Journal of Thermal Analysis and Calorimetry, Vol. 83 (2006) 2, 373–378

CALORIMETRIC ANALYSIS OF THE CROSS-LINKING REACTION OF EPOXIDIZED POLYBUTADIENES

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Liquid polybutadienes were epoxidized with hydrogen peroxide-acetic acid confirming the influence of the microstructure on the epoxy content. Thermal cross-linking of the epoxidized products was studied by DSC and a different behaviour due to epoxy content as well as to microstructure was found. A correlation between enthalpy/epoxy ratio and vinyl content was also observed. The addition of a radical initiator as dicumyl peroxide (DCP) yielded exothermal effects of cross-linking in the original polybutadienes, confirming the higher reactivity of the vinyl groups. In the epoxidized products, the introduction of DCP gave a peak split, which was explained by the overlap of two cross-linking mechanisms, due to residual double bonds and epoxy groups. From the DSC data, the isothermal curves of cross-linking conversion were calculated as a function of time, for a better comparison of the performances and properties of the epoxidized polybutadienes.

Keywords: *cross-linking, DSC, epoxidation, kinetics, polybutadiene*

Introduction

Low molecular mass epoxidized polybutadienes are useful intermediate products since the epoxide groups allow cross-linking as well as functionalization reactions leading to a large number of practical applications in the field of binders, plasticizers, printing inks, stabilizers, adhesives, components in composites and epoxy resins, oil additives, etc. [1, 2]. The epoxidation of liquid polybutadienes has been extensively studied by some authors [3–10] that thoroughly investigated reaction kinetics, reactivity of the double bonds and experimental conditions related to the epoxidation degree. Many types of peracids, such as performic, peracetic and *m*-chloroperbenzoic acid have been used for epoxidation, because the reaction should occur in homogeneous phase without side reactions [11, 12].

Cross-linking of epoxidized polybutadienes can be achieved by simple thermal treatment in the presence of radical initiators or without [10, 13, 14]. Moreover, the introduction of epoxy-hydroxy functionalized polybutadiene in cationic UV-curable systems leads to the incorporation of the oligomer into the epoxy cross-linked network [15].

Non-isothermal DSC measurements are widely used in kinetic study of cure reaction of epoxy [16–19], phenolic [20, 21] and polyester [22] resins. In a precedent work, the same investigation technique was applied also to another reaction of liquid polybutadienes, such as the maleinization [23].

In this paper, the epoxidation of some liquid polybutadienes of different microstructure was reported and the thermal cross-linking of these products was studied by non-isothermal DSC. The use of a radical initiator, as dicumyl peroxide (DCP), was also considered.

Experimental

Materials

Commercial liquid polybutadienes with different *m.w.* and microstructures were chosen. Polyoil samples were kindly supplied by Hüls Werke, now Degussa (Germany). Lithenes and other polybutadienes were kindly supplied by Revertex Ltd., now Sinthomer (England). The *m.w.* were determined via GPC, with THF as solvent, through calibration with three polyisoprene standards (Polymer Laboratory). The microstructure was determined via FTIR analysis on carbon disulfide solutions [24]. The characteristics of the polybutadienes used are reported in Table 1. DCP and other chemicals were from Aldrich.

Epoxidation of polybutadienes

Each polybutadiene sample (5.4 g corresponding to 0.1 mol of double bonds) was epoxidized in benzene solution (250 mL) by introducing different amounts of

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1388–6150/$20.00

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Table 1 Characteristics and thermal behaviour of pure polybutadienes compared with 1% DCP mixtures

Polybutadiene	*m.w.*	Microstructure /%			T^{peak} /°C		ΔH /J g^{-1}	
		1,4 *trans*	1,4 *cis*	1,2	pure	DCP	pure	DCP
Polyoil 110	1580	22.9	74.5	2.6	180	181	6.0	16.8
Polyoil 130	2830	20.0	77.2	2.8	–	181	<0.5	12.1
Lithene 5000	4650	31.9	25.0	43.1	184	187	12.4	53.8
Lithene PH	2960	35.1	25.8	39.1	190	184	13.3	35.0
20046-8	1051	28.9	36.6	34.5	–	182	<0.5	33.0
20048-4	1540	28.4	48.2	23.4	–	181	<0.5	25.3
38369-4	5250	44.5	38.2	17.3	184	182	2.5	18.6

glacial acetic acid and 35% hydrogen peroxide. A sulfonic acid resin (Dowex 50W-X8, 18 g) was introduced as catalyst. The reaction was carried out in nitrogen atmosphere at 60°C under reflux for 120 min. At the end, 250 mL of water were added and the organic phase, after separation, was thoroughly washed with a saturated solution of sodium carbonate. The benzene solution was then dried with anhydrous sodium sulfate and the solvent was distilled off at 75°C under vacuum.

The epoxy group content of the epoxidized polybutadienes was determined by titration with hydrochloric acid in dioxane [25]. This reagent was prepared approximatively 0.2 N by adding concentrated hydrochloric acid to dioxane purified by distillation over potassium hydroxide. A resin sample, containing 0.002–0.004 equivalents of epoxide, was dissolved in 25 mL of hydrochloric acid-dioxane, kept at room temperature for 15 min, then added with 25 mL of neutral cresol red ethanolic solution (0.001%). The residual acid not consumed for chlorohydrin formation was back titrated with standard 0.1 N methanolic potassium hydroxide to the yellow-violet end point. Blank tests, without resin, and resin acidity in pure dioxane were determined by the same procedure and the titration results were consequently calculated. The epoxy content was expressed as milliequivalents (meq) of epoxide-bound oxygen per g of resin. FTIR analyses on polybutadiene films, before and after epoxidation, were performed on KBr pellets by means of a Mattson Genesis II spectrophotometer, through absorbance measurements at 966, 913, 741–728 cm^{-1}, corresponding respectively to 1,4-*trans*, 1,2 and 1,4-*cis* peaks.

DSC analyses

The DSC analyses were carried out on a Mettler TA 3000 calorimeter equipped with a Mod. 20 DSC cell. Resin samples were sealed in the standard aluminium pans of 40 μL and submitted to DSC analysis in the range from 50 to 350°C at the heating rate of 10°C min^{-1} under nitrogen flux. The data were processed on a personal computer with the aid of the Mettler TA 70 Graphware.

Samples of about 15 mg were taken from the pure polybutadienes because of their low cross-linking enthalpy (≤50 J g^{-1}), whereas a lower amount, 6 mg, was taken from the epoxidized resins owing the higher enthalpy (>250 J g^{-1}). Relative standard deviations of replicate measurements were estimated about 18 and 5% respectively. For tests carried out in the presence of 0.5–2% mass/mass of DCP as radical initiator, the required amount of solid DCP was added to the resin in 10 mL vials; the mixtures were stirred some minutes at 60°C, then submitted to DSC analysis.

Results and discussion

Epoxidation of polybutadienes

The epoxy content of the epoxidized polybutadienes was in the range from 2 to 5 meq g^{-1} of resin, as shown in Table 2. In Fig. 1, these values are plotted *vs.* the total content of 1,4 microstructure showing a significant linear correlation (coefficient about 0.9), according to the literature data on polybutadiene epoxidation which aknowledge that the vinyl groups are practically unreactive in the experimented conditions [2]. Some authors, however, have recognized

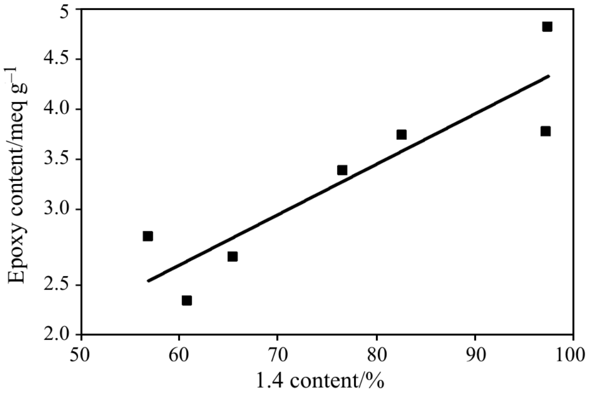

Fig. 1 Correlation between epoxy content of epoxidized polybutadienes and total 1,4 microstructure content

Table 2 Kinetic results of thermal cross-linking of epoxidized polybutadienes

Epoxidized polybutadiene	Epoxy content/meq g^{-1}	T^{peak}/°C	ΔH /J g^{-1}	ln k_0	E_A /kJ mol^{-1}	n
Polyoil 110	4.83	208	789	38.1	170	2.0
Polyoil 130	3.87	293	325	44.4	228	0.8
Lithene 5000	2.91	258	594	24.1	127	0.2
Lithene PH	2.33	311	302	102.2	512	1.3
20046-8	2.72	314	288	113.0	569	1.2
20048-4	3.51	308	307	93.6	468	1.2
38369-4	3.84	316	310	66.6	345	1.0

the higher reactivity of the 1,4-*cis* microstructure with respect to the 1,4-*trans* (about 1.5:1) [7], but in our case this difference cannot be evidenced, probably because of the limited range of variation of the 1,4 microstructure in the tested samples. The difference in epoxy content between Polyoil 110 (4.83 meq g^{-1}) and Polyoil 130 (3.87 meq g^{-1}), which have the same microstructure, could arise from the higher *m.w.* of the latter (near twice) and higher viscosity (about four times at 20°C).

The comparison of FTIR spectra showed a decrease of the double bond absorption peaks (e.g. at 940–980 and 735 cm^{-1}) and the appearance of peaks assigned to epoxides (e.g. at 880 cm^{-1}) [11]. Some small microstructure changes due to epoxidation were observed, although the vinyl content was found practically unchanged.

DSC data processing

The evaluation method of kinetic results from DSC non-isothermal measurements included in the Mettler TA 70 Graphware was discussed by Widmann and Riesen [26] and reported in the previous paper [23]. A kinetic equation can be written as:

$$\ln\frac{d\alpha}{dt} = \ln k_0 - \frac{E_A}{RT} + n\ln(1-\alpha) \qquad (1)$$

where α – extent of reaction, dα/d*t* – reaction rate in s^{-1}, k_0 – frequency factor, n – order of reaction.

The values of dα/d*t* and α can be calculated from DSC curves on the assumption that the differential conversion dα corresponds to a proportional enthalpy change d*H*. Hence, k_0, the activation energy E_A and the order of reaction n can be determined with the aid of a multiple linear regression. It is assumed that 20 experimental value triplets of dα/d*t*, *T* and α are available from DSC measurements for drawing the regression plane through the experimental points using the method of least squares. The confidence limits for n, E_A and lnk_0 are respectively <0.05, <10 kJ mol^{-1}, and <1. These values enable to calculate the isothermal conversion as a function of the reaction time by integration of Eq. (1):

$$\alpha = 1 - e^{-kt} \qquad \text{if } n = 1 \qquad (2)$$

$$\alpha = 1 - [kt(n-1)+1]^{\frac{1}{1-n}} \qquad \text{if } n \neq 1 \qquad (3)$$

where k is the kinetic constant in s^{-1} calculated for a given temperature.

Thermal cross-linking of polybutadienes

At first, DSC analyses of pure polybutadienes were carried out in the range from 50 to 350°C in order to evaluate thermal effects due to cross-linking under nitrogen. The results are reported in Table 1, where small exothermal effects in the range 180–190°C are shown. DCP addition to polybutadienes yielded higher exothermal peaks due to radical-initiated cross-linking [10, 13] in the same temperature range. DCP was chosen as radical initiator owing its better solubility in polybutadiene and lower dissociation enthalpy with respect to other initiators such as AIBN or benzoyl peroxide. In fact, the dissociation enthalpy of 1% DCP solution in silicon oil was about 6.5 J g^{-1} with a temperature peak at 180°C. For a given sample, however, the enthalpy was proportional to the DCP concentration, as can be seen by DSC curves of Lithene 5000 plotted in Fig. 2.

Moreover, the cross-linking enthalpies of polybutadienes in the presence of 1% DCP regularly increased with 1,2 microstructure content and confirmed, according to Zuchowska [10], the higher reac-

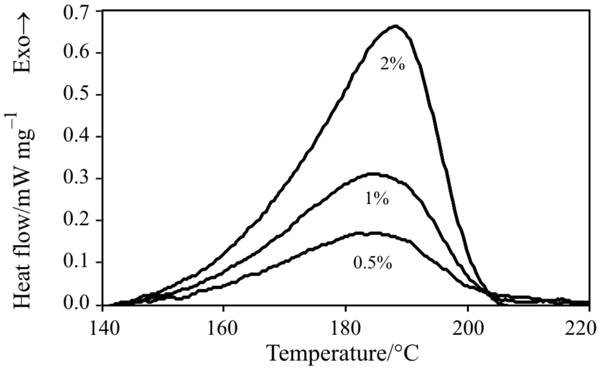

Fig. 2 DSC curves of Lithene 5000 with different amounts of DCP

tivity of the vinyl groups compared to the other unsaturations (about 4:1).

Thermal cross-linking of epoxidized polybutadienes

The kinetic results of thermal cross-linking of the epoxidized polybutadiene samples are collected in Table 2. The highest thermal effect, but with a peak at the lowest temperature, was shown by Polyoil 110, having the highest epoxy content. A reaction order of 2.0, however, indicates that the cross-linking reaction of this oligomer proceeds, at high conversion, more slowly with respect to the other polybutadienes ($0.2<n<1.3$) [26]. Moreover, the differences between the Polyoils could be ascribed to the different epoxy content.

On the other hand, the microstructure can affect the thermal behaviour of the epoxidized products. Figure 3 shows the DSC curves of epoxidized polybutadienes: different shapes of the traces and shift of the exothermal peaks are evidenced for the various oligomers. Moreover, the activation energy values indicate a different dependence of the kinetic constants on the temperature.

In Fig. 4, a correlation curve between enthalpy/epoxy ratio and 1,2 content shows that, except for Polyoils, the thermal effect due to an epoxy group regularly rises with increasing the vinyl group content, starting from about 30%. This suggests an involvement of the vinyl group, at higher concentration, in the cross-linking mechanism.

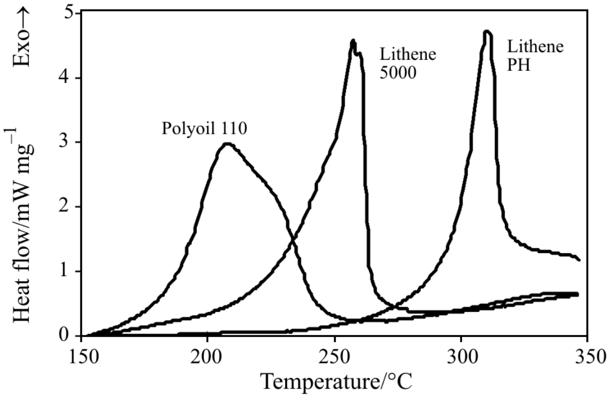

Fig. 3 DSC curves of epoxidized polybutadienes

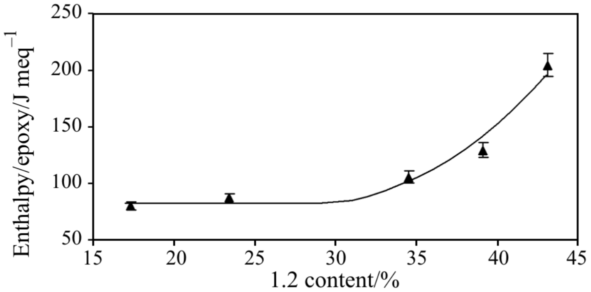

Fig. 4 Correlation curve between enthalpy/epoxy ratio and 1,2 microstructure content in epoxidized polybutadienes

Thermal cross-linking of epoxidized polybutadienes in the presence of DCP

Some modifications of the DSC curves were induced by DCP addition to epoxidized polybutadienes, as it can be seen in Fig. 5. Except for Polyoil 110, the exothermal effect was splitted into two peaks, one at about 180°C and the other close to the temperature peak observed without DCP. The results of these DSC analyses are reported in Table 3. In the case of epoxidized Polyoil 110, the peak split cannot be observed because of the lower cross-linking temperature. However, the peaks at about 180°C were smaller than those at higher temperature, except for epoxidized Lithene PH, which was the sample with lowest epoxy content.

These results suggest that, in the presence of DCP, two cross-linking mechanisms are involved: one is due to the residual double bonds, the other to the epoxy groups; the latter seems to be little affected by the former, except when a low epoxy content is joined to high vinyl content, as in the case of epoxidized Lithene PH. This can be justified by a fast consumption of double bonds promoted by DCP before the epoxy groups begin to react. Hence the exothermal effect at higher temperature could be decreased by a low content of residual unsaturations. The comparison between DSC curves of Lithene PH is reported in Fig. 6.

In order to compare the kinetic data with those yielded by pure epoxidized samples, only the peaks at

Table 3 Kinetic results of thermal cross-linking of epoxidized polybutadienes in the presence of 1% DCP. T_1^{peak} and ΔH_1 are related to the peak at lower temperature, T_2^{peak}, ΔH_2 and the other values to the peak at higher temperature

Epoxidized polybutadiene	T_1^{peak}/°C	ΔH_1/J g^{-1}	T_2^{peak}/°C	ΔH_2/J g^{-1}	ln k_0	E_A /kJ mol^{-1}	n
Polyoil 110	–	–	211	771	23.8	116	0.9
Polyoil 130	179	36	294	309	34.5	183	0.6
Lithene 5000	181	83	251	491	34.6	170	0.6
Lithene PH	184	243	313	238	40.2	219	0.1
20046-8	181	46	315	325	99.2	502	1.1
20048-4	181	71	305	280	85.7	430	1.0
38369-4	182	34	317	261	48.4	258	0.5

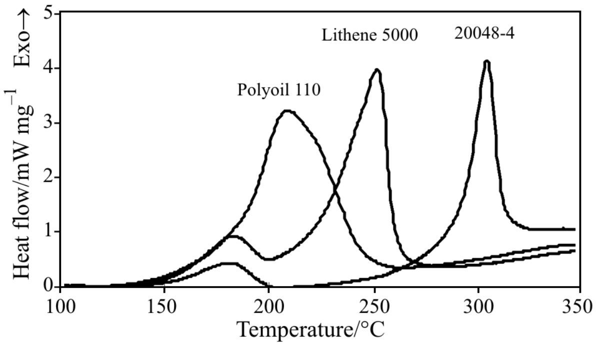

Fig. 5 DSC curves of epoxidized polybutadienes in the presence of 1% DCP

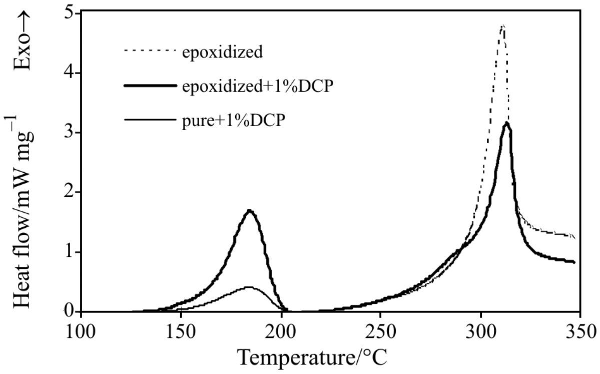

Fig. 6 Comparison of DSC curves of Lithene PH

higher temperature were considered. The activation energy values were generally decreased, showing a lower dependence of the kinetic constants on the temperature. Moreover, the reaction order was somewhat lower ($0.1<n<1.1$), indicating a swift reaction at higher conversion. A better comparison of the cross-linking behaviour of epoxidized polybutadienes with and without DCP can be made on the basis of the curves showing the extent of isothermal reaction calculated by the Eqs (2) or (3), because this calculation contemplates all the parameters of the kinetic model. As shown in Fig. 7, the reaction rate of epoxidized Polyoil 110 at 200°C was initially higher without DCP until some time had elapsed, while in the case of epoxidized Lithene 5000 the yield without DCP was always higher. Since other epoxidized polybutadienes react too slowly at 200°C, the comparison was made at 300°C, as reported in Fig. 8, which confirmed that the addition of DCP at this temperature generally yields higher conversion values at the same time.

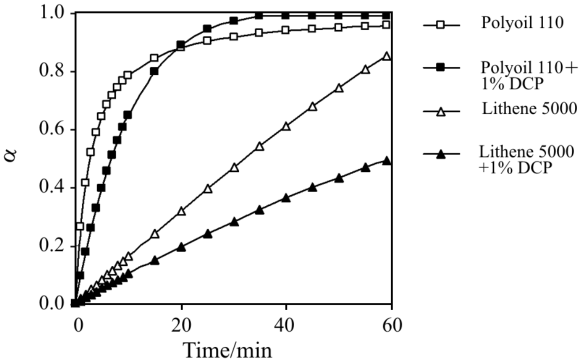

Fig. 7 Extent of isothermal cross-linking reaction (α) *vs*. time for epoxidized polybutadienes at 200°C

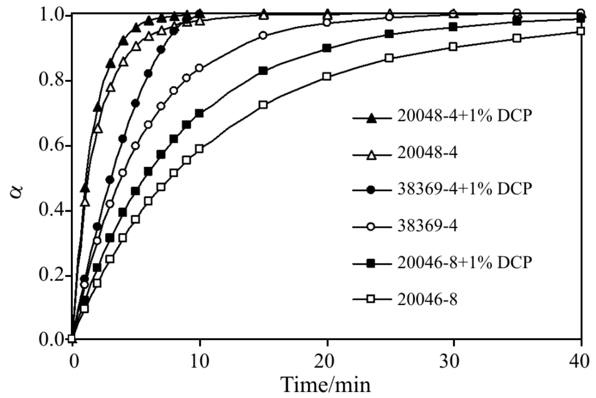

Fig. 8 Extent of isothermal cross-linking reaction (α) *vs*. time for epoxidized polybutadienes at 300°C

Conclusions

The epoxidation of liquid polybutadienes has confirmed the influence of the microstructure on the epoxy content of the products and the higher reactivity of the 1,4 microstructure. The calorimetric analysis of thermal cross-linking using DSC has shown a different behaviour of epoxidized polybutadienes in dependence on the epoxy content as well as on the microstructure. Moreover, for a 1,2 microstructure content higher than 30%, a correlation between enthalpy/epoxy ratio and vinyl content was found, suggesting an involvement of this group in the cross-linking mechanism.

The addition of DCP as radical initiator to the original polybutadienes increased the exothermal effect due to cross-linking of double bonds. The cross-linking enthalpies confirmed the literature data which ascribed higher reactivity to 1,2 microstructure. In the epoxidized products, the introduction of DCP gave a peak split, suggesting an overlap of two cross-linking mechanisms: one at lower temperature (about 180°C) due to the residual double bonds, the other caused by the epoxy groups and little affected by the former, with exceptions which have been justified.

The DSC data were processed according to kinetic model which enables to calculate the isothermal curves of cross-linking conversion as a function of the time. These curves can be used for a better comparison of the cross-linking behaviour of the epoxidized polybutadienes with or without the addition of DCP.

Therefore, the results confirm that the calorimetric analysis is a powerful method to investigate the cross-linking reactions of the epoxy resins.

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Received: June 28, 2005
Accepted: October 17, 2005

DOI: 10.1007/s10973-005-7145-2