EPOXY GLUES FILLED BY SYNTHETIC WOLLASTONITE BASED ON THE RICE HUSK ASH

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Abstract

By the method of differential scanning calorimetry (DSC), there was studied the influence of naturally occurring Miwoll 10-97 and synthetic wollastonite obtained from calcium carbonate and rice husk ash, the components' ratio 1.2:1, on the process of epoxy resin ED-20 curing by aminophenol AF-2. The experiment showed the presence on the DSC diagrams of both based epoxy compositions and those containing wollastonite, two exothermic peaks. The first peak was manifested in the region of 50-130 °C, the second - in the region of 170-200 °C. With an increase in the time from the beginning of the combination of the hardener with the other components of the composition, the thermal effect of the first peak gradually decreased, which is associated with a decrease in the number of unreacted functional groups. The first exothermic peak disappeared in less than 24 hours. The introduction of wollastonite into the composition led to a shift in the temperature of the onset of the first exothermic peak to higher temperatures and a noticeable decrease in the thermal effect of curing of ED-20 as compared to the base composition. This fact is associated with the competitive interaction of the amine hardener with the epoxy groups ED-20 and wollastonite. These effects are higher in the presence of naturally occurring wollastonite in contrast with synthetic one. This is preconditioned by higher porosity and lower pH of the Miwoll 10-97 surface at a certain extent. The degree of cure of the composition with wollastonite, is higher than unmodified, which is associated with a general increase in the number of reaction centers in the composition, which includes wollastonite. The second peak exotherm appearing at DSC-diagrams in the elevated temperatures area is connected with the processes of compositions' postcuring and is less intensive in contrast with the first peak exotherm for all investigated compositions. Both naturally occurring and synthetic wollastonite improve bonding strength, wear resistance and gelling time of epoxy compositions that allow for their perspective application as adhesives and glues.

Keywords: Epoxy polymers, wollastonite, aminoalkylphenol, rice husk ash, differential scanning calorimetry, adhesive properties, wear resistance, diameter and the volume of the pores.

Introduction

Wollastonite is of a certain interest for modification of epoxy glues as it can enhance the strength of cured glue joint. This is related to both anisodiametrical needlelike shape of its particles and acid-alkali balance of its surface.[1] The latter could affect the curing process of epoxy compositions.

Due to limited supply of naturally occurring wollastonite and the shortage of its deposits in many countries, the tendency to obtain synthetic wollastonite on the base of various by-products is rapidly developing.

In particular rice husk ash is a promising effective raw material for the production of synthetic wollastonite, since it contains a large amount of amorphous reactive silicon dioxide [2,3].

Obtaining a synthetic calcium silicate using silicon dioxide from rice husk is relevant, especially for Vietnam, where the deposits of this natural mineral are missing, and rice recycling waste is available in large quantities.

The purpose of the present research is evaluation of the influence of synthetic wollastonite obtained on the base of rice husk ash on the curing process of epoxy oligomers and adhesive strength of glue joints on their base.

Object and methods of research

Epoxy composition were obtained on the base of epoxy-diane resin, grade ED-20 (GOST 10587-84) cured by aminoalkylphenol AF-2 (Technical conditions 2494-052-00205423-2004). The ratio "resin-hardener" was 100:30 weight parts [4].

As a filler, there was used synthetic wollastonite obtained on the base of rice husk ash and calcium carbonate at the components' ratio equal to 1:1.2 at 1100 °C during three hours [5]. Naturally occurring wollastonite, grade Miwoll 10-97 (Technical conditions 5777-006-40705684-2003) was used for comparison. Wollastonite was introduced in the amount of 10 weight parts per 100 weight parts ED-20.

In order to fix exotherm effects at compositions curing, there was used differential scanning calorimeter DSC 1 STAR System produced by the company Mettler Toledo (USA), rate of samples heating accounted for 10 degrees/min, the tests were carried out in air. The degree of cure was determined under the method [6].

Adhesive strength of glue bonding aluminum-aluminum was determined by the pull-off test under the All-Union standard GOST 32299-2013.

The wear resistance of the materials was measured on the vertical Optimetra at a specific pressure of the counter on the test surface of the sample 1 MPa, the slide speed - 1 m / s, without lubrication

Working life of compositions was determined by the gelling time.

pH of aqueous suspensions of fillers was determined by the pH-meter, grade SevenMulti at 20 °C.

The diameter and the volume of the pores was determined under the BJH-method at the surface area analyzer and the pores size "Nova 1200e" ISO 15901-2.

Deaeration of the samples was carried out during three hours, at the temperature of 150 °C and the vacuum 2 Pa.

Results and discussions

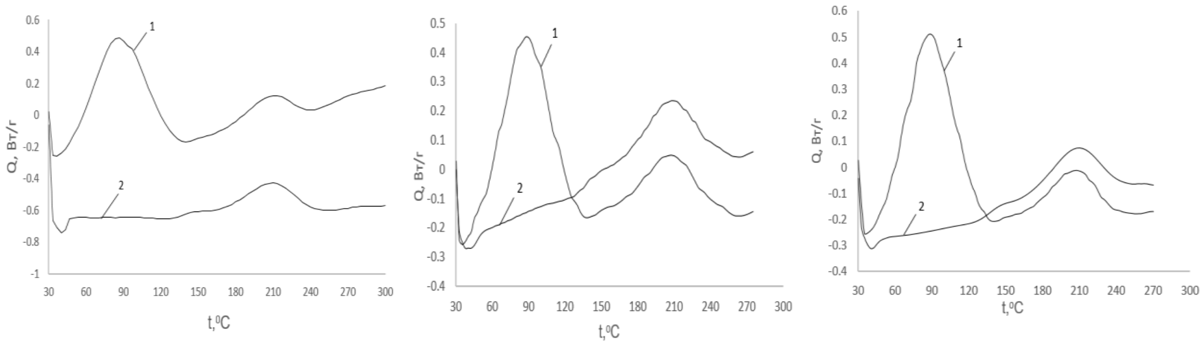
As curing of epoxy glues filled with wollastonite occurs in the presence of its solid surface, the character of the components' interaction at the phase boundary has an impact on this process and the properties of the obtained adhesive compositions.

Along with that, such properties of wollastonite as its porosity and acid- alkali characteristics of its surface contribute the most [7] (table 1).

Table 1.

Characteristics of porosity and surface pH of naturally occurring and synthetic wollastonite

Type of the filler	pH of the surface	Total pores volume, cm^3/g	Average pores diameter, nm
Synthetic wollastonite	11,50	0,010	3,67
Miwoll 10-97	9,70	0,017	3,49



(a) *(b)* *(c)*

Fig. 1. DSC-diagrams of the epoxy compositions, non-modified (a), filled with synthetic (b) and naturally occurring (c) wollastonite taken at the various time intervals after the components' mixing (hours): 1-0; 2-24

The exothermic nature of the process of curing epoxy resins amines makes an informative use for its study of the method of differential scanning calorimetry (DSC) [6].

The evaluation of wollastonite's impact on the curing process of epoxy resin demonstrates the presence of two peak exotherms on DCS-diagrams [8] for both based aminoepoxy compositions and those filled with wollastonite. The peaks are appearing in the temperatures area 50-130 °C and 170-240 °C, respectively (fig. 1).

It was stated that the main process of curing of epoxy compositions filled with wollastonite initiates at a higher temperature T_0 in contrast to the based composition (Fig. 1, table 2). This is also demonstrated by the gelling time of epoxy compositions (table 3).

Table 2.

Thermodynamic characteristics of the first (in a numerator) and the second (in the denominator) the peaks of the curing of epoxy compositions, basic and filled with natural and synthetic wollastonite

Characteristics	Basic composition	Synthetic wollastonite	Miwoll 10-97
Starting time			
ΔH, J /g	207/31	175/39	165/18
T_0, °C	43/176	50/172	55/190
T_m, °C	85/209	88/207	88/208
T_e, °C	134/236	126/239	123/233
After 1 hour			
ΔH, J /g	141/39	104/41	87/22
T_0, °C	69/171	52/172	53/182
T_m, °C	89/207	89/208	88/203
T_e, °C	139/238	126/240	118/222
After 2 hours			
ΔH, J /g	100/41	89/42	101/26
T_0, °C	50/194	60/173	49/187
T_m, °C	90/208	88/209	91/207
T_e, °C	132/242	130/239	129/234

Note: T_m - the temperature of the maximum exothermic process

T_e -the temperature of the end of the exothermic process.

Enthalpy (*ΔH*) of active curing lowers at a greater extent, whereas temperature T_0 grows in the case of filling with naturally occurring wollastonite in comparison with synthetic one (table 2). This could be connected with the greater pores volume and the lower pH of natural wollastonite' surface (table 1).

Independently of composition, with the increase in curing time for systems at room temperature enthalpy of the first curing peak typically lowers (table 2). This is related to the decrease in the number of unreacted functional groups that can be involved into curing reaction.

The curing process both for the based epoxy composition and filled with wollastonite alike terminates before 24 hours of their curing at room temperature. This could be proved by the lack of DSC-diagrams (fig. 1) taken in 24 hours after components mixing, peak exotherm related to the reaction behavior.

The curing degree of epoxy compositions filled with wollastonite is reduced as opposed to the based composition. Moreover, this effect is more pronounce when naturally occurring calcium silicate is applied (table 3).

This is connected with general decrease in the number of reaction centers in the composition, due to the interaction of epoxy resin with the surface of the wollastonite.

The second peak exotherm appeared at DSC-diagrams in the area of elevated temperatures is significantly lower in intensity if compared with the first one (fig.1, table 2) for the based composition and filled with wollastonite alike. It is connected with the reaction of epoxy and amine groups which did not react earlier due to steric difficulties

It worth mentioning, that the thermal effect of postcuring process is remarkably lower in the presence of naturally occurring wollastonite as opposed to the synthetic calcium silicate.

Along with that, as opposed to the first exothermic process, the presence of synthetic wollastonite in the composition leads to the shift of initiation of the second peak exotherm at the first-time interval to the area of lower temperatures (fig. 1, table 2). This could be explained by the increase in reaction capacity of remaining epoxy groups due to their polarization caused by hydrogen bonds formation with OH-groups of wollastonite.

When samples' curing time at room temperature is increased up to 24 hours, high-temperature peak at DSC-diagrams does not disappear, as opposed to the first exothermic process. Thus, the increase in the curing degree for both based composition and those filled with wollastonite is possible at the elevation of curing temperature.

Table 3.

Gelling time, adhesive strength and the curing degree of epoxy compositions filled with wollastonite

Characteristic	Basic composition	Synthetic wollastonite	Miwoll 10-97
Lifetime, min.	20	25	27
Curing degree, %	0,52	0,48	0,39
Pull-off strength, MPa	1,86	2,81	2,43

The studies have shown (table 3), that breakaway strength of epoxy compositions filled with naturally occurring and synthetic wollatonite is typically growing. This could be explained by the presence of adhesive active silanol groups in calcium silicate surface. Adhesive strength is higher in the case of applying wollastonite synthesized on the base of rice husk ash.

As the reaction of curing epoxy resin with amines has an exothermic character (fig. 1), in the process of cross-link structure' formation, there occurs the generation of hydrogen bonds between HO-groups of resin and oxygen atoms of a filler [9].

This effect is more pronounced when synthetic wollastonite is applied that should promote growth of interfacial interactions between polymer matrix and a filler and contribute to its modifying effect.

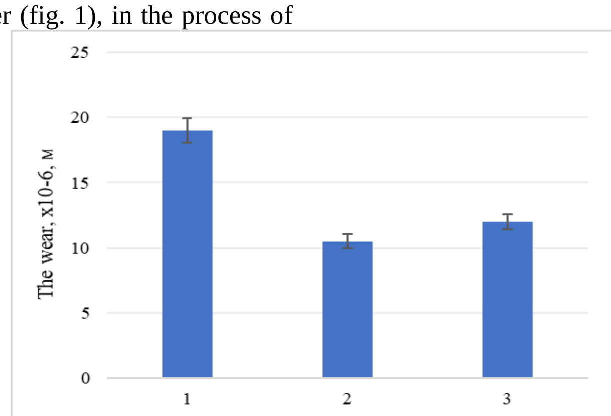


Fig. 2. The dependence of the wear of epoxy compositions from the type of filler used:
1 - based; 2 - Miwoll 10-97; 3 - synthetic wollastonite

Filling of epoxy composites, both natural and synthetic wollastonite, is essential, about the same degree, increases their wear resistance (fig. 2)

It is connected with the interaction of epoxy resin and wollastonite, causes braking of the propagation of cracks on the border of the filler-polymer matrix, as well as a result of micro-cracking in the region of the top of cracks and changes to its trajectory [11].

It is important that the use of rice-processing waste as raw materials to obtain wollastonite makes epoxy adhesives more economically competitive, and moreover, accelerates the processes of their disposal after the service is completed, due to the biodegradability of rice husk [10].

Conclusions

It was stated by the DSC-method that filling of epoxy compositions with both naturally occurring and synthetic wollastonite can inhibit their curing that was exhibited in the shift of initialization of exothermic process to the area of elevated temperatures and the gelling time growth.

This could be seen as the positive effect as it enables to prepare the greater volume of an adhesive composition consentaneously that is less labour-consuming.

Just as naturally occurring so synthetic wollastonite significantly increases adhesive strength and wear resistance of epoxy materials that confirms the efficiency of their application in the compositions applied for gluing of metal structures.

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