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ИССЛЕДОВАНИЕ МЕТОДОМ ДСК ВЛИЯНИЯ МАСЛА КАУЧУКОВОГО ДЕРЕВА, СОЕВОГО МАСЛА И ИХ ЭПОКСИДИРОВАННЫХ ПРОИЗВОДНЫХ НА ПРОЦЕСС ОТВЕРЖДЕНИЯ ЭПОКСИАМИННЫХ КОМПОЗИЦИЙ

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Растительные масла и их эпоксидированные производные представляют большой интерес в качестве модификаторов эпоксидных полимеров, как получаемые на основе возобновляемого сырья, характеризующееся биоразлагаемостью и оказывающие пластифицирующее действие. Введение в рецептуру эпоксидных материалов ненасыщенных жирных кислот также является эффективным. В связи с этим, большой интерес в качестве модификатора эпоксидных полимеров представляет масло каучукового дерева, содержащее порядка 28% по массе свободных жирных кислот. Модификация эпоксидных полимеров маслом каучукового дерева обуславливает улучшение целого комплекса их эксплуатационных характеристик. Поскольку структура эпоксидных материалов формируется в присутствии модифицирующих добавок, важной является оценка влияния их на процессе отверждения методом ДСК. Установлено, что модификация эпоксидных композиций как соевым, так и маслом каучукового дерева и их эпоксидированными производными, замедляет отверждение эпоксидных композиций, что проявляется в сдвиге начала первого экзотермического процесса в область более высоких температур и росте их жизнеспособности. Этот эффект проявляется в меньшей степени в случае применения масла каучукового дерева из-за присутствия в его составе большого количества свободных жирных кислот. При нагревании исследованных композиций, не зависимо от их состава, в процессе отверждения в районе 200 °С появляется второй экзотермический эффект, существенно меньший по интенсивности, по сравнению с первым, связанный, вероятно, с процессами доотверждения (реакцией не прореагировавших ранее из-за стерических затруднений эпоксидных и аминных групп). На это накладывается химическое взаимодействие между эпоксидной смолой и маслом каучукового дерева, которое происходит в близком температурном интервале.

Ключевые слова: масло каучукового дерева, соевое масло, свободные жирные кислоты, эпоксидные полимеры, метод дифференциально-сканирующей калориметрии

DSC STUDY OF INFLUENCE OF RUBBER SEED OIL, SOYBEAN OIL AND THEIR EPOXIDED DERIVATIVES ON PROCESS OF CURING EPOXYAMINE COMPOSITIONS

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Vegetable oils and their epoxidized derivatives are of great interest as modifiers of epoxy polymers, since they are obtained on the basis of renewable raw materials. The unsaturated fatty acids could also serve as effective modifiers of epoxy materials. In this regard, rubber seed oil, containing about 28% by weight of free fatty acids is a promising modifier of epoxy polymers, which enhances several performance characteristics. Since the structure of epoxy materials is formed in the presence of modifying additives, it is important to estimate their influence on the curing process by differential scanning calorimeter. It was found that the modification of both soybean and rubber seed oils and their epoxidized derivatives decelerates the curing of epoxy compositions. The increase in the temperature of the beginning of the interaction exothermic process of epoxy and amine groups and an increase in the gel time of the compositions were displayed. In the process of curing compositions in the region of 200 °C, a second exothermic effect appears, which is significantly less intensive than the first one. This could be associated, probably, with the processes of additional hardening (the reaction of epoxy and amine groups that did not react earlier due to steric difficulties). This peak is superimposed by a thermal effect due to the chemical interaction between the epoxy resin and the components of rubber seed oil, which occurs in a close temperature range.

Key words: rubber seed oil, soybean oil, free fatty acids, epoxy polymers, differential scanning calorimetry

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INTRODUCTION

Vegetable oils and their epoxidized derivatives are of great interest as modifiers of epoxy polymers, since they are obtained on the basis of renewable raw materials, characterized by biodegradability [1–4]. The efficiency of modification by unsaturated fatty acids of epoxy materials is shown [5, 6] on the example of ricinoleic and oleic acids.

In this regard, a by-product obtained from the seeds of *Hevea brasiliensis,* non-edible rubber seed oil (RSO) [1], containing about 28% by weight free fatty acids [4] has a great potential for epoxy polymers modification.

EXPERIMENTAL PART

The compositions were prepared on the basis of epoxy-diane resin ED-20 (GOST 10587-84): epoxy number – 20.2%;. Aminophenol AF-2 was used as a hardener: dynamic viscosity at 50 °C – not more than 1.5 mPa·s; mass fraction of titrated nitrogen – 15.66%.

The amount of hardener in the base composition was determined by the equimolar ratio of the reacting groups [epoxy group]:[amino group] – 30 parts per hundred of epoxy resin (pph).

As modifiers used: the liquid part of the RSO from the province of Vung Tau (Vietnam), obtained after centrifugation and filtration, the composition of which is given in [7], epoxidized rubber seed oil (ERSO), obtained by the method described in [8], with a content of epoxy oxygen – 5.2% by weight and an acid number of 42.8 mg KOH/g; soybean oil (SO) (GOST R 53510-2009); epoxidized soybean oil (ESO) (TU 0253-061-07510508-2012) with an epoxy oxygen content of 6.2% by weight and an acid number of 0.5 mg KOH/g. The optimal content of modifying additives was 10 pph [9].

A differential scanning calorimeter DSC 1 STAR System of Mettler Toledo (USA) was used to record the thermal effects during the curing of the compositions. The heating rate of the sample was 10 deg/min. The tests were carried out in air atmosphere.

The viability of the compositions was determined by the gel time. Gel-Sol analysis was carried out through extraction of polymer films (after 7 days of their preparation) with hot acetone for 6 h in the Soxhlet apparatus.

RESULTS AND DISCUSSION

Modification of epoxy polymers by rubber seed oil and the product of its epoxidation causes improvement of the whole complex of their operational characteristics [7, 10].

The properties of epoxy materials depend on the cross-linked structure formed in the presence of modifiers. Therefore, it is important to estimate the effect of modifying additives on the curing process, which makes it possible to regulate the rate of spatial structure formation.

Since the process of curing epoxy resins with amines is exothermic, it is most rational to use the differential scanning calorimetry method to estimate the effect of modifiers on the curing process [11]. Heat of the reaction was determined by DSC peak area (ΔH), the beginning (T_0) and end (T_e) temperatures of active curing, the temperature of the maximum peak (T_M), its width ($\Delta T = T_e - T_0$) and height [12].

Table 1

Thermodynamic characteristics of the first peak curing AF-2 modified epoxy compositions

***Таблица 1.* Термодинамические характеристики первого пика отверждения АФ-2 модифицированных эпоксидных композиций**

Characteristics	The composition				
	ED-20+AF-2	ED-20 + AF-2 + RSO	ED-20 + AF-2 + SO	ED-20 +AF-2+ ERSO	ED-20 + AF-2 + ESO
At the initial point in time					
ΔH, J/g	207	211		189	195
T_0, °C	43	49		53	52
Tm, °C	85	90		93	90
Te, °C	134	138		143	142
Peak height, mW	6	5		4	6
ΔT, °C	89	92		90	90
After 60 min					
ΔH, J/g	141	153	114	158	148
T_0, °C	49	48	48	50	52
Tm, °C	89	92	89	93	92
Te, °C	139	140	127	143	143
Peak height, mW	4	4	3	4	4.5
ΔT, °C	90	92	79	93	91
After 120 min					
ΔH, J/g	100	132	107	124	115
T_0, °C	50	37	51	52	53
Tm, °C	90	92	93	96	94
Te, °C	137	138	136	145	144
Peak height, mW	2	3	3	3	3
ΔT, °C	87	101	85	93	91

Analysis of DSC diagrams showed (Fig. 1, 2) that they are characterized by two exothermic peaks. By increasing the holding time of samples at room temperature, the enthalpy of curing and the height of the first peak naturally decrease, which is associated with a decrease in the number of non-reacted functional groups of components of the epoxy composition.

At the same time, the curing process of epoxy composition modified RSO begins at a higher temperature (T_0) than the base composition (Table 1) and the temperature of its maximum increases at the initial stage of curing. This indicates that this modifier slows down the curing reaction; obviously, due to the dilution effect. This correlates with an increase of the viability of the composition with the modification of RSO, and it is accompanied by the decrease of the gel fraction content (Table 2).

The use of RSO as a modifier further shifts the beginning of the exothermic curing process to the region of higher temperatures (Table1). This can be attributed to the lower reactivity of epoxy groups of epoxidized vegetable oils compared to ED-20 [13, 14].

Soybean oil, much more than RSO, inhibits the curing process of ED-20 aminophenol AF-2 (Fig. 2). Thus, after mixing the components and exposing them for an hour at room temperature, the main exothermic peak of curing is not observed in the DSC diagrams. Interestingly, it appears only after 2 h of exposure of the composition at room temperature. This correlates with the greater viability of epoxy compositions modified by SO compared to RSO (Table 2).

This effect may be due to the fact that soybean oil, similarly to RSO, acts as a diluent, but unlike rubber seed oil, SO does not contain free fatty acids that can possess a catalytic effect on the curing process of epoxy oligomers [15].

Table 2

Viability and gel fraction content of epoxy compositions

***Таблица 2.* Жизнеспособность и содержание гель-фракции эпоксидных композиций**

Modifier	No modifier	SO	ESO	RSO	ERSO
Gel time, min	30	50	45	45	35
Gel fraction, %	96.1	93.5	95.2	89.2	91.8

When used as a modifier, epoxidized soybean oil promotes/induces thermal curing effect of epoxy compositions and the height of its peak is significantly less, as well as the temperature of the beginning of active curing is significantly higher, compared with the use of ERSO (Table 1). Consequently, ESO has a greater inhibitory effect on the curing process of the AF-2 epoxy resin.

The curing process of both non-modified epoxy compositions and those containing vegetable oils and their epoxidized derivatives practically ends in less than 24 h of their exposure at room temperature. This is evidenced by the fact that there is no exothermic peak associated with this reaction in the DSC diagrams (Fig. 1 and 2), taken one and two days after the mixing of the components.

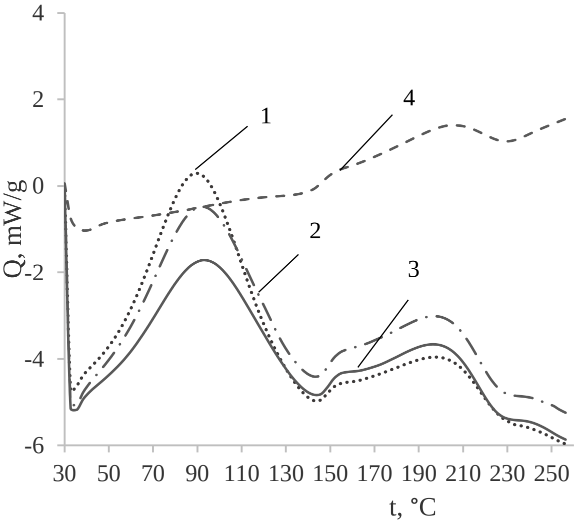


Fig. 1. DSC-curves of modified RSO epoxy compositions taken at different intervals after mixing: 1 – immediately after mixing 2 – 1 h; 3 – 2 h; 4 – 24 h

Рис. 1. ДСК-кривые модифицированных МКД эпоксидных композиций, снятые через различные промежутки времени после смешения: 1 – сразу после смешения; 2 – 1 ч; 3 – 2 ч; 4 – 24 ч

When all the investigated compositions are heated in the region of 200 °C, a second exothermic effect is observed, which is significantly less intense than the first one (Fig. 1 and 2, Table 3). This could be associated with the processes of additional hardening (reaction of epoxy and amine groups which did not react earlier due to steric difficulties).

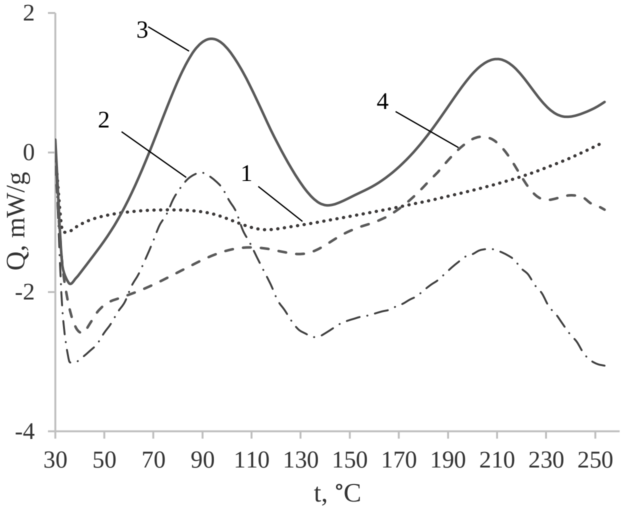


Fig. 2. DSC-curves of modified SO epoxy compositions taken at different intervals after mixing: 1 – immediately after mixing; 2 – 1 h; 3 – 2 h; 4 – 24 h

Рис. 2. ДСК-кривые модифицированных 10 мас.ч СМ эпоксидных композиций, снятые через различные промежутки времени после смешения: 1 – 0 мин.; 2 – 1 ч; 3 –2 ч.; 4 – 24 ч

As a result of modification of epoxy polymers RSO and SO as well as their epoxidized derivatives, this process is shifted to the region of lower temperatures (Table 3). This may connected with the large number of non-reacted functional groups in compositions containing vegetable oils due to their dilution effect as palm oil [16].

Table 3

Thermodynamic characteristics of the second peak curing AF-2 modified epoxy compositions

***Таблица 3*. Термодинамические характеристики второго пика отверждения эпоксидных композиций**

Characteristics	The composition				
	ED-20 +AF-2	ED-20+ AF-2+ + RSO	ED-20 + +AF-2+ SO	ED-20 + AF-2+ +ERSO	ED-20 + AF-2+ +ESO
1	2	3	4	5	6
At the initial point in time					
ΔH, J/g	31	34		38	24
T_0, °C	176	164		157	169
Tm, °C	209	201		206	200
Te, °C	236	226		229	220
Peak height, mW	1	1		1	1
ΔT, °C	60	62		72	51
After 60 min					
ΔH, J/g	39	36	83	27	20
T_0, °C	172	163	162	175	172
Tm, °C	207	200	208	206	201
Te, °C	238	225	243	228	220
Peak height, mW	1	1	2	1	1
ΔT, °C	66	62	81	53	48

1	2	3	4	5	6
After 120 min					
ΔH, J/g	41	27	22	33	16
T_0,°C	194	171	181	162	175
1	2	3	4	5	6
After 120 min					
Tm,°C	209	201	208	206	201
Te,°C	242	224	232	230	220
Peak height, mW	1	1	1	1	0.7
ΔT, °C	58	53	50	68	45
After 24 h					
ΔH, J/g	40	30	20	21	28
T_0, °C	173	158	180	167	172
Tm, °C	208	203	204	201	206
Te, °C	238	238	224	223	228
Peak height, mW	1	0,6	0.9	0.8	0.9
ΔT, °C	65	80	44	56	56
After 48 h					
ΔH, J/g		20	24	18	20
T_0, °C		177	179	183	178
Tm, °C		207	207	209	206
Te, °C		234	230	228	227
Peak height, mW		0,8	0.9	1	0.9
ΔT, °C		57	51	45	49

It can be assumed that the following reactions can take place in the modified compositions at elevated temperatures: epoxy groups with carboxyl groups of fatty acid, which was observed during epoxidation of RSO [17], as well as triglycerides of higher fatty acids with an amine hardener to obtain fatty acid amides [18, 19].

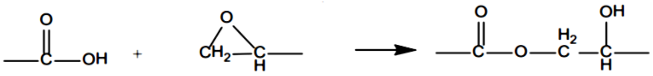
These reactions do not appear as individual peaks on the DSC curves, but probably contribute to the overall effect, as indicated by the increase in the enthalpy of the second process (Table 3) immediately after mixing the components in modified RSO and ERSO compositions.

To confirm the possibility of interaction of rubber seed oil with epoxy resin, spectra of DSC ED-20 and its mixture with RSO were taken. The results shown in Fig. 3 indicate the presence of a chemical interaction between these components.

This reaction begins at a higher temperature (T_o = 188 °C) and the thermal effect (7.4 J/g) is significantly lower than in modified RSO epoxy compositions with AF-2 (Table 3). With the growth of the exposure time of the mixture ED-20 – RSO, the temperature of this peak and the thermal effect increase.

Thus, it can be assumed that the second exothermic process in the cured AF-2 compositions containing RSO is the imposition of several chemical reactions, namely, the additional curing of ED-20 and the interaction of epoxy resin and rubber seed oil.

Indeed, the literature [20] describes the esterification reaction between epoxy and carboxyl groups occurring at temperatures of 120 – 160 °C according to the following scheme:



$$-C(=O)-OH + CH_2(-O-)CH- \longrightarrow -C(=O)-O-CH_2-CH(OH)-$$

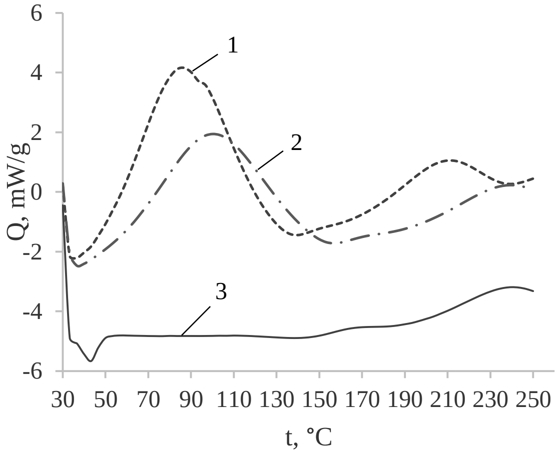


Fig. 3. DSC curves 1 – ED-20 and its mixture with RSO (in a ratio of 10:1); 2 – immediately after their mixing and 3 – after 60 min of their exposure at room temperature

Рис. 3. ДСК кривые 1 – ЭД-20 и смеси ее с МКД в соотношении 10:1, 2 –снятые сразу после смешения и 3 – через 60 мин

Homopolymerization of ED-20 takes place at a much higher temperature (T_o = 259 °C), than the process of its interaction with rubber seed oil (Fig. 3).

And the thermal effect of this reaction (4.7 J/g) is significantly lower than all previously described.

CONCLUSION

By DSC method it was found that modification of epoxy compositions by both soybean and rubber seed oils and their epoxidized derivatives slows down the curing process of epoxy compositions, which is manifested in the shift of the beginning of this exothermic process to higher temperatures and the growth of their viability. This results in a less density of crosslinked structure of the materials.

When all the investigated compositions are heated during the curing process in the region of 200 °C, a second exothermic effect appears, which is significantly less in intensity than the first. It, associated, in our opinion, with the processes of - additional curing (reaction of epoxy and amine groups that did not react earlier due to steric difficulties). This is superimposed by the chemical interaction between the epoxy resin and the rubber tree oil, which occurs in a close temperature range.

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