

Modified Soybean Oil as a Nonvolatile Additive for Polymers

II. Acids Bonded on Oil

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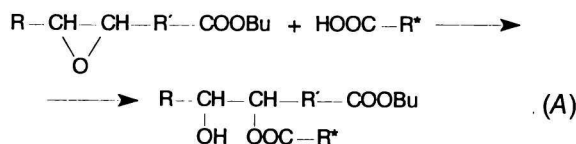
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The commercial epoxidized and with butanol esterified soybean and sunflower oil was by means of epoxy groups chemically modified with low-molecular compounds having a dissociating hydrogen. Compounds containing in their molecules nitrogen, sulfur, chlorine, bromine, and phosphorus atoms were bonded on the oil, whereby it is possible to consider for most of them a special effect. The molecular mass increase of modified soybean oil was reached by transforming it into a magnesium, calcium, strontium, barium, zinc or bismuth salt. The thermal analysis has proved that these materials can be used as nonvolatile additives for polymers processed at enhanced temperatures, which is closely linked with the creation and protection of the environment. The conditions of this general method for fixation of compounds on carriers of epoxidized groups, rate constants of reaction and the mechanism of its catalysis were discussed.

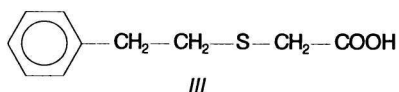
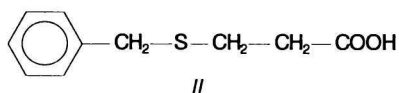
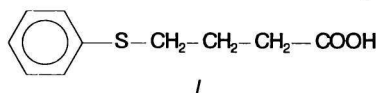
We reported in the previous paper [1] on the possibility of chemical modification of commercial epoxidized and with butanol esterified soybean and sunflower oil by amino compounds, which were bonded on oil by means of an epoxy group. We found in the temperature range between 130 to 170 °C that it is unconditionally necessary to apply a reaction catalyst for its fast course and that also in the case of bonding a highly basic amine. In the role of catalysts compounds capable of rendering a dissociating hydrogen have shown to be suitable. The aim was to bond some low-molecular compounds with a special effect, which could be used in the form of a nonvolatile additive for polymers. The amines are bonded on the oil by strong C—N bonds, resistant against temperatures used by the processing of *e.g.* polyolefines; in this respect the calcium form of the additive is outstanding. Materials of this type were developed for rubber, whereby the carrier of the epoxy group was a modified castor or linseed oil [2, 3]. Another type of bond with epoxide after the reaction is formed by carboxylic group, or by another compound with an acidic hydrogen [4, 5]



Reactions of type (A) of modified soybean and sunflower oil epoxy group are dealt with in this paper. If R* group is characterized by a special effect, it is possible to consider the modified oil as a nonvolatile additive for polymers.

EXPERIMENTAL

Epoxybutylester S (EBS) was a commercial epoxidized and with butanol esterified soybean and sunflower oil with the determined content of epoxy oxygen of 4.75 mass % [1]. Thiocarboxyl acids, as γ -phenylthiobutyric acid (I), β -benzylthiopropionic acid (II) and S-phenylethylthioglycolic acid (III)



and also 3-(4-hydroxy-3,5-di-*tert*-butylphenyl)propionic acid were delivered from the Research Institute of Macromolecular Chemistry, Brno. Diethanolamide of maleic acid was synthesized from diethylamine and maleic anhydride in chloroform. Monophenylphosphoric, dichloroacetic, 2-(4-chlorophenyl)-1-chloropropionic, and monobromoacetic acids, further *p*-chlorophenol, 3,5,3,5-tetrabromo-2,2-dihydroxydiphenyl, 2-mercaptobenzothiazole, benzyltrimethylamine, tribenzylamine, and triethanolamine were commercial compounds and purified before use [6]. The used nitrogen was purified from oxygen traces at room temperature, the used solvents were anal. grade.

Procedures and Apparatus

The reactions of EBS epoxide with low-molecular compounds were carried out in sealed ampoules in

nitrogen atmosphere by a previously described procedure [1]. In a standard experiment 5 g of EBS was used and the other components of the system were dosed in a certain mole ratio to the epoxy group in the system. Solvents were dosed if they were needed for the homogenization of the sample. After the reaction the oil was shaken with a sodium hydroxide solution, acetic acid and finally with water and it was dried *in vacuo* to the constant mass. If water-insoluble alcohol was present as solvent, it was removed by distillation in water azeotrope. After the analysis of oil for the characteristic element (N, S, P, Cl, or Br) the result of the reaction was expressed as the mass fraction (*w*%) of EBS epoxide reacted with the given compound. In the case that these were water-soluble acids, it was possible to determine the conversion by determination of the unreacted acid by a procedure described previously for an unreacted amine [1]. In the case of the water-soluble acid, 3-(4-hydroxy-3,5-di-*tert*-butylphenyl)propionic acid which in addition has no characteristic element, it was proceeded in such a way that the acid was extracted by means of an aqueous hydroxide solution and it was precipitated after acidifying. The retained acid was washed and the amount of it was determined by means of alkalimetric titration.

If the compound was not bound on EBS by an ester group, it was possible to prepare its calcium form [1], or a salt of another metal. The modified EBS was obtained by extraction with hot dioxane. The product was subjected to the analysis for the characteristic element.

The reaction between EBS epoxide and the compound containing dissociable hydrogen was described by the rate constant in the case of a bimolecular reaction of the second order with the excess of one component according to the relations reported previously [7].

Thermal analysis of samples for the modified EBS was performed on air by the apparatus Derivatograph System F. Paulik–J. Paulik–I. Erdey (MOM, Budapest).

RESULTS AND DISCUSSION

The possibility of bonding compounds with a carboxy group on EBS epoxide in the presence of the most used catalyst, the tertiary amine, is quoted in Table 1. For the formulation of the composition of the systems the knowledge from amine bonding on EBS was used [1]. A significant fact found was that the reaction of mentioned acids is under given conditions fast and that the use of a catalyst is not inevitable, and may in the case of bonding a diethanolamide of maleic acid containing a nitrogen atom it has even a negative influence on the reaction. That is a fundamental difference in comparison with a similar amine bonding on EBS [1].

We studied the influence of the catalysis of the reaction of EBS epoxide with thiocarboxylic acids differing in the position of the sulfur atom in the chain (Table 2) in more detail. Also in spite of relatively low temperature at the reaction and short time of acting conversions higher than 50 % of EBS epoxide reacted with acid were gained. In compli-

Table 1. Influence of the Amine Catalyst and Used Solvent on the Reaction of Acids and EBS Epoxide

Acid ^a	Catalyst ^a	Solvent ^b	θ /°C	<i>t</i> /h	Reacted epoxide ^c <i>w</i> /%
S-Phenylethylthioglycolic acid (1.2 : 1)	–	–	170	2	73.2
	Benzyl-dimethylamine (0.05 : 1)	–	170	2	80.3
	Benzyl-dimethylamine (0.2 : 1)	–	170	2	80.7
↓ Diethanolamide of maleic acid (1.2 : 1)	–	Dimethylformamide	160	8	41.5
	Triethanolamine (0.3 : 1)	Dimethylformamide	160	8	42.1
	–	Dimethylformamide	170	16	78.0
	–	Hexanol	170	16	75.4
	Triethanolamine (0.3 : 1)	Dimethylformamide	170	16	61.6
	Triethanolamine (0.3 : 1)	Hexanol	170	16	63.5
	Benzyl-dimethylamine (0.3 : 1)	Dimethylformamide	170	16	63.5 (40.6) ^d
	Benzyl-dimethylamine (0.3 : 1)	Hexanol	170	16	78.5 (61.7) ^d
	↓				

a) Mole ratio of compound with regard to the EBS epoxide content in the system; b) For homogenization of the sample 2.5 cm³ of solvent per 1.0 cm³ of EBS was used; c) values obtained from S resp. N determination in the product; d) in the presence of benzyl-dimethylamine (0.45 : 1).

Table 2. Influence of the Amine Catalyst on the Reaction of Thiocarboxylic Acids with EBS Epoxide at 130 °C for 1 h

Acid (1.2 : 1) ^a	Catalyst (0.1 : 1) ^a	Reacted epoxide w/%	Change ^b %
S-Phenylethylthioglycolic acid pK = 2.25 ^c	—	59.5	—
	Benzyl-dimethylamine	70.3	+ 18.2
	Tribenzylamine	62.0	+ 4.2
β-Benzylthiopropionic acid pK = 4.27 ^c	—	54.4	—
	Benzyl-dimethylamine	65.3	+ 20.0
	Tribenzylamine	56.4	+ 3.6
γ-Phenylthiobutyric acid pK = 4.47 ^c	—	50.3	—
	Benzyl-dimethylamine	62.3	+ 23.9
	Tribenzylamine	47.3	- 0.6

a) Mole ratio with regard to the EBS epoxide content in the system; b) conversion change against the noncatalyzed sample; c) referred according to literature [4].

ance with theoretical considerations [4] the mass fraction of reacted epoxide depends on pK of bonded acid. In this case the dissociation degree of the carboxy group is influenced by the position of the sulfur atom in the chain. The influence of the catalyst based on tertiary amine depends on the ability to interact with epoxide and therefore it can be strongly decreased by interaction with the present

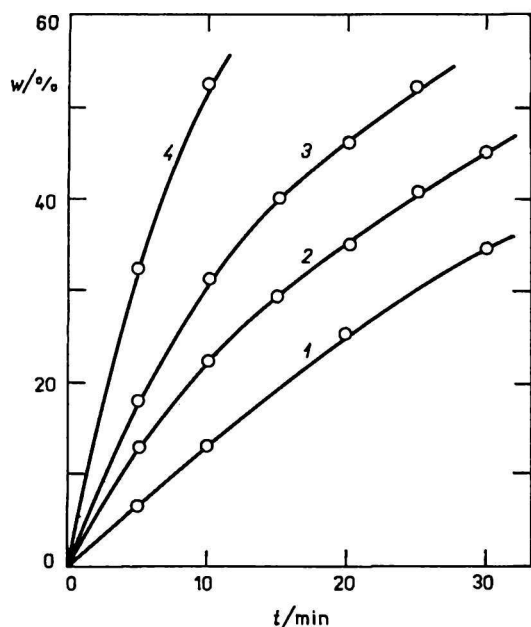


Fig. 1. Influence of time on the mass fraction of EBS epoxide reacted with S-phenylethylthioglycolic acid (in the mole ratio 1.2 : 1 with regard to epoxide) at 130 °C (2, 72.9 % in 6 h) under simultaneous presence of benzyl-dimethylamine catalyst (0.1 : 1) at 110 °C (1, 69.5 % in 6 h), 130 °C (3, 79.7 % in 6 h), and 170 °C (4, 82.0 % in 6 h).

acid [7]. In the case that the question is of strongly basic catalyst and strongly dissociated acid, in an extreme case the deactivation of the catalyst may occur, and especially a decreasing of the active concentration of acid which is bonded in the system. In accordance with that in Table 2 the catalysis of the dissociated γ-phenylthiobutyric acid by the more basic benzyl-dimethylamine proves to be more significant than the same catalysis of the more dissociated S-phenylethylthioglycolic acid. It is possible to observe an opposite influence in the case of using the less basic tribenzylamine, but it is with its low catalytic activity practically of no importance.

Fig. 1 illustrates the initial time sections of the reaction of the selected thioacid with EBS epoxide and also the possibilities of the system by influence of catalysis, temperature, and time. Values gained at 130 °C were used for calculation of reaction rate constants [1] (Fig. 2). This temperature was chosen with the effort to reach restriction of side reactions as much as possible. From Fig. 2 were determined reaction rate constants of the reaction of S-phenylethylthioglycolic acid with EBS epoxide, and that of a noncatalyzed one, k_0 , as a catalyzed one with benzyl-dimethylamine (in the mole ratio 0.1 : 1 with regard to epoxide), k_t [1]

$$k_0^{130} = 2.4 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$k_t^{130} = 3.9 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

From the determination of the mentioned rate constants of relatively strongly dissociated thiocarboxylic acid it follows that:

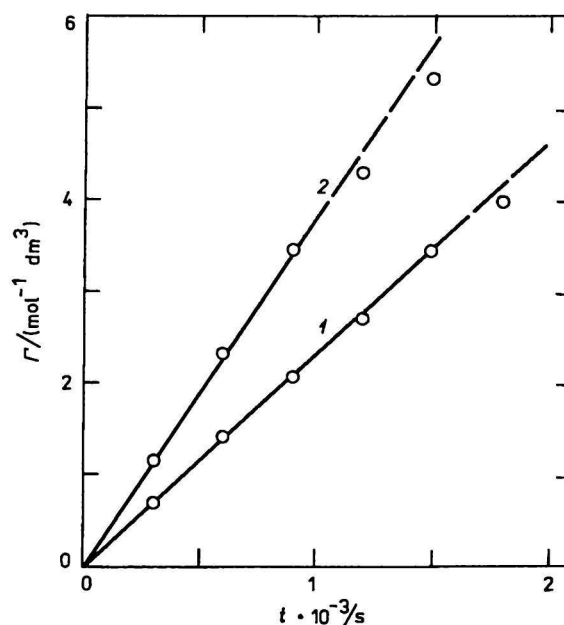
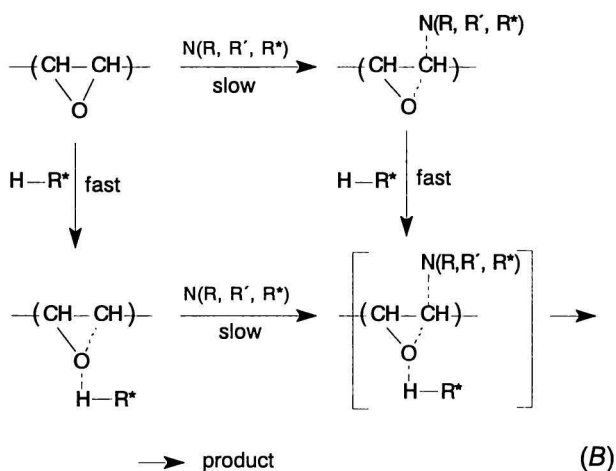


Fig. 2. Dependence of Γ [1] on time as a basis for the estimation of the rate constant of the reaction of S-phenylethylthioglycolic acid (1.2 : 1) with EBS epoxide at 130 °C. 1. Noncatalyzed reaction; 2. reaction catalyzed with benzyl-dimethylamine (0.1 : 1) (Fig. 1, curves 1 and 2).

- the relatively small influence of the catalyst on the basis of a tertiary amine was proved;
- the reaction is faster than the reaction of a strongly basic amine also in the presence of a catalyst [1], whereby during bonding of the acid the reaction temperature also of 110 °C is actual;
- the reaction is faster than the reaction of the same thiocarboxyl acid with epoxide bonded on a grafted polypropylene [4].

These comparisons can be discussed by the well-known mechanism of acting of the pair amine—acid on an epoxide, whereby one component of the pair is a catalyst and the other one a bonded compound. The epoxide group can be a terminal one [4, 8—12], or it can be on another place in the molecule [13—17], as it is in the case of EBS. In the second case it is immediately a difference in the readiness of both compounds for addition on epoxide



According to the conception of the scheme (B) the acting of the nucleophilic agent on the C—O epoxide bond from the carbon side is made difficult by space hindrances. For the fast reaction course the common participation of the electrophilic agent in a relatively high concentration during the opening of the epoxide ring is necessary. In the case of the terminal epoxide the space factor does not so much exhibit itself and the strongly basic amines are bonded on epoxide easily even without the catalyst assistance. From the viewpoint of acting of the electrophilic agent on the C—O bond its access to the epoxide from the oxygen side is not influenced by the epoxide position in the molecule; therefore in both cases adequate rates of the reaction of epoxide with acid are reached also without the use of catalyst.

The mentioned comparison of rate constants has only an intimation character, because in the case of the modification of EBS the question is of a homogeneous system, while by bonding compounds on grafted polypropylene with epoxide groups the

question is of a heterogeneous system [4, 5, 12]. This conditions also the difference of the possibility for the course of side reactions, mainly epoxide: while epoxide bonded on polypropylene powder is fixed on its surface, EBS epoxide in homogeneous phase can substantially react also with groups formed by the reactions, as are —OH and —NH groups formed in the reactions with primary amines. The problem of the possible participation of —OH groups in the further reaction was discussed previously [1], here in the case of the reaction of epoxide with strongly dissociated acids it is possible to complete it with a possible esterification, in consequence of which more material is bonded on oil, as it corresponds to the epoxide content in the oil [4]. From the viewpoint of the discussed interaction amine—EBS epoxide according to the scheme (B) it is possible to attribute to the influence of the formed —NH group during bonding of primary EBS only a small importance for the consumption of epoxide by this side reaction. In this sense it is possible to consider also the improbability of the reaction of the hindered —NH group during bonding of the HALS type compounds on EBS [1].

With the catalyzed reaction of epoxide also a noncatalyzed reaction simultaneously takes place, which is expressed by the obtained total reaction rate constant $k_t = k_0 + k_{cat}c_{cat}$, where k_{cat} is the rate constant of the catalyzed reaction and c_{cat} the catalyst concentration. This form is valid in that case, when further possible influences are neglected, as for instance autocatalysis of the reaction [13] and the influences of such solvents which are donors or acceptors of hydrogen bond [9] are not competitive.

The common influence of the pair amine—acid on EBS epoxide according to the scheme (B) brings in the practice two problems:

1. For the reaction of amine with epoxide it is difficult to find such catalyst with a hydrogen capable to dissociate that will not bond at working temperature at least partly on the EBS epoxide; but here is no complication as for the interaction amine—catalyst, while the catalyst is a higher alcohol [1];
2. The tertiary amine catalyst used for the reaction of acid with epoxide admittedly has no precondition to be bonded on epoxide, but here is a serious problem of its interaction with acid.

But from the practical point of view the first problem brings also an advantage to bond on EBS simultaneously two compounds, when the reactivities of acidic and amine components are suitably balanced in the system. In that way materials with combined special effect can be obtained whereby a synergistic effect of both compounds would be the optimum. Another procedure of bonding two compounds could be carried out in such a manner

that the first compound is bonded in moderate conditions and the unreacted epoxide is preserved.

On EBS epoxide it is possible to bond also further compounds with dissociating hydrogen, as for instance compounds with —OH groups on the aromatic ring acidified by halogen, further mercaptans, eventually inorganic acids. In Table 3 are stated some examples of bonding of such compounds on EBS epoxide, whereby it is possible to consider for them a special effect [18–21]. The yield of the modified oil in the given conditions is in the range of 78–92 % with regard to the added EBS. As it was referred previously [1], EBS can be modified after the hydrolysis of the ester group in the form of a calcium salt. Table 4 states the possibilities for

Table 3. Influence of Reaction Conditions on the Content of EBS Epoxide Reacted with Compounds Containing Dissociable Hydrogen

Compound (1.2 : 1)	$\theta/^\circ\text{C}$	t/h	Reacted epoxide w/%
Dichloroacetic acid	25	4	64.5 ^b
Dichloroacetic acid	130	4	93.6 ^b
Dichloroacetic acid	170	4	101.3 ^b
Monobromoacetic acid	150	8	77.4 ^b
Monobromoacetic acid	170	4	83.8 ^b
2-(4-Chlorophenyl)-1-chloro-propionic acid	150	8	90.8
2-(4-Chlorophenyl)-1-chloro-propionic acid	170	4	100.5
<i>p</i> -Chlorophenol	170	8	58.1
3,5,3,5-Tetrabromo-2,2-dihydroxydiphenyl	170	8	48.1
3-(4-Hydroxy-3,5-di- <i>tert</i> -butylphenyl)thiopropionic acid	170	16	48.3 ^b
Monophenylphosphoric acid	150	8	34.3 ^c
Monophenylphosphoric acid	170	8	22.7
2-Mercaptobenzothiazole	170	8	32.1

a) Determined from the analysis of the characteristic element in the product; b) determined from the analysis of the unreacted acid amount after reaction; c) in the presence of benzyldimethylamine catalyst (0.1 : 1).

Table 4. EBS Salts with Bonded Dispiro[5,1,5,3]-7,15-diazahexadecane (EBS—D) Formed by Precipitation of Salts of Various Metals from (EBS—D)Na^a

Precipitant Me ⁿ⁺	(EBS—D) _n Me ⁿ⁺	
	w(N)/%	w(P)/%
MgCl ₂	4.0	
CaCl ₂	3.5	
Sr(CH ₃ COO) ₂	3.5	
BaCl ₂	3.5	
ZnCl ₂	3.0	
Bi(NO ₃) ₃	2.3	
CaCl ₂ ^b		1.1
CaCl ₂ ^c	0.8	

a) The original EBS—D material contained 4.0 mass % N; 1 mass % (EBS—D)Na solution was precipitated with a 5 mass % salt solution; b) Monophenylphosphoric acid was bonded on EBS; c) 2-Mercaptobenzothiazole was bonded on EBS.

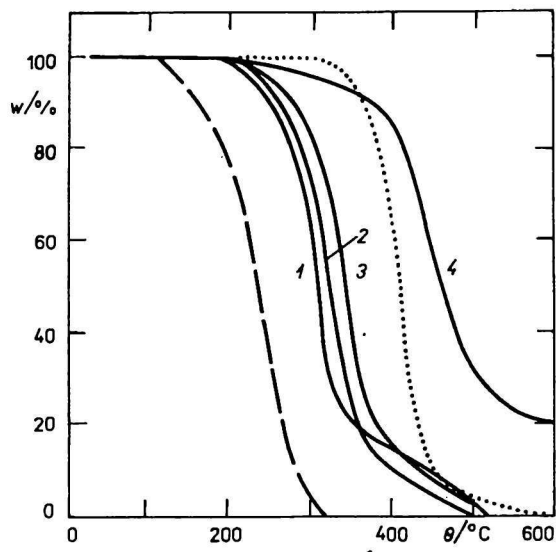


Fig. 3. Course of TG curves at thermolysis of selected synthesized materials on the basis of modified EBS. 1. EBS heated at constant temperature for 16 h at 170 °C; 2. EBS with bonded *S*-phenylethylthioglycolic acid; 3. EBS with bonded 3-(4-hydroxy-3,5-di-*tert*-butylphenyl)propionic acid; 4. EBS with bonded monophenylphosphoric acid in the form of a Ca²⁺ salt; dashed line — Antioxidant 4; dotted line — Irganox 1076.

the preparation also of other salts by this procedure for EBS with a bonded Cr stabilizer of the HALS type. As far as the aim was to increase the molecular mass of the additive, preparation of bismuth^{III} salt is worth of attention. Another process of synthesis starting from EBS salt and enabling to bond also compounds with an ester bond was not successful, because during the hydrolysis of the ester group of EBS the epoxide groups were damaged. Other methods, starting from oleic acid were beyond the frame of this work.

In Fig. 3 is illustrated the course of thermolysis of selected materials, which after mixing into polymers are considered to exhibit a special effect. Similarly as in the previous paper [1] it can be stated that compounds on the basis of modified EBS are characterized at least with such a resistance against thermal decomposition under the access of air as the EBS itself. From the course of thermolysis of commercial thermooxidative stabilizers Antioxidant 4 and Irganox 1076 the different intention concerning the retention of the additive in the polymer after it was thermally treated is evident. Our intentions with the structure modification of EBS follow the possibility to protect the polymer during its subjection to heat and its application. Table 5 summarizes the characteristic thermolysis data of modified EBS (also taken over from the previous paper [1]) about prepared materials also from the point of view of their possible application at increased temperature. Calcium forms of additives are again

Table 5. Thermoanalytical Characteristics of EBS with Bonded Selected Compounds

Bonded compound		θ_{init}^b	θ_{max}^c	$R(300)^d$	$R(600)^d$
Type	w/% ^a	°C	°C	mass %	mass %
– (EBS alone ^e)	–	190	320	65	0
T	23.9	220	340	82	0
T (Ca ²⁺ salt)	21.9	220	430	87	6
D	38.1	240	355	84	0
D (Ca ²⁺ salt)	27.6	240	430	92	8
Diethanolamine	24.5	195	330	74	0
Diethanolamine (Ca ²⁺ salt)	22.4	240	430	88	8
Diethanolamide of maleic acid	31.0	205	330	79	0
S-Phenylethylthioglycolic acid	31.2	200	340	80	0
3-(4-Hydroxy-3,5-di- <i>tert</i> -butylphenyl)propionic acid	27.5	210	345	85	0
Monophenylphosphoric acid	13.3	200	320	78	9
Monophenylphosphoric acid (Ca ²⁺ salt)	5.6	240	455	95	21
Dichloroacetic acid	18.2	195	280	59	0
2-(4-Chlorophenyl)-1-chloropropionic acid	38.3	190	320	63	0
<i>p</i> -Chlorophenol	17.4	130	340	68	0
Monobromoacetic acid	22.8	210	280	53	0
3,5,3,5-Tetrabromo-2,2-dihydroxydiphenyl	40.5	200	290	51	0

a) Content of bonded compound in the modified EBS; b) temperature of initial decomposition of material from DTG curve; c) temperature at which the sample is decomposed at the maximum rate (from DTG curve); d) $R(\theta)$: undecomposed residue of sample at 300 °C resp. 600 °C; e) EBS was heated at 170 °C for 16 h in advance.

characterized with high resistance. Material containing halogen is more easily decomposed, which was proved previously [6] by its effect on polypropylene. While the values θ_{init} , θ_{max} , and $R(300)$ are evaluating the material up to temperatures at which polypropylene is processed, the value $R(600)$ is a value of a mass residue at an extreme temperature. In the case of calcium salt form, the form can comprise in addition calcium compounds in the form of hydroxide or carbonate and in the case of a low epoxide conversion also calcium bonded on unreacted EBS. The value of $R(600)$ reflects in this way also the purity grade of the synthesized material.

Other possibilities of application of in this manner prepared material are everywhere, where they exhibit the advantage against low-molecular compounds. An example for the application of compounds bonded on EBS by an ester bond is the possibility of hydrolysis of this bond under certain conditions and in such a way to gradually release (dose) the active component. Yet it is possible to suggest that in principle it is not excluded to adapt these and previous results also for modified inland rape oils.

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