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Adhesive Compositions based on Heptene-1 Copolymer with Maleic Anhydride

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Abstract

Adhesive compositions based on hepten-1-maleic anhydride co-polymer and ED-16 epoxide resin were prepared and some physical and physico-chemical properties of these adhesive compositions were determined. The ability of the prepared adhesive composition to bond aluminum and steel plates was also studied. Adhesive compositions of hepten-1-maleic anhydride copolymer and ED-16 epoxy resin in different ratios (10, 15, 20, 25, 30 s.c. copolymer to 100 s.c. ED-20 epoxide resin) were prepared. Curing of ED-16 epoxy resin with co-polymer (CP) was studied and the effect of temperature and amount of co-polymer on curing was determined. The adhesive properties of aluminum and steel plates were studied by hardening under different conditions. It was determined that the strength of the adhesive compositions prepared in different mass ratios of joint polymer and ED-16 epoxy resin for aluminum plates with a ratio of ED-16:CP=100:25 to fracture resistance. was higher for When the adhesive composition with this composition is cured at 160, 180, 200 0 C for 3 hours, the strength against sliding breakage for duralumin plates were 24.8, 26.2 and 25.8 MPa. The tensile strength ¬and dielectric properties of the adhesive composition prepared in the ratio of ED-16:CP=100:25 were determined.

Keywords: heptene-1; maleic anhydride; copolymer; epoxy resin; adhesive composition; degree of swelling;tensile strength; dielectric constant.

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1.İntroduction

The curing of epoxy adhesive compositions with of polybasic carboxylic acids is the oldest method, which has not lost its significance at the present time. The anhydrides of maleic, phthalic, pyromellitic, chlorendic, tetrahydrophthalic acids used as hardeners of epoxy compositions have a number of disadvantages: some are prone to sublimation, others are toxic and do not mix well with epoxy resins, etc. [1]. The search for new hardeners for epoxy compositions is one of the urgent problems of the chemistry of composite materials. The presence of reactive anhydride units in the molecular chain of copolymers of maleic anhydride with various monomers creates prerequisites for their use as hardeners for epoxy compositions. While retaining the basic characteristics of typical hardeners, maleic anhydride copolymers could improve the physical and mechanical properties of cured epoxy compositions. The possibility of using anhydride-containing copolymers in the composition of epoxy compositions is already reported in a number of works [2,11]. This paper presents the results on the preparation and study of the properties of adhesive compositions based on a heptene-1 copolymer with maleic anhydride and epoxy resin ED-16, as well as, the use of these compositions for gluing aluminum and steel plates [3-7,10].

2.Experimental part

In this work, an industrial grade epoxy resin ED-16 with a molecular weight of 520 and a content of 16.5% epoxy group and 1.8% hydroxyl group was used. The heptene-1-maleic anhydride (HML) copolymer was synthesized by the radical copolymerization of heptene-1 (HP) with maleic anhydride (MA) in the presence of azobisisobutyronitrile according to our method [3]. HML with equimolar content of HP and MA had an intrinsic viscosity of 0.18-0.20 $m*gr^{-1}$. The compositions were prepared as follows: finely ground copolymer and epoxy resin of a certain mass ratio were thoroughly mixed at 80-90 ^{0}C for 3-5 minutes until a homogeneous mass was formed. Then diethylamine (curing accelerator) and powdered alumina are added to the mixture as a thixotropic additive. The composition was placed in a thermostat at a given temperature for a certain time. The beginning of gelation, the time of hardening and complete curing were noted [2,7]. The cured composition was treated with acetone and dried in a vacuum oven at 40-50 ^{0}C. The degree of curing was determined by the ratio of the masses of the cured sample before and after treatment with acetone. To study the deformation-strength properties, the composition was cured in a special form with dimensions of 50x10x5 mm. The strength properties were determined from stress-elongation curves taken on a Haunsfield tensile testing machine equipped with an automatic computer recorder. Thermal stability was determined from TG curves taken in a nitrogen atmosphere on a Shimadzu model TGA-50 instrument. The dielectric properties were determined by the well-known method [4,5,9,10]. The shear stress of the adhesive composition on the metal plates was also determined from the stress-elongation curves. For this purpose, a homogeneous adhesive composition prepared at 80-90 ^{0}C is applied to the surfaces of metal (duralumin, steel) plates pre-treated with a chromium mixture and degreased with acetone, and the latter are glued overlapping each other (the area of the bonded surface is 10x10 mm). Later, the plates with a clamp were kept in a thermostat at a given temperature for a certain time.

3.Results and Discussion

Curing of epoxy compositions with anhydrides of polybasic carboxylic acids is usually carried out at 120-200^{0}C. The degree of curing depends mainly on the mass ratio of components, temperature and heat treatment time. Compositions of the following composition were prepared and the influence of these factors on the time of the onset of gelation, and hardening, and the degree of hardening were studied:

Consistency 1. Epoxy resin - 100 m. p.

Table1

Copolymer	15 m. p.
Aluminum oxide	5 m. p.
Diethyl amine	1 m. p.

Consistency 2. Epoxy resin - 100 m. p.

Table2

Copolymer	20 m. p.
Aluminum oxide	5 m. p.
Diethyl amine	1 m. p.

Consistency 3. Epoxy resin - 100 m. p.

Table3

Copolymer	25 m. p.
Aluminum oxide	5 m. p.
Diethyl amine	1 m. p.

Consistency 4. Epoxy resin - 100 m. p.

Table4

Copolymer	30 m. p.
Aluminum oxide	5 m. p.
Diethyl amine	1 m. p.

Curing condition of composition (mass Al_2O_3-5gr, diethyl amine)

Table5

Mass of copolymer, for 100 gr	Temp,^{0}C	Thermal treatment time, hour	Starting of gel formation, min	Starting of curing, min	Curing degree, %
15	180	3	66	92	68.9
20	180	3	55	77	88.1
25	180	3	43	70	96.8
30	180	3	40	61	98.5
25	140	3	105	150	63.2
25	160	3	80	110	80.1
25	200	3	35	65	98.1
25	180	2	44	67	66.3
25	180	4	42	68	98.8

For overlap-bonded steel and galvanized iron plates at various temperatures and compositions, the shear stress at failure and relative change were determined from stress-strain curves taken on a Hounsfield tensile testing machine.

Destructive adhesive shear stress (σ), at various curing temperatures and mass parts of the copolymer-curing agent.

Curing time - 3 hours

Table6

Metal	Curing temperature, ^{0}C	Б, MPa for gluing agents			Б, MPa with commercial epoxy glues
		2	3	4	
Steel	160	9,6	15,1	17,0	-
	180	19,5	24,0	22,3	7,5
	200	17,7	27,1	24,0	-
Galvanized iron	160	8.0	14.5	11.5	-
	180	15.3	19.8	17.6	7.0
	200	14.0	18.9	14.5	-
Duralumin	160	8.8	24.8	13.8	-
	180	20.0	26.2	23.8	10.4
	200	20.6	25.8	24.0	-

Curing temperature 180^0C, time 3 h.

Table7

Properties	Compositions			
	1	2	3	4
Shear stress at destruction point, MPa	12,1	15,8	19,6	18,1
Relative elongation, %	1,8	1,3	1,5	1,3
Thermal resistance (by TG) ^{0}C		255	280	285
The dielectric constant (10^6 hz)		3,2	3,1	3,5
Dielectric loss tangent (10^6 hz)		0,009	0,012	0,01
Swelling degree, %				
Toluene		4,2	3,1	3,5
Chlorobenzene		4,5	2,7	2,0
Hexane		2,8	1,7	1,8

Features of thermal degradation of epoxy adhesive composites were studied using thermal analysis methods - thermogravimetric method (TG) and differential scanning calorimetry (DSC) in linear heating mode at a rate of 10 ^{0}C/min in an argon atmosphere in the temperature range of 20-1000 ^{0}C. Figure 1 shows the thermograms of the original epoxy resin and samples of the cured composition.

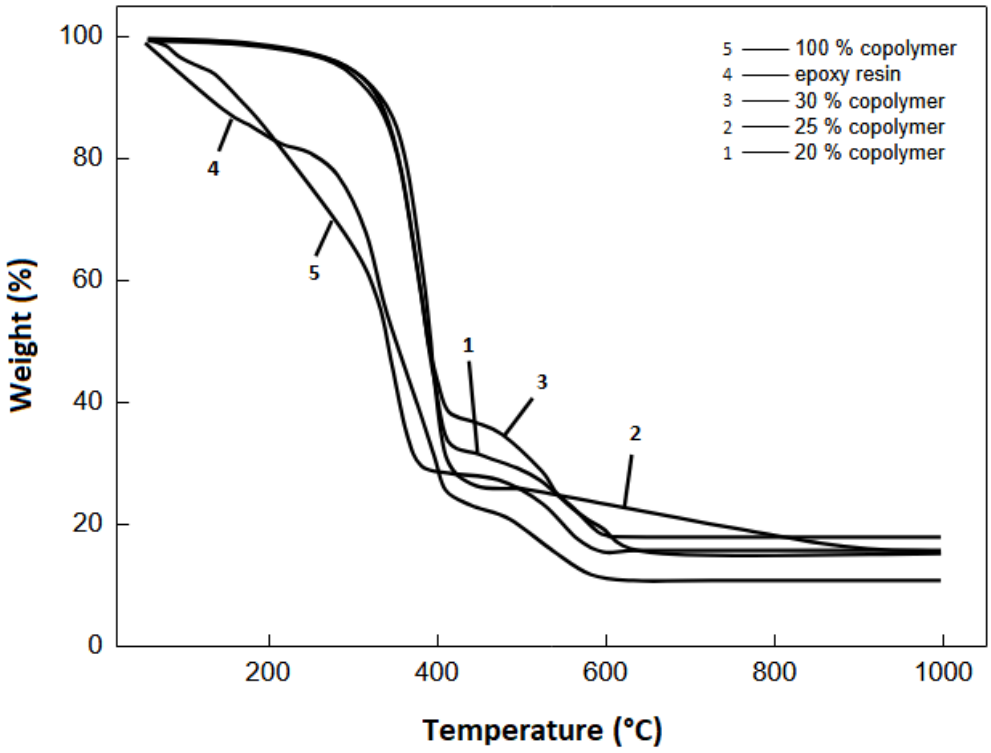

Figure1: Thermograms of the original epoxy resin and samples of the cured composition

4.Conclusion

Based on the results of the work performed, adhesive compositions based on a copolymer of heptene-1-maleic anhydride and epoxy resin ED-16 were prepared, and some physical and physico-chemical properties of these adhesive compositions were determined. The ability of the prepared adhesive composition to bond aluminum and steel plates was also studied. Adhesive compositions of a copolymer of heptene-1-maleic anhydride and epoxy resin ED-16 were prepared in various ratios (10, 15, 20, 25, 30 x copolymer per 100 x epoxy resin ED-20). The curing of epoxy resin ED-16 with a copolymer (CP) was studied and the effect of temperature and the amount of copolymer on curing was determined. The adhesive properties of aluminum and steel plates were studied by hardening under various conditions. It has been determined that the strength of adhesive compositions prepared at different mass ratios of suture polymer and epoxy resin ED-16 for aluminum plates at a ratio of ED-16:CP=100:25 to fracture resistance. was higher when curing the adhesive composition with this composition at 160, 180, 200 0 C for 3 hours, the tensile strength in sliding for duralumin plates was 24.8, 26.2 and 25.8 MPa. The tensile strength and dielectric properties of the adhesive composition prepared in the ratio ED-16:CP=100:25 were determined. The tensile strength of the adhesive composition prepared in this proportion was 19.6 MPa, the dielectric constant was 3.1 (at a frequency of 10 6 Gs), the dielectric loss tangent was 12 10 -3 (at a frequency of 10 6 Gs). Xs). The results obtained show that these materials have good electrical insulating properties. Based on the TG curve, it can be said that the adhesive composition prepared in the ratio ED-16:CP=100:25 is resistant to a temperature of 400 0 C. The degree of swelling (α%) of the adhesive compositions prepared in different mass ratios and cured in different solvents . The swelling coefficients of the cured adhesive composition in toluene, chlorobenzene and hexane were 3.1, 2.7 and 2.0, respectively, when the adhesive composition was prepared in a mass ratio of 100:25. From the obtained results, it can be seen that as the mass amount of the copolymer in the adhesive composition decreases, the degree of swelling in the solvent increases, while the adhesive composition prepared in a mass ratio of 100:10 dissolves in the tested solvents.

References

[1]. Chunfu Chen, Bin Li, Masao Kanari and Daoqiang Lu . Epoxy Adhesives. Chapter Metrics Overview . 2019

[2]. Kablov, E.N., Chursova, L.V., Lukina, N.F. et al. A study of epoxide–polysulfone polymer systems for high-strength adhesives of aviation purpose. Polym. Sci. Ser. D 10, pp. 225–229 (2017). https://doi.org/10.1134/S1995421217030066.

[3]. Kochergin, Y.S., Pyrikov, A.V., Kulik, T.A. et al. Investigation of epoxide adhesive compositions cured with polyoxypropylene triamine. Polym. Sci. Ser. D 3, pp. 47–49 (2010). https://doi.org/10.1134/S1995421210010077

[4]. Petrova, A.P., Lukina, N.F., Dement'eva, L.A. et al. Film structural adhesives. Polym. Sci. Ser. D 8, pp. 138–143 (2015). https://doi.org/10.1134/S1995421215020148

[5]. Fedoseev, M., Gurina, M., Sdobnov, V. and Kondyurin, A. (1996), Study of the Reaction of Epoxides with Carboxylic Acids by IR and Raman Spectrometry. J. Raman Spectrosc., 27: pp. 413-418.

https://doi.org/10.1002/(SICI)1097-4555(199605)27:5<413::AID-JRS947>3.0.CO;2-T

[6]. Vyatkina, M.A., Gorbatkina, Y.A., Gorbunova, I.Y. et al. Effect of Oligomeric Copolyimides on the Properties of Epoxy Binders. Mech Compos Mater 58, pp. 857–866 (2023). https://doi.org/10.1007/s11029-023-10074-1

[7]. Konoplin, A.Y., Baurova, N.I. Thermogravimetric Analysis of a Weld-Bonded Joint with Various Types of Adhesive Materials. Polym. Sci. Ser. D 15, pp. 166–170 (2022). https://doi.org/10.1134/S1995421222020125

[8]. Gur'eva, L.L., Kuzub, L.I., Tarasov, A.E. et al. Epoxy Nanocomposites Containing Silver Nanoparticles with Oligostyrylcarboxylate Ligands. Polym. Sci. Ser. B 64, pp. 209–218 (2022). https://doi.org/10.1134/S1560090422020105

[9]. Sirotin, I.S., Son, V.X., Gorbunova, E.A. *et al.* The Composition and Some Properties of Epoxy Oligomers Based on Hexachlorocyclotriphosphazene and Diphenylolpropane. *Polym. Sci. Ser. D* **15**, pp. 457–463 (2022). https://doi.org/10.1134/S1995421222030261

[10]. G. Fantin et al., "Functionalization of poly(organophosphazenes)—III. Synthesis of phosphazene materials containing carbon-carbon double bonds and epoxide groups," Eur. Polym. J. **29**, pp. 1571–1579 (1993).

[11]. J. Sun, X. Wang, and D. Wu, "Novel spirocyclic phosphazene-based epoxy resin for halogen-free fire resistance: synthesis, curing behaviors, and flammability characteristics," ACS Appl. Mater. Interfaces **4**, pp. 4047–4061 (2012).