X-ray diffractometer (Siemens AG, Karlsruhe, Germany) with Cu Kα radiation in the 2θ range of 2° to 70°.

2.4.2. Fourier transform infrared spectroscopy

The Fourier Transform Infrared (FTIR) spectra of silica nanoparticles, silica/zeolite-A nanocomposite, and PVAc adhesives were measured using a Bruker Tensor 27 spectrophotometer (Germany) in the wavenumber range of 400–4000 cm^{-1}.

2.4.3. Scanning Electron Microscopy (SEM)

Morphology of silica, silica/zeolite-A nanocomposite, and its components as well as the surface morphology of the modified PVAc adhesive were studied using MIRA3 FEG-SEM (Tescan, Czech) scanning electron microscope. Size distribution of silica nanoparticles was measured using the manual microstructure distance measurement software (Nahamin Pardazan Asia Co, Iran).

2.5. Shear strength analysis

The silica/zeolite-A nanocomposite-modified PVAc was employed to bind wood joints. The effect of adding the silica/zeolite-A nanocomposite on the bonding strength of PVAc was studied through block shear tests. Maple wood prepared according to American Society for Testing and Materials (ASTM) D1002. 0.3 ml adhesive was applied to the surface of the wood and the samples were pressed under 2 kN force. Before testing, the glued samples were conditioned to room temperature for two weeks. The shear strength of wood joints was measured in three conditions: including dry (room temperature) condition, wet condition, and an elevated temperature (100°C). In wet conditions, the samples were immersed in water for 3 h; then, they were directly taken out of the water and the excess water was wiped off from the samples. Prepared according to ASTM D2295, the samples in wet, dry, and elevated temperature conditions were of the same size. The block shear tests were carried out by Instron 4465 (USA).

2.6. Thermo-Gravimetric Analysis (TGA)

TGA of the samples was carried out using 13–15 mg of samples on a TGA/DSC-1 and Mettler Toledo instrument while heating them from 25 to 740°C at a heating rate of 10°C.min^{-1}. In order to avoid unwanted oxidation, TGA measurements were performed under high-quality nitrogen atmosphere.

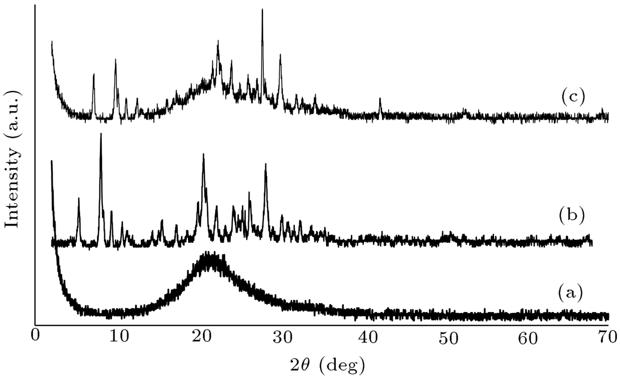


Figure 1. X-Ray Diffraction (XRD) patterns of (a) silica nanoparticles, (b) zeolite-A, and (c) silica/zeolite-A 1:1.

2.7. Investigation of water resistance

In order to evaluate the resistance of adhesives against water, the wood samples adhered by silica/zeolite-A nanocomposite-modified PVAc adhesives were immersed in distilled water, and separation of the woods from each other was visually investigated.

3. Results and discussion

3.1. XRD analysis

To investigate and approve the structure of the prepared silica/zeolite-A nanocomposite, XRD patterns within $2\theta = 2° - 70°$ were considered. Figure 1 shows the XRD patterns of silica nanoparticles, zeolite-A, and silica/zeolite-A nanocomposite. As shown in Figure 1(a), the main broad peak of silica nanoparticles appeared at $2\theta = 22.5°$, which is indicative of the amorphous structure of silica with low crystallinity [11]. The characteristic peaks of zeolite-A emerged at $2\theta = 7.36°$, 10.06°, 22.57°, and 30.15°, as shown in Figure 1(b) [27]. According to the XRD patterns of the silica/zeolite-A nanocomposite presented in Figure 1(c), silica/zeolite-A nanocomposite has both profiles, as observed in the XRD patterns of pristine zeolite-A and silica nanoparticles. This indicates that the silica/zeolite-A nanocomposite contains both zeolite-A and silica nanoparticles; therefore, the amorphous structure of silica nanoparticles and crystalline structure of zeolite-A would not change after composition. Moreover, the main peaks of zeolite-A were shifted to higher 2θ values after composition. Then, the role of composition of silica molecules and zeolite-A in reducing the spaces between the planes in atomic lattice of zeolite-A was observed.

3.2. FTIR studies

The pristine silica nanoparticles, silica/zeolite-A nanocomposite, and PVAc adhesive modified by silica/zeolite-A nanocomposite additive were characterized using FTIR technique. In FTIR spectra of silica nanoparticles (Figure 2(a)), the main peaks appearing at wavenumbers of 460 cm^{-1}, 784 cm^{-1}, and 1085 cm^{-1} are related to the angular deformation and asymmetric stretching vibrations of Si–O–Si bonds, respectively [20]. Figure 2(b) shows the FTIR spectra of silica/zeolite-A nanocomposite in which the characteristic peaks at 466 cm^{-1} and 794 cm^{-1} are attributed to Si–O–Si bond of silica nanoparticles, and the broad peak at 1032 cm^{-1} is related to the overlap between the Si–O–Si bond of silica and asymmetric stretching vibrations of bridge bonds of Si–O (Si) and Si–O (Al) in zeolite-A [27,28]. Delocalization of characteristic FTIR peaks of silica nanoparticles in silica/zeolite-A nanocomposite with respect to that of pristine SiO_2 indicates the existence of physicochemical interactions between SiO_2 and zeolite-A in nanocomposite structure. Figure 3(a) illustrates the FTIR spectra of unmodified PVAc. The characteristic peaks of FTIR spectra of the unmodified commercial-grade PVAc at 1630 cm^{-1} and 1460 cm^{-1} are related to the stretching vibrations of carbonyl bond and etheric C–O bond of PVAc, respectively. The broad peak at 3445 cm^{-1} is attributed to O–H bond stretching vibrations. Figure 3(b) shows the FTIR spectra of the modified PVAc with 1% silica/zeolite-A nanocomposite. This curve exhibits the peaks related to the unmodified PVAc resin and silica/zeolite-A nanocomposite with some delocalization of the main peaks, which is also indicative of the presence of some interaction between silica/zeolite-A nanocomposite and polymer. The peaks appearing at 470 cm^{-1} and 815 cm^{-1} are related to Si–O–Si bonds of silica in silica/zeolite-A nanocomposite, and those at 1632 cm^{-1} and 3425 cm^{-1} are related to PVAc resin.

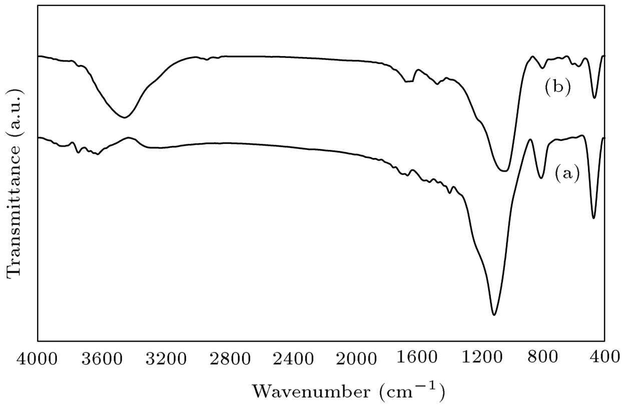


Figure 2. Fourier Transform Infrared (FTIR) spectra of (a) silica, and (b) silica/zeolite-A nanocomposite.

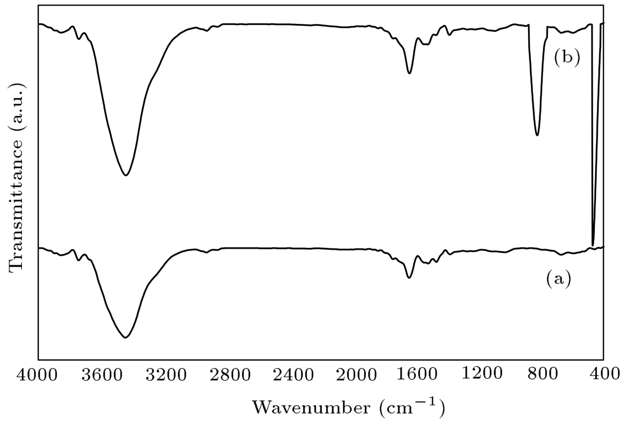


Figure 3. Fourier Transform Infrared (FTIR) spectra of (a) unmodified Polyvinyl acetate (PVAc) and (b) modified polyvinyl acetate with silica/zeolite-A.

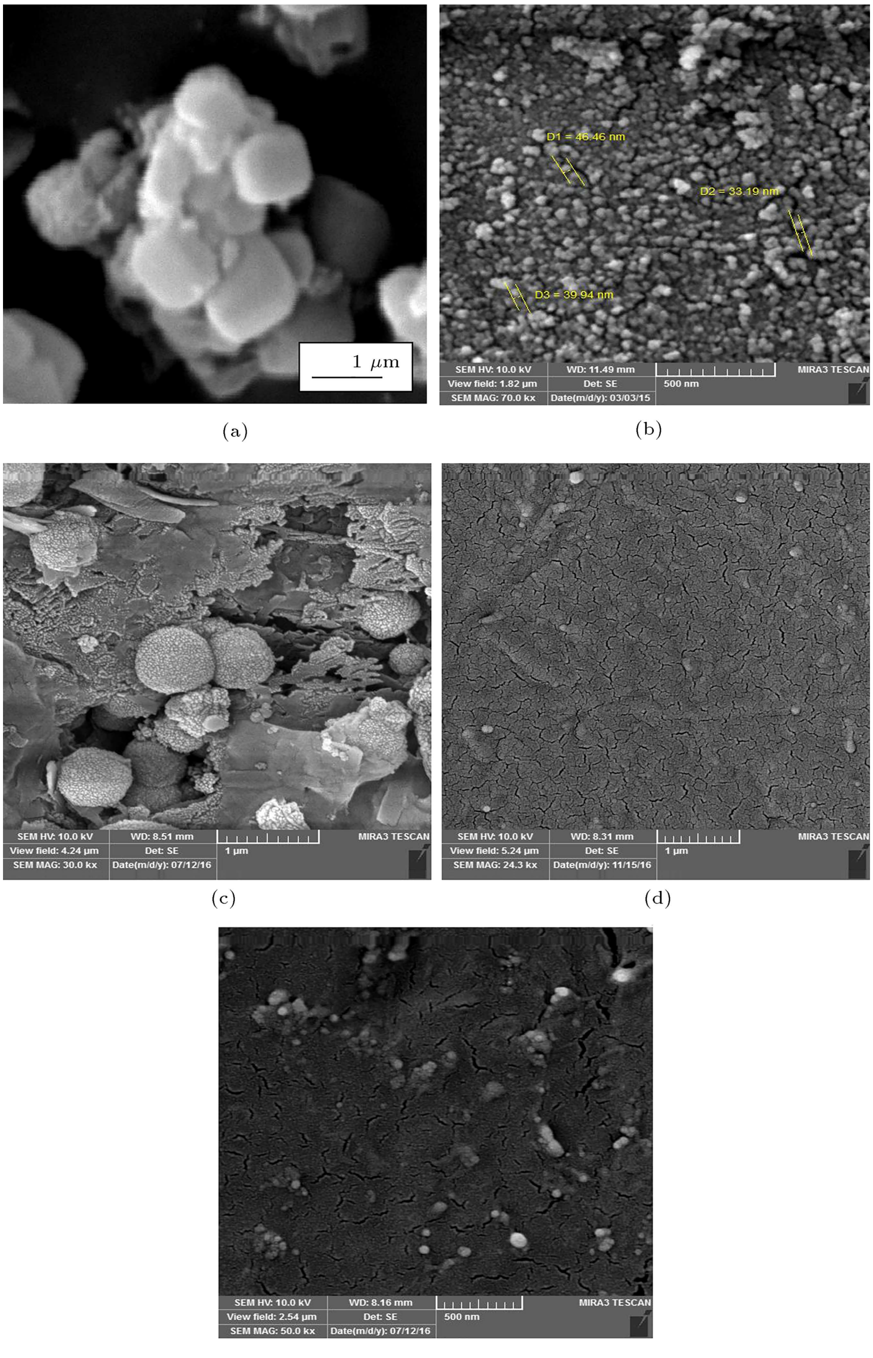
3.3. Morphological analysis

SEM technique was employed to study the surface morphology of zeolite-A, silica nanoparticles, silica/zeolite nanocomposite, and PVAc modified by silica/zeolite-A nanocomposite. Figure 4(a) shows the SEM image of zeolite-A with micron-sized particles. Figure 4(b) illustrates the SEM image of silica nanoparticles. As shown in Figure 4(c), the SEM image of silica/zeolite-A nanocomposite confirmed the presence of silica nanoparticles on the surface of zeolite-A. The SEM micrographs of the PVAc modified by 1% and 4% silica/zeolite-A nanocomposite are presented in Figure 4(d) and (e), respectively. Both of the modified PVAc adhesives show the good dispersion of the additive in the PVAc matrix. Further, the PVAc modified by 1% additive has a smoother surface and lower additive aggregation than the 4% additive contained one.

3.4. Bond strength

3.4.1. Dry state

Mechanical properties of the PVAc adhesive modified by silica/zeolite-A nanocomposite were identified to determine how they were influenced by the nanocomposite additive. The values of bond strength measured on block shear samples are given in Figure 5. Addition of silica/zeolite-A nanocomposite to the PVAc significantly increased the shear strength in the dry condition. The intermolecular forces between the silica/zeolite-A nanocomposite additive and PVAc matrix may enhance the shear strength of the modified PVAc adhesive. In other words, improvement in the shear strength could be a result of the interactions among the functional groups of PVAc and hydroxyl groups of silica nanoparticles, thus leading to physical crosslinking with polymer chains [29]. Moreover, adding a high percentage of silica/zeolite-A nanocomposite (> 5%) would lead to wood failure under approximately 20 MPa force, thus proving the positive effect of nanoparticles on the bonding strength of glue line. Therefore, silica/zeolite-A nanocomposite could make



(a) (b)

(c) (d)

(e)

Figure 4. FESEM micrographs of (a) zeolite-A, (b) silica nanoparticles, (c) silica/zeolite-A 1:1, (d) modified polyvinyl acetat with 1% silica/zeolite-A, and (e) modified polyvinyl acetat with 4% silica/zeolite-A.

the glue line of PVAc even stronger than the wood, causing a failure in the wood rather than in the glue line [12]. The presence of nanoparticles in the polymer matrix can significantly increase the mechanical properties of the polymer by filling up the weak region in the adhesive. In addition, good dispersion of silica/zeolite-A nanocomposite into the polymer matrix, as shown in Figure 4, caused an increase in the interactions at the polymer-nanocomposite interfaces [13,30].

3.4.2. Wet state

Figure 6 shows the effect of adding the silica/zeolite-A nanocomposite additive to PVAc matrix on the shear strength of wood joints after three hours of immersion in water. Pristine PVAc showed weak resistance after exposure to water. Adding nanocomposite additive to the PVAc matrix caused a slight increase in the shear strength of wood joints. PVAc containing a 2% silica/zeolite-A nanocomposite additive exhibited

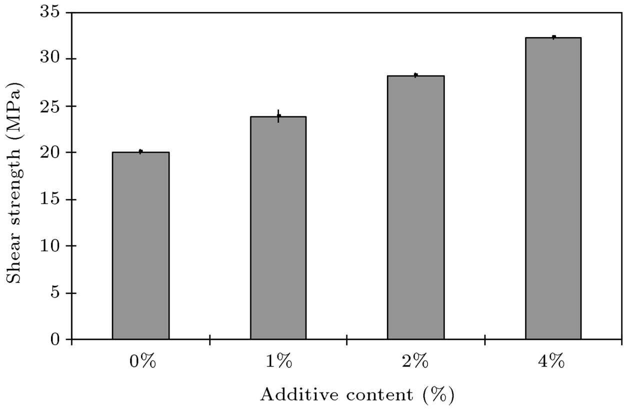


Figure 5. Shear strength of joints bonded of Polyvinyl acetate (PVAc) modified by silica/zeolite-A nanocomposites.

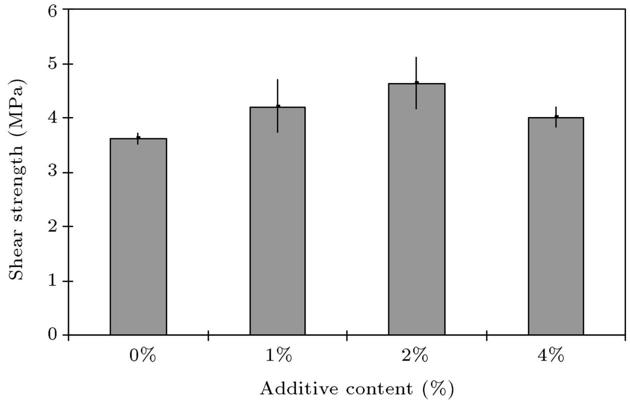


Figure 6. Shear strength of joints bonded of Polyvinyl acetate (PVAc) modified by silica/zeolite-A nanocomposites after keeping in water for three hours.

the highest shear strength in aqueous media. Higher amount of additive caused a decrease in the shear strength value of the adhesive due to the hydrophilic behavior of Zeolite-A, obtained from microporosity and capillary effect of zeolite-A aluminosilicate [31]. The optimum percentage of the additive (2%) leads to a 27% increase in the shear strength of the modified PVAc with respect to that of the unmodified PVAc.

3.4.3. Elevated temperatures

Shear strength values of both modified and unmodified PVAc at 100°C are presented in Figure 7. Loading the silica/zeolite-A nanocomposite into the PVAc matrix had a positive effect on the matrix adhesive performance at elevated temperatures (100°C). Upon increasing the silica/zeolite-A nanocomposite content of PVAc matrix, the shear strength of the adhesive-contained wood joints increased. The shear strength value of PVAc containing 4% wt additive was 84% higher than that of pristine PVAc at elevated temperatures (100°C). The enhanced resistance against elevated temperatures could be related to the presence of silica nanoparticles in nanocomposite additives. Characterized by high thermal insulation, silica nanoparticles are homogeneously distributed throughout the PVAc matrix. Small size (< 50 nm) and huge relative surface area of silica nanoparticles make strong interactions among the polymer chains.

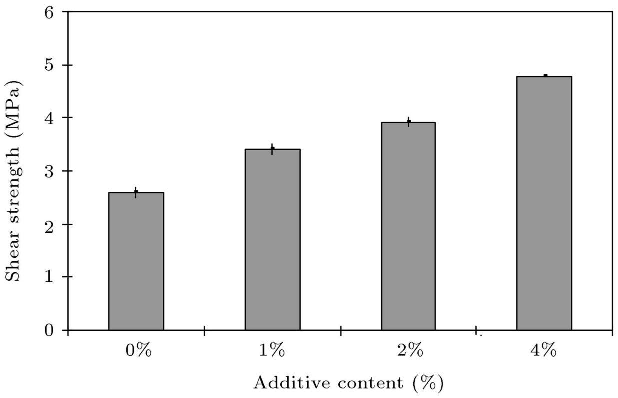


Figure 7. Shear strength of joints bonded of Polyvinyl acetate (PVAc) modified by silica/zeolite-A nanocomposites at elevated temperatures (100°C).

3.5. Thermal properties

The thermal stability of both unmodified and modified PVAc was estimated through Thermo-Gravimetric Analysis (TGA). Figure 8 shows the mass loss of pristine PVAc and silica/zeolite-A nanocomposite containing PVAc adhesive. The direction of changes in the thermal stability depends on temperature [32]. According to Figure 8, there is no weight loss platform in temperature values under 300°C which approves the high stability of the prepared adhesives in this range of temperatures as well as the absence of any water or other impurities in the adhesive formulation. Based on the results from TGA diagram, it can be concluded that the thermal stability of both modified and unmodified PVAc is quite similar.

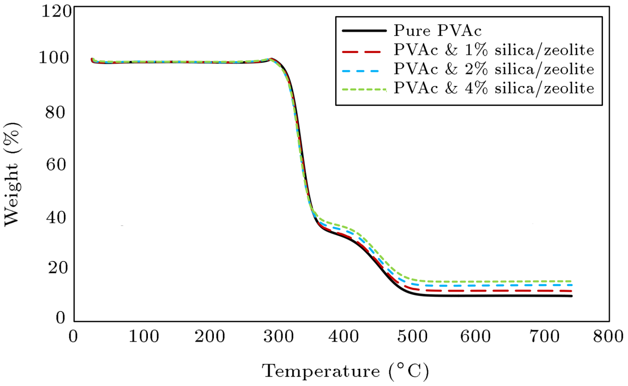


Figure 8. Thermal stability of both unmodified and modified Polyvinyl acetate (PVAc) with silica/zeolite-A nanocomposite.

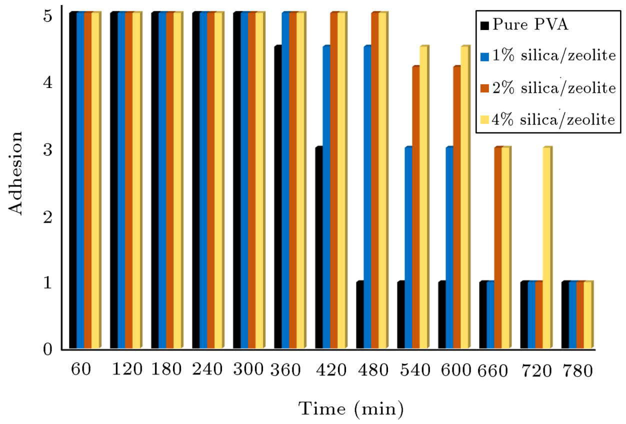


Figure 9. Water resistance of both unmodified and modified Polyvinyl acetate (PVAc) with silica/zeolite-A nanocomposite.

3.6. Water resistance

Figure 9 shows the results of water resistance tests for pure PVAc and PVAc adhesives modified by different weight percentages (1–4% wt) of silica/zeolite-A nanocomposite. Y-axis shows the adhesiveness of two pieces of wood attached to each other by adhesive samples in distilled water as 5: complete adhesion, 4: few separations, 3: medium, 2: much, and 1: separated. The pieces of wood attached to each other by pristine PVAc were completely separated after seven hours of soaking in the distilled water. Further, Figure 9 shows the water resistance of the PVAc containing silica/zeolite-A nanocomposite additive. As shown in this figure, the PVAc containing silica/zeolite-A nanocomposites can be more water resistant than pristine PVAc. Upon increasing the percentage of the nanocomposite additive, water resistivity would increase and complete separation of wood joints would be deferred.

4. Conclusion

In this study, the effect of silica/zeolite-A nanocomposite on promoting the properties of Polyvinyl acetate (PVAc) as a wood adhesive was investigated. The nanocomposite additive could enhance the mechanical performance of PVAc glue line in dry and wet states and at elevated temperatures. The shear strength of wood joints was improved as silica/zeolite-A nanocomposite was inserted to PVAc. Thermal stability of the modified PVAc was similar to that of the unmodified PVAc. Nanocomposite additive containing PVAc exhibited better stability in water. Moreover, SEM analyses indicated that at 1% and 4% loadings, silica/zeolite-A nanocomposites were dispersed well in the matrix. Furthermore, the results of X-Ray Diffraction (XRD) and FTIR analyses confirmed the preparation of the silica/zeolite-A nanocomposite.

Acknowledgments

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