Journal of Thermal Analysis, Vol. 23 (1982) 135—141

THERMAL DEGRADATION OF EPOXIDIZED POLYDIENES III. THERMAL BEHAVIOUR OF SOME CROSS-LINKED EPOXIDIZED POLYDIENES

ALI A. Z. EL FAYOUMI

Chemistry Department, University of Bahrain, P. O. Box 1082 Manama, Bahrain

(Received June 23, 1981)

DTA and TG has been used to study the thermal stability of cross-linked epoxidized polydienes. Cross-linking has been achieved using some derivatives of hydroxycarbostyrils, triazines and phthalimide. The new properties of the polymers after curing are interpreted on the basis of the results of DTA and TG.

The relation between the flexibility imparted to epoxidized polydienes after curing with phthalic anhydride, ethyl acetoacetate, ethyl cyanoacetate, methyl methacrylate, diethyl succinate and acrylonitrile has been elucidated via DTA and TG techniques [1].

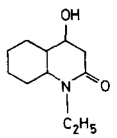
The elasticity and flexibility of epoxidized polydienes are highly affected by the structure, reactivity and concentration of the curing agents. Some curing agents have been considered as flexibilizers and diluents for epoxidized polydienes [2]. Other curing agents have been considered as hardeners for epoxidized polydienes, as suggested by El Fayoumi [3]. It is shown that the rate of heating, the concentration of the polymerizing agent and the extent of curing can each influence the DTA curve for a particular system, and the shapes and positions of the DTA peak, depend on the nature of the epoxides as well as on the type of polymerizing agent.

Materials and methods

The rubbers used in this work were of the polybutadiene type. The following elastomers were dissolved in dry benzene, precipitated by ethanol and then dried at 23° under reduced pressure. The purified rubbers were epoxidized using freshly-prepared peracetic acid (PAA), the strength of which was determined as 0.5 mol/l. Stock polymer solution was prepared for use in the curing reactions. The rubbers were (1) Europrene cis 1.4 (ANTC, Italy), $\eta_{\text{int}} = 2.45$; and (2) Cariflex Br 11 (Compagnie Française des produits Chimiques, Shell, France), $\eta_{\text{int}} = 2.24$. Preparation and purification of the epoxidized polybutadiene, and isolation, purification and drying of the final products were carried out before study by DTA and TG as described earlier [4, 5].

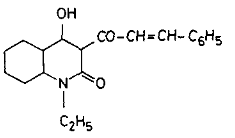
The polymerizing agents were

1. 1-Ethyl-4-hydroxy-carbostyril (EHC).
2. 3-Cinnammoyl-4-hydroxy-1-phenylcarbostyril (CHC).
3. 3-Hydrazine cinnammoyl-5,6-diphenyl-1,2,4-triazine (TZ).
4. Phthalimide (PM).



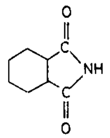
EHC

1-ethyl-4-hydroxycarbostyril



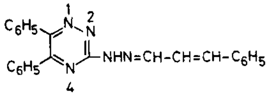
CHC

3-cinnammoyl-4-hydroxy-1-phenylcarbostyril



PM

Phthalimide



TZ

3-hydrazine cinnammoyl-5,6-diphenyl-1,2,4-triazine

EHC and CHC were synthesized as described in [6].
TZ was synthesized as described in [3]

The DTA apparatus used was basically similar to that described by Anderson and Freeman [7]. The analysis was performed under nitrogen at atmospheric pressure at a heating rate of 12°/min up to 1000°. About 1 g of well-dried cured epoxypolydiene samples were intimately mixed with equal weights of aluminium oxide. The mixture was packed around the thermocouple well, whose bottom was located 0.5 in from the bottom of the sample tube. The packed sample tube was weighed before and after a DTA run so that the percentage weight loss could be calculated. An equal weight of aluminium oxide was placed in the reference tube.

Chevenard thermobalance was used for TG studies.

Results and discussion

Studies were carried out on the cured reactions by DTA and TG techniques to study the following subjects:

1) The modification in the structure.

2) The relation between the change in flexibility imparted to the cured products and the change in the temperatures at which scission of the cross-links occurs.

3) The relation between the results obtained form DTA and TG.

4) The kinetic data derived from TG curves and their relation with the new properties of the cured polymers.

5) The extent of the reaction determined from the start of precipitation and characterized by activation energies derived from TG.

6) The degree of cross-linking and its relation with the thermal stability of the cured polymers.

Modification in the epoxidized polydiene structure was elucidated by the following procedure:

a) Consumption of epoxy groups, which is determined by qualitative, quantitative and IR analyses, may reveal the reactivity of the epoxy groups, the change in the structure of the starting epoxy polymer and the role of the curing agent in the reaction. Epoxy group opening will yield a hydroxy group, leaving a carbonium ion acting as an active center on which a residual part of the curing agent is grafted, or an ether cross-link could exist between two polymer molecules. Accordingly, the higher the consumption of epoxy groups, the higher the cross-linking density, and the greater the insolubility of the product and the increase in thermal stability (Tables 1 and 2). IR analysis revealed the disappearance of the band specific for epoxide groups at 3010 – 3060 cm^{-1} in the modified product.

b) The swelling values in Table 1 revealed the existence of cross-linking, which varied according to the curing system. Cross-linkage formation was supported by the use of IR by monitoring the absorption band (1100 cm^{-1}) specific to the ether bond.

c) As a result of the change in the structure a change in properties should occur and the applications as well will be modified. The new properties appearing in the cured products included:

1. Insolubility of the products.
2. Chemical resistance towards 18 M H_2SO_4, 12 M HCl, glacial ethanoic acid and 12 M NaOH.
3. The flexibility and elasticity of the EPB are varied depending on the structure, reactivity and concentration of the curing system.

Table 1

Determination of epoxy and swelling values for cured epoxidized polydienes using different curing agents

Curing agent g/g epoxy	Start of ppn., min	Reaction product yield, %	Time, h	F, %	Epoxy value, α %	Swelling value, %	x	Y
PM	60	60	7	25	2.9	46	45	hard resin
EHC (1/1)	120	91.2	12	—	1.4	38.1	21	hard, resinous
CHC (1/1)	60	62	10	—	2.8	44.6	14	canary-yellow solid
TZ (0.5/1)	120	50	5	10	1.2	37.2	17	orange, tough, very poorly elastic

F Percentage of the dissolved polymer in the remaining fluid of the reaction mixture.
Y The state of the modified polymer after period x.
x Duration of flexibility of EPB after curing, in days.

Table 2

Exothermic and endothermic processes revealed by DTA for the epoxidized polydienes cured with different curing agents

Curing agents	Endothermic processes						Exothermic processes	
	Melting		Cross-link bond scission		Depolymerization		Oxidation	
	Temp. °C	Peak °C	Temp. °C	Peak °C	Temp. °C	Peak °C	Temp. °C	Peak °C
PM	20–190	125	260–400	325	400–630	450–530*	190–260	225
EHC	20–120	95	200–430	415	430–685	460–685*	120–200	150
CHC	30–100	65	160–330	240	330–650	575	100–160	120
TZ	20–100	65	200–395	280–350*	395–650	450–625*	100–200	135

* Plateau.

4. The drastic decrease in the flexibility on using TZ, EHC and CHC showed that TZ and EHC could be used as hardeners for epoxidized polydienes.

The results in Table 1 showed that the flexibility decrease in the cured polymer agreed with the swelling values, revealing the relations between the consumption of the epoxy groups, the swelling values, the cross-linking density, the change in solubility, the start of polymer precipitation in the reaction medium, the extent of reaction and the flexibility decrease in the cured polymers. The results showed that the use of PM, EHC, TZ and CHC as curing agents for EPB changed the flexibility retention of the EPB to 45, 21, 17 and 14 days, respectively.

d) The results obtained by DTA and TG agree as regards the behaviour mentioned above on the use of the different curing systems (Table 2).

DTA and TG studies

The thermal degradations of the modified products have been studied.

On the basis of the results of DTA and TG, the modification in the structure and the new properties imparted to the new polymers may be summarized as follows:

1) The cross-linking density, as determined by the swelling values (Table 1), is directly proportional to the insolubility, the change in flexibility of the EPB, the comsumption of the epoxy groups, the reactivity of the curing agents, and the concentration of the curing agents.

The strength of the cross-link formation means that the activation energy required should be high. Endothermic cross-link scission processes have been shown to occur at high temperatures, in the following order: EHC > TZ > PM > CHC. The sequence for the increase of the cross-linking density or the decrease of the swelling values is as follows: TZ $\sim$ EHC > CHC > PM.

The polymers started to precipitate after

50, 60, 120 and 120 min

on using PM, CHC, EHC and TZ, respectively. This result shows that the rate of precipitation polymerization is higher on using PM, CHC, EHC and TZ, and also means that cross-linked polymers are formed in the same order; this agrees with results on the thermal cross-link bond scission obtained from the DTA curves. The above deduction was supported by the kinetic data obtained by TG (Table 3), as the curing agents PM and CHC required less activation energy for the process of curing than did TZ and EHC.

2) From Table 2 it is clear that the melting, depolymerization and oxidation temperatures of the modified products obtained by the reaction of different curing agents with epoxidized polydienes follow the order given in Diagram A.

These results agree with the flexibility decrease of the obtained cross-linked products, since the epoxidized polydienes on exposure to direct and diffuse sunlight were changed to hard resinous blocks after 2 months, whilst cured epoxypolybutadiene when exposed to direct and diffuse sunlight retained its flexibility and elasticity for periods of 45, 21, 17 and 14 days for the samples cured with PM, EHC, TZ and CHC, respectively. Thus, some curing agents, such as TZ, EHC and CHC, could be considered as hardeners for epoxy polybutadienes.

The efficiency of the curing agents in producing hard and tough rubbers decreased in the order: TZ > EHC > CHC > PM.

From a comparison of the above arrangements one can observe a close relation between the DTA results and the degree of flexibility.

The higher the melting, depolymerization and oxidation temperatures, the higher the cross-linking density and the decrease in the flexibility, as shown in Diagram A.

From the results obtained it is clear that all samples underwent degradation at relatively mild temperatures. The weight loss recorded by TG for samples cured with PM, CHC, EHC and TZ was 100, 140, 150 and 160, respectively, and complete degradation occurred at 500, 600, 620 and 630°. It can thus be concluded that the decrease in flexibility of epoxy polydienes after curing influences both the initial

Table 3

Activation energy and order (n) of thermal degradation of cured epoxidized polydienes

Curing agent	E, kJ/mol	n
PM	28.6	0
CHC	65.1	2
EHC	67.6	2
TZ	72.2	2

Diagram A

From the results in Table 2, the following sequences could be deduced for each thermal process and the behaviour of each cured product using different curing agents

Thermal process	Peak temperature	Range difference, °C
Depolymerization	TZ > EHC > CHC > PM	TZ ≃ EHC > CHC > PM 255 255 320 230
Cross-link bond scission	EHC > TZ > PM > CHC	EHC > TZ > CHC > PM 230 195 170 140
Melting	PM > EHC > CHC ≃ TZ	PM > EHC > TZ > CHC 170 100 80 70
Oxidation	PM > EHC > TZ > CHC	TZ > EHC > PM > CHC 100 80 70 60

and the final weight losses. The range of weight loss seems to be broadened by a decrease in flexibility or an increase in hardening. The stability of the cured epoxidized poydienes towards weight loss exhibited the following order

$$TZ > EHC > CHC > PM$$

The activation energy for the thermal degradation has been derived from the TG curves using the equation of Bikales [7]:

$$\Delta \log R_t = n\Delta \log w - (E_a/2.303R) \cdot \Delta(1/T)$$

where w is the weight of active material remaining and R_t is the reaction rate (dw/dt) (mg/min). The plot of $\Delta \log R_t$ versus $\Delta \log w$ should be linear when $\Delta(1/T)$ is constant. The slope of the resulting line will give a value for n, and the intercept will give a value for E_a. The values of the reaction order (n) and activation energy (E_a) are given in Table 3.

Conclusion

The elasticity and flexibility of the cured epoxy polydienes are decreased, indicating the usefulness of the studied curing agents as hardeners for epoxidized polydienes. They can be used with bitumen to see what improvements can be made in road asphalt. The degree of flexibility determines to a great extent the temperature at which the thermal cross-link scission occurs in DTA. The temperature range of total weight loss is broadened by a decrease in the flexibility of epoxidized polydienes.

References

1. A. A. Z. EL FAYOUMI and S. ABOU ALI, Ind. J. Chem., 16 (1978) 395.
2. A. A. Z. EL FAYOUMI, A. A. IBRAHIM, Y. AKHNOOKH and A. A. SALEH, Indian Technol., 19 (1981) 145.
3. A. A. Z. ELFAYOUMI and H. ZAHER, J. of Faculty of Education-Ain Shams University, Egypt 8 (1981) 203.
4. A. A. Z. EL FAYOUMI, J. KALAL and F. SVEC, Spornik, 18 (1972) 45.
5. A. A. Z. EL FAYOUMI, A. A. IBRAHIM, Y. AKHNOOKH and A. A. SALEH, J. of University of Kuwait (Science) 8 (1981) 203.
6. A. A. SAYED, S. M. SAMI, A. A. Z. EL FAYOUMI and E. A. MOHAMED, Acta Chim. Acad. Sci. Hung., 94 (1977) 131.
7. N. M. BIKALES, Characterisation of Polymer, Wiley-Interscience, (1971) p. 226.

ZUSAMMENFASSUNG — DTA und TG wurden zur Untersuchung der Thermostabilität von quervernetzten epoxidierten Polydienen eingesetzt. Die Quervernetzung wurde unter Verwendung einiger Derivate von Hydroxycarbostyrilen, Triazinen und Phtalimid durchgeführt. Die neuen Eigenschaften der Polymere nach einer Wärmebehandlung wurden aufgrund der Ergebnisse der DTA und TG gedeutet.

Резюме — Методы ДТА и ТГ были сипользованы для изучения термоустойчивости эпоксидных полидиенов с поперечными связями. Образование поперечных связей в полимерах было достигнуто использованием некоторых производных карбостирола, триазина и фтальимида. На основе данных ДТА и ТГ объяснены новые свойства полимеров, приобретенные в результате вулканизации.