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THE INFLUENCE OF THE MODIFICATION OF THE MONTMORILLONITE KSF AND K10 ON THE HYDROLYTIC STABILITY OF UF COMPOSITES

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Abstract

In this work, the hydrolytic stability of composites based on the urea-formaldehyde resin (UF) and montmorillonite-MMT (K10 and KSF) as a formaldehyde (FA) scavenger was investigated. K10 and KSF were activated by sodium chloride (NaCl) for the purpose of modified Na-MMT. The degree of activation was determined using specific surface measurement by Sir's method. Evaluation of MMT activation was performed by determining free and liberated FA after acid hydrolysis of synthesized crosslinked UF/MMT composites. The specific surface area (SSA) of montmorillonite KSF and K10 calculated by the Sear's method are 270 m^2/g and 119 m^2/g, respectively. After modification of MMT, the SSA of Na-KSF is 48.6 m^2/g and 71 m^2/g for Na-K10. The amount of free formaldehyde is 0.6% for both UF/K10 and UF/Na-K10 and 0.4% and 0.12% for UF/KSF and UF/Na-KSF composites. The content of liberated FA are 2.1% and 2.2% for UF/K10 and UF/Na-K10 composites and 1.2% and 2.3% for UF/KSF and UF/Na-KSF composites, respectively. It was concluded that the UF composite with modified KSF has a smaller content of free formaldehyde (0.2%) compared to UF composites with pure and modified K10. The UF composite with pure KSF has the highest resistance to acid hydrolysis and the lowest released FA percent.

Keywords: Montmorillonite, Urea-formaldehyde resin, Formaldehyde, Hydrolytic stability

INTRODUCTION

Chemically, UF adhesives are duromers. They belong to the group of thermosetting aminoplastic resins, formed by polycondensation reactions of urea and formaldehyde (FA) (Samaržija-Jovanović et al. 2020, p. 3575). The biggest disadvantage of using UF resins is the emission of FA from the panels and low resistance to moisture. This leads to the hydrolytic degradation and subsequent emission of FA. FA emission can be affected by external factors such as temperature, humidity, air movement over the panel surfaces, changes in air velocity and local formaldehyde concentrations in the space where the material is located; as well as internal factors, type of wood and percentage of moisture in it, types and chemical composition of used binders, additives that are added, surface treatment, etc.

The reversibility of methylation reactions is one of the most important characteristics of UF adhesives and is responsible for its poor resistance to hydrolytic degradation in conditions of increased humidity and temperature, and at the same time affects the emission of FA from the finished product.

The World Health Organization (WHO) refers to FA as a compound that can be carcinogenic, while in 2004, the International Agency for Research on Cancer (IARC) included FA in the group of substances that have been proven to be carcinogenic to humans, with emissions higher than 5.65 ppm. Its harmful effect is reflected on the respiratory organs, where it can cause irritation in the case of lower concentrations, but it can leave permanent consequences and cause chronic diseases in the case of high concentrations. The first reaction to formaldehyde is irritation of the respiratory organs, while the other symptoms that occur are: nausea, headache, dizziness, abdominal pain, irritation in the oral cavity. When it comes to the carcinogenicity of formaldehyde, data showing this is very scarce. Most studies state that it is cancerogenic after prolonged exposure to it, especially to workers in the wood industry (production of boards and formaldehyde adhesives), and to workers in the medical industry where formalin is used (Kalinić, 1995, p. 259).

Modified clays are increasingly being used for the reinforcement of polymeric materials (El Achaby, 2013, p. 310) and as scavengers of formaldehyde in cross-linked UF composites (Samaržija-Jovanović et al. 2020, p. 3575). Clays, such as montmotillonite (MMT), are used to modify the characteristics of certain polymers (Krupskaya et al., 2017, p. 49). Montmorillonite (MMT) is an aluminum phyllosilicate with hydroxyl groups and water. It may contain other cations (calcium, magnesium, sodium, iron). Out of all the phyllosilicates, MMT is the most promising due to its natural abundance on a high scale (Ke and Stroeve, 2005). MMT is a derivative of pyrophyllite. The difference between the crystal structure of MMT and pyrophyllite is that the latter is neutral while the former has deposits due to isomorphic substitution. The high value of cation exchange capacity (CEC) is one of the properties of MMT that defines it as a good adsorbent. It is known that MMT has two types of charges. In addition, negative charge originates from the mentioned isomorphic substitution (permanent charge) which does not depend on the pH value and contributes to 80% of the CEC value, there is also a variable edge charge which makes up the other 20% of the total CEC value.

The goal of this work was to examine the effect of modification of the MMT on hydrolytic stability modified UF/MMT composites.

MATERIAL AND METHODS

Materials

Urea (Alkaloid-Skopje, Republic of North Macedonia); 35% Formaldehyde Unis-Goražde, Bosnia and Herzegovina); Montmorillonite-K10 and KSF (Sigma-Aldrich Chemistry, Germany) with specific surface area (SSA) of 220-270 m^2/g and 20-40 m^2/g were used. All the other materials and solvents used for analytical methods were of analytical grade.

Modification of montmorillonite

Activation of MMT was performed in such a way that 11.66 g of MMT (K10 and KSF) were treated with 250 cm^3 of 1M NaCl solution with constant stirring for 24 h, after which Na-MMT was washed with deionized water until negative reaction to chloride ions. After removal of the chlorides, the clay was dried in an oven at 100°C (Ainurofiq et al., 2014, p. 131). The activated samples are referred to as Na-K10 and Na-KSF later in text.

Characterization of the MMTand modified MMT

The SSA of adsorbents was determined using the Sear's method (Sears, 1956, p. 1981). The volume (V) required to raise the pH from 4 to 9 is recorded and the specific surface area was calculated by the **Eq. (1)**:

$$SSA\ (m^2/g) = 32 \cdot V - 25 \tag{1}$$

Synthesis of modified UF/MMT composites

Synthesis of UF/K10 composites with molar ratio of UF/U = 0.8 with pure and modified MMT takes place using the procedure (Jovanović et al. 2015, p. 59715).

Determination of the hydrolityc stability of modified UF/K10 composites

The percentage of free and liberated FA was determined by the sulphite method (Walker, 1964). The percentage of free FA content was calculated from **Eq. (5)**:

$$FA(\%) = \frac{V \cdot c \cdot E \cdot 100}{1000 \cdot a} \quad (5)$$

where V is the voume of HCl (cm^3), c is the contrentration of HCl ($moldm^{-3}$), E, is the equivalent weight of FA, and a is the weight of the samples (g).

The synthesized UF composites were subjected to hydrolysis according to the procedure (Samaržija-Jovanović et al. 2011, p. 1159).

RESULTS AND DISCUSSION

FA emitted from UF resins can come from several sources: (a) unreacted FA resin; (b) FA which is released when the ether bonds are converted to methylene bonds; and (c) FA which is released due to hydrolytic degradation of weak bonds in the crosslinked resin. All these factors form the sources and generative processes for longterm FA emission. Decreasing the content of FA in the formulation of such resins decreases the amount of terminal CH_2OH groups, which are surely more reactive than the methylene ones. However, a lower F/U molar ratio allows producing a crystalline framework, which reasonably hinders the penetration of water in the bulk of the material, thus making the reactive moieties less available for hydrolysis (Park and Causin, 2013, p. 532).

Since the SSA is inversely proportional to the particle size, the smaller particles will have a larger specific surface area and the other way around. SSA has several consequences, and that means there is a possibility of the adsorption and absorption of various substances. The values of specific surface area of KSF and K10 determined by the Sear's method are 269.5 m^2/g and 119 m^2/g, respectively, and is shown in Figure 1.

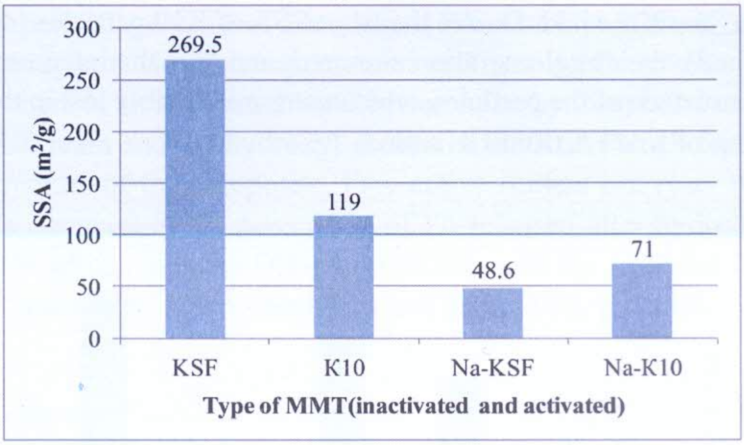

Figure 1. The SSA of pure and activated MMT determined by Sear's method.

This is intriguing because the determined values of the specific surface area by the BET method are 20-40 m^2/g for KSF, and 220-270 m^2/g for K10. One of the possible causes for such differences in the obtained results is the possible agglomeration of K10 particles. BET method measures the specific surface area of a dry solid which is available for the adsorption of N_2. Sear's method gives the number of silanol groups accessible for chemical reactions in an aqueous environment (Yuan , 2017, p. 8724). After modification of MMT, the values of the specific surface area of Na-KSF and Na-K10 are 48.6 m^2/g and 71 m^2/g.

Free and liberated FA of UF/KSF and UF/K10 composites

The hydrolysis of hardened resins is considered to be the main factor that influences the long-term emission of formaldehyde from the panel. The hydrolysis of UF resins depends on their chemical structure and the degree of crosslinking. The presence of crystallyne regions in hardened UF resins affects the degree of hydrolysis of cured UF resins (Stuligross and Kousky, 1985, p. 281). That is, UF resins with a lower FA/U mole ratio will be less susceptible to hydrolysis than those with a higher FA/U mole ratio. Since the FA/U ratio is low and is 0.8, it is not expected of the resin to have a branched structure, which means that it has fewer terminal methylol groups, i.e. there are more stable methylene groups (Lubis and Park,. 2018 p.759).

Figures 2 and 3 shows the percentage of free and liberated FA from pure UF resin, modified UF resin with unmodified MMT, and UF/Na-KSF and UF/Na-K10 composites. The lowest percentages of free FA and liberated FA of 0.12% and 1.2% are shown by the UF/Na-/KSF and UF/KSF composite, respectively.

KSF has a higher SSA (269.5 m^2/g) compared to K10 (119 m^2/g) which is determined by the Sear's method. Due to the large SSA of K10 particles (determined by BET method), their agglomeration occurred, and thus the interconnection of groups on the surface of the particles, which were irreversibly lost in this process for the binding of free FA from UF resin.

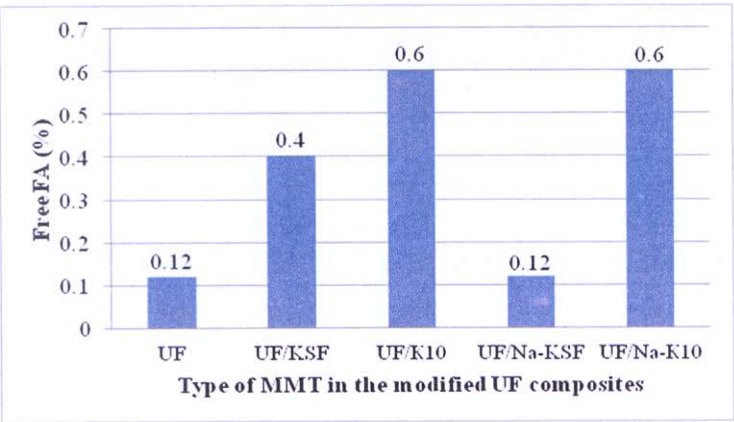

Figure 2. Content (%) of free FA from pure UF resin, UF resin with unmodified MMT and modified UF/MMT composites with activated MMT composites

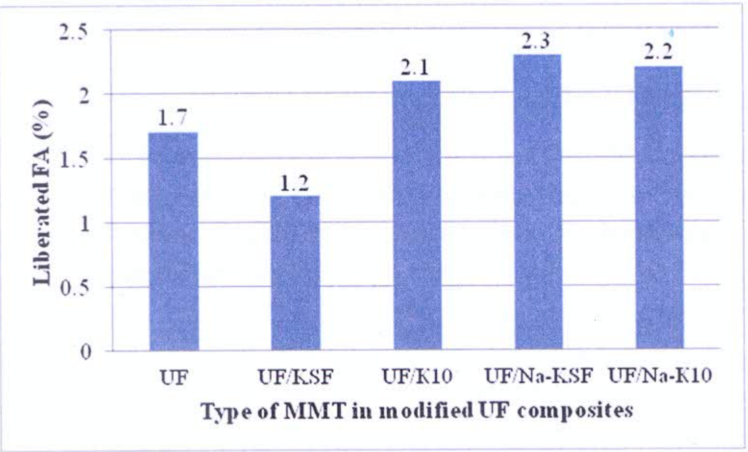

Figure 3. Content (%) of liberated FA from pure UF resin, UF resin with unmodified MMT and modified UF/MMT composites with activated MMT composite

The UF/KSF composite shows a higher resistance to acid hydrolysis, due to the lower percentage value of the released FA, which is 1.2%. It is considered that in this sample, at elevated temperatures and in an acidic environment during hydrolysis, there is an additional bond between the hydroxyl and methylol groups of the UF resin and the hydroxyl groups of the KSF, which further strengthens the structure of the composite. Free active centers can react with FA and thus cause a decrease in the percentage of FA released after hydrolysis. In this way, the KSF which contains OH-groups reacts with the liberated FA from UF resins as a "scavenger" of FA (Abdullah and Park, 2010, p. 3181).

CONCLUSION

Based on the experimental data, the following can be concluded:

- The lowest content of free formaldehyde is in the modified UF / Na-KSF composite and is 0.12%.
- UF / KSF composite has the highest resistance to acid hydrolysis and the content of released formaldehyde is equal to 1.2%.

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