Influence of the acid-base surface centers of fiber fillers on the curing process of epoxy composites

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Abstract – Considered the influence of the acid-base surface centers of basalt and glass fibers on the modified epoxyamine compositions curing process. It is shown that the removal of a lubricant from the surface of the fibers with heat leads to the decrease of the Brensted acid level on their surface, whereupon the process of structuring slows down and the activation energy of the curing process increases at the initial stage.

Key words – epoxyamine composites, basalt fiber, glass fiber, acid-base centers, curing.

I. Introduction

The epoxy composite materials are widely used for restoration and repairing of the building constructions. One of the significant parameters in solving of problem of their quality and durability is strength of adhesion connections between components on the phase boundary. Regulating the interactions on the contact area it is possible to control the formation process of composite materials.

II. Analysis of the existing solutions

Physical-mechanical properties, performances of epoxypolymer materials and composites largely depend on technical properties of oligomer binder, structuring process, adhesive interface interaction, intermolecular and other kinds of interactions [1].

Specificity of the epoxy polymers processing is that curing processes and workpieces moulding occure at the same time. That is why it is really necessary to know mechanism and features of the curing process kinetics to rational manipulation of the structuring process and obtaining of the workpieces with defined technical properties.

It is well known that the solid surface may have some influence on the curing process as a result of the absorption interaction with components of the epoxy binder. The introduction of fibrous fillers into the epoxypolymer system results in a wide range of interactions, from weak physical to chemical interactions on the interface filler-binder [2]. Obviously, the nature of these interactions largely depends on the surface chemistry of the fillers and on the composition of the curing oligomer-oligomer system. There is almost no information about the influence of surface active centers of basalt and glass fibers on the interaction processes of the epoxy system and on the basic performance. Therefore we have studied the influence of acid-base surface centers of the fiber fillers on the curing process of the modified epoxyamine composites.

III. The methodology of the experiments

This research studied an epoxy oligomer ED-20 solidificated with polyethylene polyamine (PEPA). As the modifying additives that improve the technological properties of the binder employed such low-viscosity reactive oligomers as threefunctional epoxy oligoester Lapoksid-503 and threefunctional cyclo-carbonate oligomer Laprolat-803. Glass fiber, basalt fiber and microfiber are selected as the fiber fillers.

The fiber was used with lubricant and without it. The lubricant was removed by thermal method (400ºC for basalt fiber and 250ºC for glass fiber) and by the hexane solvent. Basalt and glass fibers were cut into pieces 3-5 mm long. The content of fiber fillers in all experiments was 25 wt. % per 100 wt. % of binder.

One of the major parameters that allow to evaluate the surface and to control changes in its characteristics in the real processes is acid-base properties which largely determine the absorption and reaction of the solid substance surface [3]. The spectroscopy method allows to define the active centers of a specific type of acidity and to evaluate their contents [4].

The dielectric method was used to investigate the curing process of fiber reinforced composites at the initial stage. This method is based on registration of the changes of volume resistivity and on evaluation of reaction rate. The curing process was studied within the temperature range 303-323 K.

The curing process rate was determined using standard methodology. The effective activation energy of curing was calculated by Arrhenius equation.

IV. Discussion of results

Investigation results of the acid-base centers of fiber fillers are given in Table 1.

As we can see, chemical properties of fiber surface depend on the chemical contents, on method of preparation and availability of the lubricant. The least amount of active centers is on the surface of glass and basalt fiber with the lubricant. Obviously, the biggest number of the active adsorption centers is on the basalt microfiber and glass washed off fiber surfaces – 22 and 25 μmol/g accordingly. Subacid Brensted centers with pKa 6.4, which possess low catalytic activity relatively to curing epoxyamine composites, make the biggest contribution into the total amount [5].

Investigations have shown that thermal treatment of glass and basalt fiber leads to the evident decreasing of the amount of acid centers (OH-group) on their surface in comparison with the washed off fiber. Obviously, it is

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associated with dehydroxylation processes of the surface under the influence of high temperature.

TABLE 1

ACID-BASE CENTERS OF FIBERS SURFACES

Filler	The concentration of active centers, q, μmol/g								
	Brensted acid				Brensted base				
	+1,5	+5,0	+6,4	∑	+7,	+8,0	+10,5	∑	Sum
Basalt microfiber	3	3	10	16	2	1	3	6	22
Basalt fiber	0,2	0,4	0,4	1	0,2	0,2	0,7	1,1	2,1
Annealed basalt fiber	1	4	1	6	8	1	3	12	18
Glass fiber	0,5	1,3	0,3	2,1	0,4	0,3	0,6	1,3	3,4
Washed off glass fiber	3	2	11	16	3	2	4	9	25
Annealed glass fiber	2	3	1	6	4	4	4	12	18

Investigation results of fiber reinforced epoxyamine composites curing processes are given in Table 2.

TABLE 2

KINETICS OF THE COMPOSITES CURING PROCESSES

Composition, wt. %	Curing process rate (ΔlgρV/Δτ) at the temperature of, *102			Eef, kJ/mol
	303 K	313 K	323 K	
ED-20:PEPA	1,0	1,7	3,6	54,7
ED-20:Laproksid-503:PEPA	1,2	2,1	3,8	49,6
Basalt microfiber	1,1	1,7	3,6	50,8
Basalt fiber	0,95	1,7	4,1	62,4
Annealed basalt fiber	0,82	1,75	3,14	57,0
Glass fiber	0,84	1,4	3,3	58,8
Washed off glass fiber	0,6	1,5	3,6	76,4
Annealed glass fiber	0,4	1,14	2,52	77,3
ED-20:Laprolat-803:PEPA	0,82	1,4	4,0	67,5
Basalt microfiber	0,85	1,78	3,65	62,8
Basalt fiber	0,95	1,6	2,6	43,4
Annealed basalt fiber	0,7	1,3	2,45	53,6
Glass fiber	0,76	1,2	2,3	47,8
Washed off glass fiber	0,54	0,9	2,0	56,2
Annealed glass fiber	0,4	0,9	2,2	72,0

As we can see from this table, an addition of the modified threefunctional epoxy oligoester Laproksid-503 into initial binder leads to insignificant change of the curing process rate at the temperature of 303 K. And at the same time the value of the effective activation energy decreased from 54.7 to 49.6 kJ/mol. An addition of thee-functional cyclo-carbonate oligomer Laprolat-803 leads to decrease of the curing process rate by 20% in comparison with the initial binder and by 40% comparing to the binder modified with threefunctional epoxy oligoester. At the same time the effective activation energy increases to 67.5 kJ/mol. That means that curing process depends on the temperature.

An addition of the microfiber into the binder modified with threefunctional epoxy oligoester leads to decreasing of curing process rate and to flowing of the reaction at lower values of the effective activation energy. We observed the same when we added basalt fiber with lubricant into the binder modified threefunctional cyclo-carbonate oligomer. That stimulates a forming of the homogeneous structure and less tense structure.

Conclusion

It has been shown, that the curing process of the epoxy basalt- and glass-reinforced composites depends on the nature of the modified oligomer composed of binder and on acid-base absorption centers of the fibers surface.

It was found that the curing process of the epoxy binder modified with threefunctional epoxy oligoester runs at low values of the interaction rate and activation energy in the presence of basalt microfiber, as well as the curing process of the epoxy binder modified with threefunctional cyclo-carbonate oligomer runs in the presence of basalt and glass fiber with the lubricant.

It was shown that the amount of acid-base centers on the annealed basalt and glass fiber surface is lower than on the washed off fiber. And due to that fact the structuring process runs slower and the value of activation energy at the first stage of curing increases.

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