Modified Soybean Oil as a Nonvolatile Additive for Polymers
I. Amines Bonded on Oil

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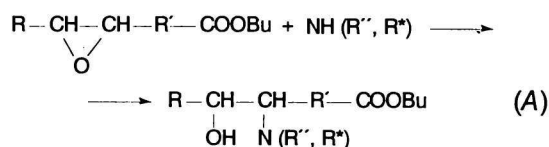SK-812 37 Bratislava

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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 an amine hydrogen. The conditions of the reaction, possibility of its catalysis and rate constants were referred. If compounds with special effect were bonded on the oil, a material with preconditions for use as nonvolatile additive for polymers was prepared. It is possible to attain the increase of molecular mass of additives by transforming them into calcium salt. The modified oil is thermally more stable than the original oil.

There is a great number of chemical compounds, which are characterized by a special effect (chemical, biological, physical, etc.), but they cannot be used frequently for their volatility at increased temperature, solubility and extractibility, toxicity, thermal lability or also bad smell [1—3]. There is an effort to bond together such compounds into larger molecules or on other molecules even up to macromolecules with the hope that their activity will not be considerably decreased by that treatment [4—7]. It is simultaneously a topic problem from the viewpoint of creation and preservation of environment.

In this paper some possibilities of chemical bonding of model amine compounds, but also of compounds with special effect (with the substituent R*), on commercial epoxidized and with butanol esterified soybean (and sunflower) oil according to a well-known scheme [8]

$$R-CH-CH-R'-COOBu + NH\,(R'',R^*) \longrightarrow$$
$$\underset{O}{\diagdown\diagup}$$

$$\longrightarrow\ \underset{OH}{R-CH}-\underset{N\,(R'',R^*)}{CH}-R'-COOBu \qquad (A)$$

are referred. The soybean oil modified in such manner can be applied as an additive with special effect for polymers. There are no reasons for restriction of their migration in polymer matrix nor for their mutual incompatibility. On the other hand, here are questions about the application of the additive in fibres [9].

EXPERIMENTAL

Epoxybutylester S (EBS) (Spolek pro Chemickou a Hutní Výrobu, Ústí nad Labem) is an epoxidized

and with butanol esterified soybean and sunflower oil. The quoted content of epoxy oxygen was 4.7 mass % [7]. Compounds of the HALS type like 2,2,6,6-tetramethyl-4-aminopiperidine (I) and dispiro-[5,1,5,3]-7,15-diazahexadecane (II) were delivered by the Research Institute of Chemical Technology in Bratislava and were purified before use by distillation, resp. recrystallization.
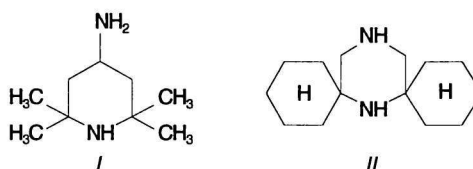
Cyclohexylamine, diethanolamine, ethylaniline, dibenzylamine, dipropylamine, dibutylamine, and piperidine were distilled before use. Glycerol, ethylene glycol, pentanol, hexanol, phenol, and the used solvents were anal. grade. The nitrogen was purified from oxygen traces on a catalyst of the composition 55 mass % MnO_2, 40 mass % MgO, and 5 mass % Cr_2O_3 at room temperature.

Procedures and Apparatus

The content of original or residual epoxy groups in original EBS or after reaction was determined by a modified method [10] using the following procedure: 1 g of EBS or carefully isolated and purified EBS after reaction was dissolved in 10 cm³ of dioxane, 20 cm³ of 0.2 M-HCl was added and after 30 min the amount of unreacted HCl was determined by means of 0.1 M-NaOH in methanol with Orthocresol Red indicator. The calculated epoxy oxygen content in EBS was (4.75 ± 0.11) mass %. In such manner determined content of the epoxy

residue in EBS after reaction was expressed as mass fraction of the reacted EBS epoxide determined by HCl (w(epoxide, HCl)/%).

Reactions of EBS epoxide with various compounds were carried out in nitrogen atmosphere in sealed ampoules, placed statically in a silicon bath at constant temperature. In a current experiment 5 g of EBS were added, and other compounds, as amine and catalyst, were dosed in addition in a certain mole ratio with regard to the content of epoxy groups in 5 g of EBS in the system (equal to 100 mole %). After the reaction the mixture was subjected to extraction of unreacted amine by multiple shaking with water and the unreacted amine was determined in extract with HCl, from which the EBS epoxide reacted with amine was estimated (w(epoxide, amine)/%). In the case that a water-insoluble amine was used in the reaction with EBS epoxide, the oil was extracted by water acidified with acetic acid. If a water-insoluble higher alcohol was used in the role of catalyst, it was distilled off azeotropically. In both cases the mass fraction of unreacted EBS epoxide was calculated on the basis of nitrogen analysis in oil, by which also the composition of all samples with bonded amine was checked. The oil product was dried *in vacuo* at room temperature up to the constant mass.

Epoxybutylester S with bonded amine (EBS—A) was subjected to saponification of butyl ester group in a flask with an azeotropic adapter for trapping the condensing vapour. 5 g of oil was heated at 115 °C with 30 cm^3 of 30 % aqueous NaOH solution until butanol ceased to distil in azeotrope with water. The solid product was dissolved in 500 cm^3 of water and the curdy product (EBS—A)$_2$Ca was precipitated with 5 % aqueous CaCl$_2$ solution. The precipitate was washed on the filter and dried on air to the constant mass. Besides of the product the precipitate contained a small amount of calcium hydroxide, eventually calcium carbonate. (EBS—A)$_2$Ca was extracted from the mixture by boiling dioxane or ethanol. By evaporation a honey-like material was obtained, which after cooling could be grind as rosin.

The reaction between EBS epoxide and amine was quantitatively characterized by the rate constant k for the case of a bimolecular reaction of the second order with the excess of one component according to the relation [8]

$$kt = \frac{1}{c_{0A} - c_{0B}} \ln \frac{c_{0B}[c_{0A} - c(t)]}{c_{0A}[c_{0B} - c(t)]} = \Gamma$$

where c_{0A} and c_{0B} are initial concentrations of EBS epoxide and amine in the system and $c(t)$ is the concentration of reacted epoxide in the time t.

The thermal analysis of the prepared materials on the basis of modified EBS was provided on air with the device Derivatograph System F. Paulik—J. Paulik—I. Erdey (MOM, Budapest).

RESULTS AND DISCUSSION

By the determination of EBS epoxide it was found that it is relatively stable also at temperature of 170 °C (Table 1). The presence of ethylene glycol at higher temperatures causes a loss of epoxide and it is possible to consider it as a compound with labile hydrogen by which it is bonded also on epoxide. This reaction can be restrained, if a reactive amine

Table 1. Influence of Temperature and Presence of Some Compounds on EBS Epoxide Decomposition

Compound[a]	$\theta/°C$	t/h	w(epoxide, HCl)/%
–	130	3	1.7
–	150	3	3.2
–	170	2	2.3
–	170	4	5.5
Ethylene glycol	130	4	4.2
Ethylene glycol	170	2	25.3
Ethylene glycol	170	4	35.7
Dimethylformamide	170	4	8.9
Ehylene glycol + Dimethylformamide	170	4	25.2

a) Mole ratio of compound with regard to the EBS epoxide content in the system 1 : 1; compounds before the epoxide determination were extracted with water.
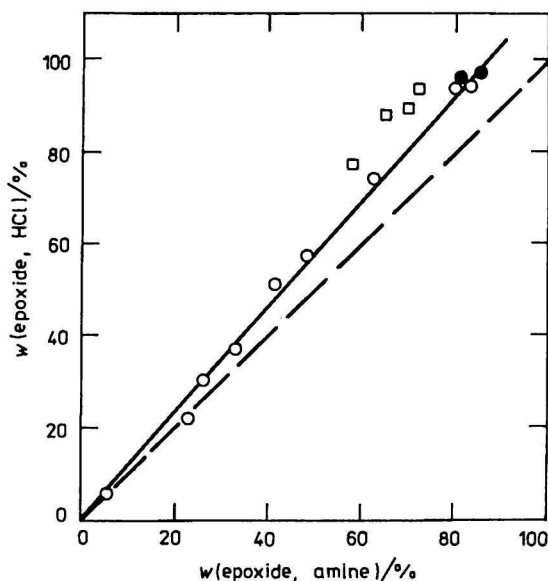
Fig. 1. Correlation between the mass fraction of reacted EBS epoxide determined on the basis of its residual amount with HCl and on the basis of unreacted amine determination at the reaction of cyclohexylamine (in the mole ratio 1.2 : 1 with regard to epoxide) with epoxide in the presence of ethylene glycol catalyst (1 : 1) at various temperatures. ○ 130 °C; ● 150 °C; □ 170 °C.

Table 2. Influence of Reaction Conditions on the Mass Fraction of EBS Epoxide Reacted with Amine Compounds for 3 h

Amine[a]	Catalyst[a]	θ/°C	w(epoxide, amine)/%
Piperidine (1 : 1)	–	100	18.4
Piperidine (1 : 1)	H_2O (1 : 1)	100	28.7
Cyclohexylamine (1.2 : 1)	–	125	0.0
	–	135	7.5
	Phenol (0.2 : 1)	135	22.7
	Pentanol (0.4 : 1)	135	17.9
	H_2O (1 : 1)	135	45.4
	–	170	44.0
	Glycerol (1 : 1)	170	77.8
	Ethylene glycol (1 : 1)	170	81.8 (89.2)[b]
	Ethylene glycol (1 : 1) + Phenol (0.2 : 1)	170	68.1
Dibutylamine (1.2 : 1)	Pentanol (1.2 : 1)	150	11.9
	Ethylene glycol (1 : 1)	150	29.3
	Ethylene glycol (1 : 1)	170	73.4
Diethanolamine (1 : 1)	–	135	22.2
Diethanolamine (1 : 1)	Pentanol (0.4 : 1)	135	40.7
Diethanolamine (1.2 : 1)	Pentanol (1.2 : 1)	170	79.2 (87.0)[b]
Diethanolamine (1.2 : 1)	Ethylene glycol (1 : 1)	170	65.1 (92.5)[d]
T (1.2 : 1)	Ethylene glycol (1 : 1)	170	89.4[d]
D (1.2 : 1)	Hexanol (1.2 : 1)	170	98.1[e]

a) Mole ratio of compound with regard to the EBS epoxide content in the system is given in parenthesis; b) for 6 h reaction; c) diethanolamine is partly soluble in oil at working temperature; d) for 12 h reaction; e) for 16 h reaction. T — 2,2,6,6-tetramethyl-4-aminopiperidine; D — dispiro[5,1,5,3]-7,15-diazahexadecane.

compound is present in the system and ethylene glycol acts as a catalyst [8].

It is possible to demonstrate it on a model system, in which cyclohexylamine (120 mole %, *i.e.* the mole ratio 1.2 : 1 with regard to epoxide) was bonded on EBS epoxide by catalytic action of ethylene glycol (100 mole %, 1 : 1). Correlating the mass fraction of EBS epoxide reacted with amine, which was obtained by determination of epoxy residue after the reaction with HCl, with that of the amine residue after the reaction of the same sample, it can be seen (Fig. 1) that in most cases w(epoxide, HCl)/% is higher than w(epoxide, amine)/%. Further, samples prepared at the highest temperature 170 °C are beyond of the common linear relation. That is not caused by the presence of bonded amine on oil, because that one with regard to the method of epoxide determination does not bond HCl irreversibly [11a]. The difference between both values of the mass fraction of reacted epoxide can be possibly attributed to epoxide consumption by other reactions than amine bonding. Besides the influence of temperature, presence of alcohol or moisture, it can be also a reaction between the formed secondary amine group and secondary alcohol in EBS with epoxide. Therefore further the w(epoxide, amine)/% was considered as a more objective evaluation of the mass fraction of epoxide reacted with amine, which was also proved by checking this value on the basis of nitrogen content determination in modified oil after reaction.

The possibility of bonding selected amine compounds on EBS epoxide is summarized in Table 2. It is evident that:

– the reaction of EBS epoxide with amine is running significantly at temperatures of approximately 100 °C only by the use of an extraordinary reactive amine, as piperidine [8, 12];

– to attain a fast reaction course, and that also in the case of strong basis amines, it is necessary to use a catalyst, as for instance a compound with labile hydrogen [8, 13];

– the reached results of mass fraction of EBS epoxide reacted with amine near to 80—90 % indicate that the assumed importance of the considered side reaction which exhausts the EBS epoxide even in severe conditions is limited;

– the reactivity of the used amine types can be arranged in the following descendent order: heterocyclic bonded amine in piperidine [8, 12] >> secondary amine in diethanolamine > primary amine in cyclohexylamine > secondary amine in dibutylamine (in case of diethanolamine it is not possible to exclude the catalytic influence of alcoholic groups).

In Table 2 possibilities of bonding of secondary amines also of the HALS type, which have a precondition of special effect (light stabilizer particularly for polyolefines) are stated.

The secondary amines in the reaction with EBS epoxide were studied in an individual experiment (Table 3), which proved that also in this case the
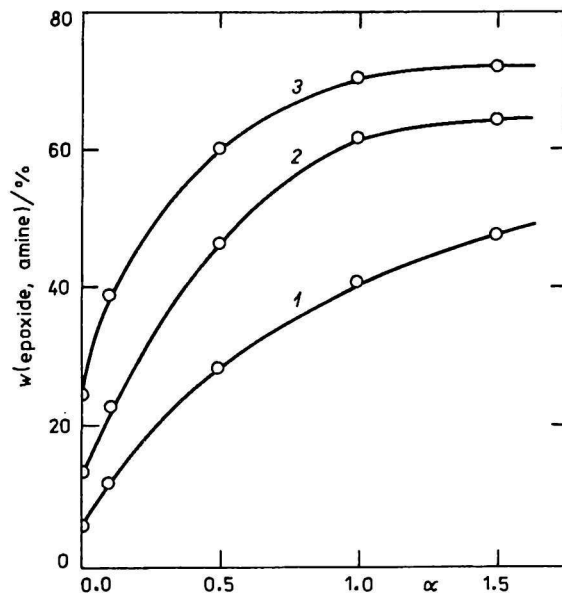
Table 3. Influence of Catalyst with Labile Hydrogen on the Reaction of Secondary Amines with Various Alkalinity with EBS Epoxide at 150 °C

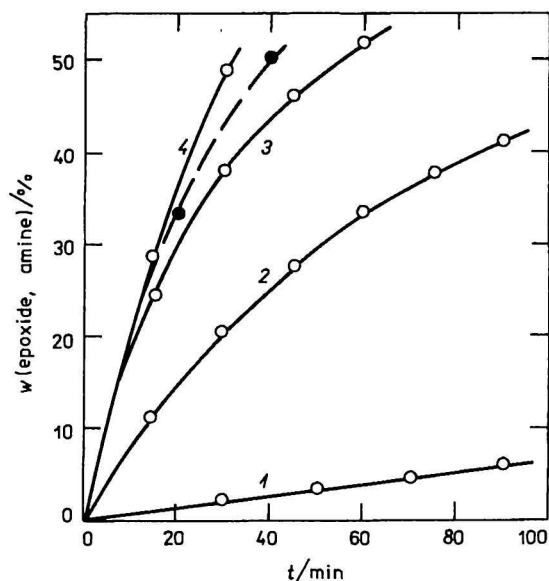| Amine[a]	Catalyst[a]	t/h	w (epoxide, amine) %	Change[b] %
Ethylaniline $pK = 5.12$	—	12	5.7	—
	Hexanol		6.0	5.3
	Phenol		56.5	891.2
Dibenzylamine $pK = 8.09$	—	6	8.6	—
	Hexanol		10.0	16.3
	Phenol		45.2	425.6
Dipropylamine $pK = 11.30$	—	3	5.7	—
	Hexanol		9.7	64.9
	Phenol		27.3	378.9

a) Mole ratio of compound with regard to the EBS epoxide content in the system 1.2 : 1; b) Conversion change against the noncatalyzed sample.

amine activity increases with its basicity, because similar conversions were obtained at various times. From the viewpoint of increased conversion of a catalytic reaction in comparison with a noncatalytic one, it can be seen that phenol, as a more acidic catalyst, is more effective for a less basic amine. On the contrary, it is more advantageous from that viewpoint to use hexanol for the reaction with a more basic amine. That is in accordance with the relations observed for the case when epoxide was bonded on powdered grafted polypropylene [8, 13]. Here exists a common principle that if the combination of bonded compound and catalyst has to be active, their mutual interaction must be strongly restrained, in order to create conditions of their individual reaction with epoxide. For that reason the combination of highly active components is unfavourable for the result of the reaction, as well as the combination of a low basic amine with a low dissociated catalyst.

The amine excess against epoxide in a mutual reaction is a question of compromise [12]. The content of alcoholic catalyst (phenol was not used in further experiments for its possible parallel reaction with epoxide [8, 13]) assumes at least its equimolar amount to epoxide in the system (Fig. 2). In the case of using diethanolamine the alcoholic catalyst acts in addition as a homogenizer of the system at working temperature. The advantage of ethylene glycol use is its water solubility. As far as the participation of both its hydroxyl groups is concerned in the catalysis, it is possible to say that the estimated needed mole ratio of catalyst to EBS epoxide does not indicate this fact. The above statement is not at variance with knowledge found during bonding amines on rubber [14] or on natural oils [15—17] and that by means of their epoxy groups, while in the second case a catalytic effect of carboxylic groups of oils was assumed.

Fig. 2. Influence of the mole ratio of ethylene glycol to the EBS epoxide content in the system (α) on the mass fraction of epoxide reacted with cyclohexylamine during 1.5 h at various temperatures. 1. 130 °C; 2. 150 °C; 3. 170 °C.

The time course of reaction of cyclohexylamine with EBS epoxide under various conditions is referred in Fig. 3, inclusive of long time treatment, as examples for the possibilities of the system. For the determination of the reaction rate constant only the temperature 130 °C was suitable, which lies

Fig. 3. Influence of time on the mass fraction of EBS epoxide reacted with cyclohexylamine (in the mole ratio 1.2 : 1 with regard to epoxide) at 130 °C (1) and in the presence of ethylene glycol catalyst (1 : 1) at 130 °C (2, 79.5 % in 12 h), 150 °C (3, 87.0 % in 12 h), and 170 °C (4, 97.5 % in 12 h); the dashed line is for the time-dependent reaction of 2,2,6,6-tetramethyl-4-aminopiperidine (1.2 : 1) in the presence of ethylene glycol (1 : 1) at 170 °C (89.4 % in 12 h).

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Piperidine (1 : 1)	H_2O (1 : 1)	100	28.7
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	–	135	7.5
	Phenol (0.2 : 1)	135	22.7
	Pentanol (0.4 : 1)	135	17.9
	H_2O (1 : 1)	135	45.4
	–	170	44.0
	Glycerol (1 : 1)	170	77.8
	Ethylene glycol (1 : 1)	170	81.8 (89.2)[b]
	Ethylene glycol (1 : 1) + Phenol (0.2 : 1)	170	68.1
Dibutylamine (1.2 : 1)	Pentanol (1.2 : 1)	150	11.9
	Ethylene glycol (1 : 1)	150	29.3
	Ethylene glycol (1 : 1)	170	73.4
Diethanolamine (1 : 1)	–	135	22.2
Diethanolamine (1 : 1)	Pentanol (0.4 : 1)	135	40.7
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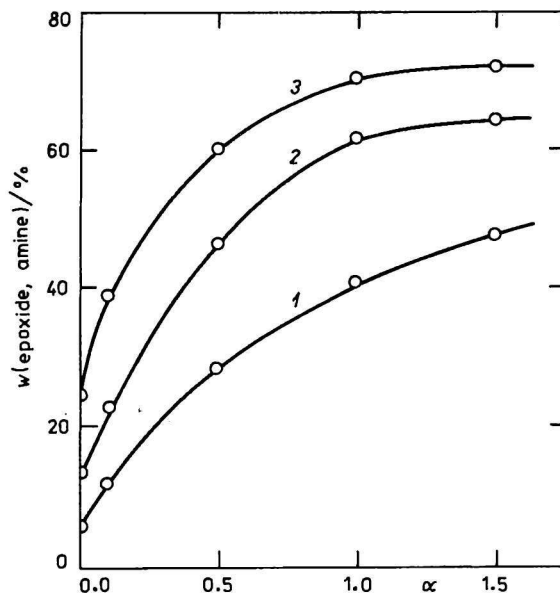
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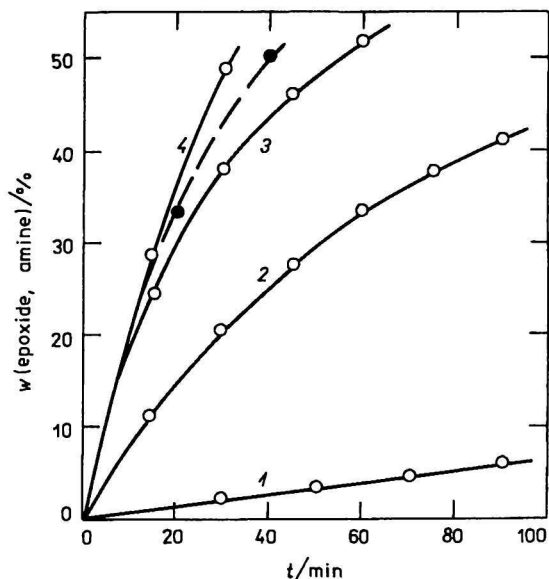| Amine[a]	Catalyst[a]	t/h	$\frac{w}{\text{(epoxide, amine)}}$ %	Change[b] %
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beneath the boiling temperature of cyclohexylamine and simultaneously restrains the occurrence of EBS epoxide side reactions. For the initial reaction stage, from curves 1 and 2 in Fig. 3 the rate constants of the reaction of cyclohexylamine with EBS epoxide and that in a noncatalyzed reaction k_0 as well as in the presence of ethylene glycol catalyst (mole ratio = 1 : 1 with regard to epoxide) k_t were graphically (Fig. 4) determined

$$k_0^{130} = 6.3 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$
$$k_t^{130} = 6.9 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

The value k_t represents the total reaction rate constant, where $k_t = k_0 + k_{cat} c_{cat}$, and k_{cat} is the rate constant of the catalyzed reaction in $\text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ at the catalyst concentration c_{cat}. The obtained values indicate the necessity of catalysis even of such a strong basic amine as cyclohexylamine, to obtain reaction rates of similar order at analogical reaction, but noncatalyzed, when the question was of the epoxide of powdered polypropylene grafted with 2,3-epoxypropylmethacrylate [8]. The mentioned rate constants can be in principle influenced by the autocatalytic effect of hydroxyl groups formed by the reaction (A) on EBS. But it is possible to neglect their influence at low conversion areas of epoxide and mainly at a simultaneous influence of a high concentration of primary alcohol used as a catalyst [14].

In Fig. 3 the initial course of bonding 2,2,6,6-tetramethyl-4-aminopiperidine on EBS epoxide is marked. It indicates the similarity with the course
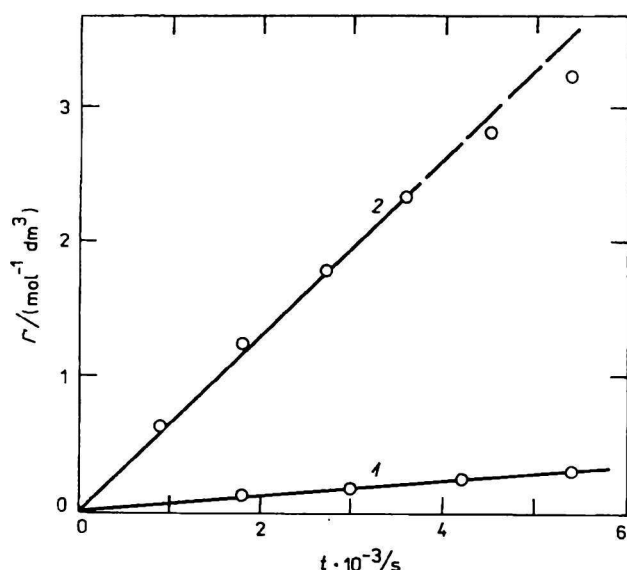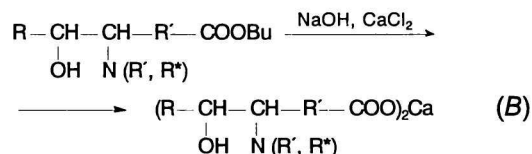

Fig. 4. Dependence of Γ on time as a basis for determination of the rate constant of the reaction of cyclohexylamine (1.2 : 1) with EBS epoxide at 130 °C. 1. Uncatalyzed reaction; 2. reaction catalyzed with ethylene glycol (1 : 1) (Fig. 3, curves 1 and 2).

of bonding of its assumed model cyclohexylamine in that direction that in case of stabilizer certain hindrances of space characteristics are demonstrated. The obtained high conversion of EBS epoxide after a 12 h reaction indicates that the secondary amino group in the stabilizer molecule in that case has no significant reactivity, which is in accordance with the previous statement [13] concerning the epoxide bonded on grafted polypropylene. Besides of the high mass fraction of EBS epoxide reacted with the compound with considered special effect, the value concerning the yield of oil after reaction is significant; in a standard experiment a 90—95 % yield with regard to EBS added into reaction was obtained.

The aim of the following experiments leading to splitting off of the butyl group from EBS in alkaline medium was not the forming of a further reactive centre for bonding of a new function [15—19], but the possibility of a synthesis of an EBS calcium salt with bonded amine

$$R-\underset{\underset{OH}{|}}{CH}-\underset{\underset{N(R',R^*)}{|}}{CH}-R'-COOBu \xrightarrow{\text{NaOH, CaCl}_2}$$

$$\longrightarrow (R-\underset{\underset{OH}{|}}{CH}-\underset{\underset{N(R',R^*)}{|}}{CH}-R'-COO)_2Ca \qquad (B)$$

With the reaction (B) the molecular mass of modified EBS is increased, which will restrain its volatility and extractibility in the case when it is applied as an additive for polymers. A significant operation is the purification of the product from impurities, particularly calcium salts not combined with EBS which can cause during thermal processing a colour change of the polymer or they can negatively influence the activity of bonded special function on EBS [11b]. The obtained yield of calcium salt was usually about 70 % with regard to the original EBS. An opposite procedure of synthesis, i.e. bonding of amine on EBS calcium form would not secure the preservation of epoxide groups for the reaction with amine in consequence of the strong alkaline medium and the high temperature during the hydrolysis.

In Table 4 are presented materials on the basis of modified EBS, where the nitrogen content is characterized in various manner. Fig. 5 on the basis of selected examples proves that these EBS derivatives are resistant against thermal decomposition on air at least as much as the original EBS, whereby the area of maximum decomposition rate of the material is markedly shifted to temperatures above 300 °C. For comparison, the thermolysis course of the nonbonded stabilizer dispiro[5,1,5,3]-7,15-diazahexadecane, which in spite of its intentionally chosen structure is at 300 °C in vapour form [20], is referred to. In this respect the synthesized materials on the basis of modified EBS have a certain

Table 4. Influence of Kind of Processing of EBS after Modification with Amine Compounds on Nitrogen Content in the Product

Modified EBS	Boiling extraction $(w/\%)^a$	$w(N)$ %
EBS—E	–	2.8
(EBS—E)$_2$Ca	Ethanol (42.0)	2.4
↓	Dioxane (13.4)	1.5
	Soluble residue $(14.6)^b$	1.2
EBS—T	–	4.3
(EBS—T)$_2$Ca	–	1.6^c
↓	Dioxane	4.8
EBS—D	–	4.0
(EBS—D)$_2$Ca	Dioxane	3.5

a) The mass fraction of the portion extracted from the mixture with Ca(OH)$_2$ resp. CaCO$_3$; b) portion soluble in boiling dioxane, insoluble in cold medium; c) The product was not purified by extraction. E — Diethanolamine; T — 2,2,6,6-tetramethyl-4-aminopiperidine; D — dispiro[5,1,5,3]-7,15-diazahexadecane.
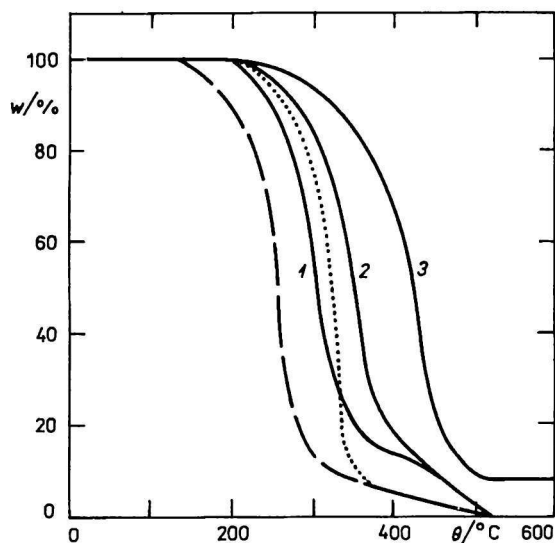
Fig. 5. Course of TG curves at thermolysis of selected synthesized materials on the basis of modified EBS. *1.* EBS heated at constant temperature for 16 h at 170 °C; *2.* EBS with bonded 2,2,6,6-tetramethyl-4-aminopiperidine; *3.* EBS with bonded dispiro[5,1,5,3]-7,15-diazahexadecane in the form of a Ca^{2+} salt; dashed line — nonbonded dispiro[5,1,5,3]-7,15-diazahexadecane; dotted line — Tinuvin 770.

advantage also in comparison with the commercial stabilizer Tinuvin 770, which is evident mainly on the example of the modified calcium additive.

It is possible to consider the application of the modified Epoxybutylester S also beyond the poly-

mer chemistry [21, 22]. Simultaneously here is offered a general method for increasing the molecular mass of amine compounds, which will enlarge the possibilities of their application.

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