

CALORIMETRIC ANALYSIS OF THE GRAFT POLYMERIZATION OF MALEIC ANHYDRIDE ONTO LIQUID POLYBUTADIENES

*F. Ferrero**

Dipartimento di Scienza dei Materiali e Ingegneria Chimica, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10100 Torino, Italy

(Received January 23, 2003; in revised form April 12, 2004)

Abstract

The kinetics of the reaction of maleic anhydride with liquid polybutadienes of various microstructures was studied by using differential scanning calorimetry (DSC). The kinetic results of thermal maleinization show a dependence from *m.w.* and polybutadiene microstructure. The introduction of a gel inhibitor as copper naphthenate has proved that crosslinking reactions also occur during the maleinization. On the other hand, the maleinization in the presence of a radical initiator as dicumyl peroxide (DCP) shows thermal effects higher than pure thermal reaction with a partial overlap of the calorimetric peaks due to maleinization and crosslinking.

Keywords: DSC, kinetics, maleic anhydride, maleinization, polybutadiene

Introduction

Liquid polybutadienes obtained by anionic polymerization, with *m.w.* in the range from 1.000 to 5.000, are mostly modified by three industrial processes: maleinization, epoxidation and chlorination [1]. The modified polybutadienes are widely applied in coating technology.

The maleinization of polybutadienes is similar to that of unsaturated natural oils and a mechanism of 'ene reaction' was suggested [2–7]. The linked anhydride generally ranges from 10 to 30% *w/w*. The maleinized resins, bearing carboxylic groups derived from hydrolysis or emiesterification by alcohols of the anhydride ring, become water soluble after neutralization and can yield coatings on various substrates by crosslinking with polyamines, polyoils, epoxy resins, etc. [8–10].

The graft polymerization of maleic anhydride onto liquid polybutadienes can be performed in two ways: a) thermally, without catalyst, by heating the reagent mixture from 180 to 230°C under nitrogen; b) with a radical initiator, as an organic peroxide, at lower temperatures [5]. Some problems arise from unwanted competing reactions

* Author for correspondence: E-mail: franco.ferrero@polito.it

as polymer crosslinking and gel formation [11] favoured by high working temperatures and long reaction times (some hours). Therefore gel inhibitors are added: copper naphthenate, acetylacetone, halogenated triazines, organophosphines, imidazoles, thiazoles, etc.

In a previous work [12] the kinetics of thermal addition of maleic anhydride to liquid polybutadienes of various microstructures was studied in batch reactor at working conditions derived from industrial processes (temperature in the range from 180 to 220°C and time from 2 to 4 h). Some samples of the reaction mixture were collected at given times and purified to yield the maleinized products. These samples were then emiesterified and titrated in order to calculate the reaction yield. A first order kinetics with respect to maleic anhydride was found and the 1,4 microstructure showed reaction rates higher than the 1,2 one. The activation energies were calculated and some properties of the final products were determined.

The procedure reported above was found too long to test liquid polybutadienes of various *m.w.* and microstructures at different working conditions. Therefore, in the present work the kinetics of the same reaction was studied by using the differential scanning calorimetry (DSC). This technique finds several applications in determination of reaction kinetics, e.g. cure reactions of epoxy [13–16], polyester [17] and phenolic resins [18, 19], and shows many advantages over other methods as rapidity, simplicity, accuracy and small sample manipulation. In this work the basic assumption was that the heat evolution recorded by DSC is proportional to the extent of maleic anhydride linked to polybutadiene chains. The kinetic data were obtained from dynamic DSC measurements during maleinization.

Experimental

Materials

Some samples of commercial liquid polybutadienes were chosen with different *m.w.* and microstructures. Polyoil samples were kindly supplied by Hüls Werke (Germany). Lithenes and other polybutadienes were kindly supplied by Revertex Ltd. (England), whereas the polybutadienediol was the Aldrich product. These oligomers were used as received.

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 by processing absorbance measurements at 10.35, 10.95 and 13.50 μm [20]. The characteristics of polybutadienes used are reported in Table 1.

Maleic anhydride, DCP and copper naphthenate were reagent grade chemicals. Copper naphthenate was used as 30% *w/w* mixture with xylene.

Sample preparation

2 g of polybutadiene were added with the required amount of pulverized maleic anhydride in a sealed 10 mL vial, to avoid sublimation, and mixed with magnetic

Table 1 Characteristics and thermal behaviour of pure polybutadienes

Polybutadiene	M. W.	Microstructure			$\Delta H/J\ g^{-1}$	$T^{peak}/^{\circ}C$
		1,4 trans	1,4 cis	1,2		
Polyoil 110	1580	22.9	74.5	2.6	6.0	180
Polyoil 130	2830	20.0	77.2	2.8	(^a)	-
Lithene 5000	4650	31.9	25.0	43.1	12.4	184
Lithene PH	2960	35.1	25.8	39.1	13.3	190
20048-4	1540	28.4	48.2	23.4	(^a)	-
38369-4	5250	44.5	38.2	17.3	2.5	184
Polybutadienediol	3550	-	-	-	3.7	187

(^a) insignificant thermal effect

stirrer at 60°C for 30 min. The heating allowed the anhydride to melt in order to obtain a homogeneous mixture with the liquid polybutadiene. The concentrations of maleic anhydride were 5, 10, 15 and 20% w/w. In some cases the copper naphthenate mixture was initially added at 1 or 2%.

Some maleinization tests were performed in the presence of a given amount (0.5, 1 or 2%) of DCP as radical initiator. In these cases solid DCP was added at the end of the mixing at 60°C and the final mixture was further stirred for 2 min.

DSC analyses

The DSC analyses were performed on a Mettler TA 3000 apparatus equipped with a DSC cell mod. 20. Samples of 14/16 mg of the mixtures prepared as above were sealed in the standard aluminium pans of 40 μ L and then submitted to DSC analysis in the range from 50 to 250°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.

Results and discussion

DSC data processing

Several methods have been developed concerning the determination of kinetic results from thermal analysis measurements. The evaluation method included in the Mettler TA 70 Graphware is based on the model equation of Wilhelmy and has been discussed by Widmann and Riesen [21]. This is briefly reported as follows. According to Wilhelmy, the kinetic equation is written as:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \quad (1)$$

where α – extent of reaction, $d\alpha/dt$ – reaction rate in s⁻¹, k – rate constant in s⁻¹, n – order of reaction

Moreover, the substitution of Arrhenius equation in Eq. (1) yields, by taking the logarithms:

$$\ln \frac{d\alpha}{dt} = \ln k_0 - \frac{E_A}{RT} + n \ln(1-\alpha) \quad (2)$$

where k_0 – frequency factor in s^{-1} , E_A – activation energy in $J\ mol^{-1}$, R – gas constant, T – temperature of the reaction mixture in K

Equation (2) is linear in three unknowns; these must be determined with the aid of a multiple linear regression. It is assumed that 20 experimental value triplets of $d\alpha/dt$, T and α are available from DSC measurements for drawing the regression plane through the experimental points using the method of least squares.

Kinetics following the Eqs (1) and (2) give very narrow confidence limits for n , E_A and $\ln k_0$, respectively <0.05 , $<10\ kJ\ mol^{-1}$, and <1 . The best confidence limits are obtained when the thermoanalytical curve is evaluated in the range of α from 0.1 to 0.8.

If it is assumed that the differential conversion $d\alpha$ corresponds to a proportional enthalpy change dH the quantities $d\alpha/dt$ and α needed for the regression analysis can be calculated from DSC curves as follows:

$$\frac{d\alpha}{dt} = \left(\frac{1}{\Delta H} \right) \frac{dH}{dt} \quad (3)$$

$$\alpha = \frac{\Delta H_{part}}{\Delta H} \quad (4)$$

where ΔH – total peak area in mJ, ΔH_{part} – partial area in mJ under the DSC curve up to the evaluation point, dH/dt – heat flux in mW above baseline at the evaluation point.

Thermal behaviour of pure polybutadienes

At first DSC analyses of pure polybutadienes were carried out in the range from 50 to 300°C in order to evaluate a thermal effect due to crosslinking reactions under nitrogen. The results are reported in Table 1 and show small exothermal peak area with temperature peak in the range between 180 and 190°C.

Thermal maleinization

In Fig. 1 four DSC curves of mixtures of Lithene 5000 with maleic anhydride are compared. The area of the exothermal peak increases with maleic anhydride concentration up to 15%, whereas at the highest concentration, i.e. 20%, the thermal effect is left unchanged. Therefore, since this value was the highest observed in thermal maleinization of all the polybutadienes it was believed that the polybutadiene sites available for anhydride grafting were practically saturated with a concentration of 15% of maleic anhydride and higher contents were not considered in the other runs.

Kinetic results obtained by computer processing of thermal data are summarized in Table 2. These show a dependence from *m.w.* and polybutadiene microstructure.

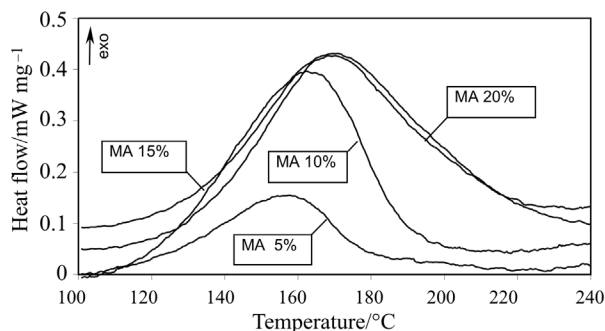


Fig. 1 DSC curves of Lithene 5000 with different amounts of maleic anhydride (MA)

The highest thermal effects are shown by Lithenes 5000 and PH which have the same microstructure and the highest content of 1,2. Moreover, with these polybutadienes the exothermal peak area ΔH regularly increases with the maleic anhydride content. On the other hand, the differences about enthalpy and activation energy between the Polyoil samples, with nearly the same microstructure, could be ascribed to the different *m.w.*

The lowest activation energy shown by the polybutadienediol proves a positive effect of the OH groups on the maleinization. Moreover, the activation energy of Polyoil 110 is much lower than those of polybutadiene 20048-4, having the same *m.w.*, but lower 1,4 *cis* and some 1,2 content. These values agree with those found in the earlier work [12]: 82 kJ mol^{-1} for a polybutadiene similar to Polyoil 110 and 109 kJ mol^{-1} for Lithene with lower *m.w.* (830), but higher content of 1,2 (62.8%). Therefore the data could confirm the hypothesis that the 1,2 microstructure reacts more slowly than 1,4 at low temperature, but the reaction rate is strongly enhanced by temperature increase. The reaction order *n* ranges from 0.8 to 2.1 and is somewhat affected by the maleic anhydride concentration.

Thermal maleinization in the presence of copper naphthenate

The samples, except for Polyoils, yield a gel when thermal maleinized in DSC chamber. In industrial process a small amount, less than 1%, of crosslinking inhibitor is added to obviate this drawback. Therefore some tests of thermal maleinization were carried out in the presence of 1 or 2% of copper naphthenate-xylene mixture. This addition to pure polybutadienes did not show any further thermal effect.

In Fig. 2 the DSC curves of Lithene 5000 with 10% of maleic anhydride added in the presence of 1 and 2% of copper naphthenate mixture were compared with the sample without inhibitor. This caused a split of the exothermal peak into two peaks, one ascribable to maleinization at about 130°C and another smaller at about 180°C . The latter was attributed to polybutadiene crosslinking on the basis of the temperature peak of pure polybutadienes, although these showed smaller peak areas. This means perhaps that the presence of maleic anhydride promotes crosslinking

Table 2 Kinetic results of thermal maleinization of polybutadienes

Polybutadiene	$\Delta H/J\ g^{-1}$			$\ln k_0$			$E_A/kJ\ mol^{-1}$			n		
	5	10	15	5	10	15	5	10	15	5	10	15
Maleic anhydride/%	-	-	-	-	-	-	-	-	-	-	-	-
Polyoil 110	-	28	-	-	13	-	-	65	-	-	1.0	-
Polyoil 130	-	7	-	-	20	-	-	87	-	-	1.0	-
Lithene 5000	35	82	132	23	23	26	98	98	113	1.0	1.2	1.8
Lithene PH	34	87	120	22	20	28	92	89	117	1.1	1.5	2.1
20048-4	11	29	22	24	24	25	106	108	113	1.3	1.3	1.0
38369-4	-	25	-	-	29	-	-	129	-	-	1.4	-
Polybutadienediol	17	23	-	9	10	-	51	55	-	0.8	1.3	-

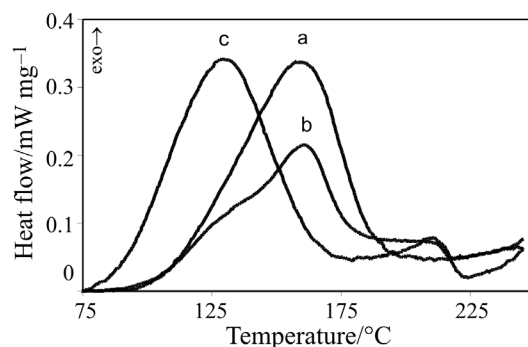


Fig. 2 DSC curves of Lithene 5000 with 10% maleic anhydride: a – without copper naphthenate, b – with 1% copper naphthenate, c – with 2% copper naphthenate

reactions also. Therefore, the exothermal maleinization peak observed without inhibitor was the result of the overlap of two peaks and this fact becomes more evident by the increase of copper naphthenate concentration.

The kinetic results obtained by data processing of maleinization peaks are reported in Table 3. The thermal effect in the presence of inhibitor was smaller than without, except for Polyols, that are mainly 1,4-*cis*. Moreover, the shift of the maleinization peak at lower temperature proves a catalytic effect of the copper naphthenate on the maleinization reaction, and can justify the use of this additive in industrial processes.

Maleinization in the presence of a radical initiator

DCP was chosen as radical initiator owing its better solubility in polybutadienes and lower dissociation enthalpy than other initiators as AIBN and benzoyl peroxide. DSC analysis of 2% DCP solution in silicon oil yielded a dissociation enthalpy of about 13 J g^{-1} with temperature peak at 180°C . The DCP addition to pure polybutadiene shows a strong exothermal peak due to radical crosslinking [11]. Moreover the ΔH values are proportional to the concentration of initiator. Lithenes yielded ΔH values higher (up to 108 J g^{-1} with 2% of DCP) than the other polybutadienes.

The maleinization of polybutadienes in the presence of DCP has shown two exothermal peaks: one at 150°C and another at 180°C ascribable to radical crosslinking. This fact was proved by the maleinization DSC curves of Lithene PH with and without radical initiator reported in Fig. 3 together with the crosslinking DSC curves. Moreover, in Fig. 4 some maleinization DSC curves of Lithene PH are shown with variable amount of maleic anhydride in the presence of 2% DCP.

The strong growth of the peak at 150°C by increase of maleic anhydride concentration has confirmed that this peak is due to maleinization, whereas the latter is slightly influenced by the maleic anhydride amount. The kinetic analysis, however, of the data was hindered by the partial overlap of these two peaks.

Table 3 Kinetic results of thermal maleinization of polybutadienes with 10% of maleic anhydride in the presence of copper naphthenate-xylene mixture

Polybutadiene	$\Delta H/J\text{ g}^{-1}$			$\ln k_0$			$E_A/kJ\text{ mol}^{-1}$			$T^{\text{peak}}/^{\circ}\text{C}$		
	0	1	2	0	1	2	0	1	2	0	1	2
Copper naphthenate/%	28	36	25	13	41	40	65	148	144	157	124	135
Polyoil 110	7	21	-	20	16	-	87	70	-	149	139	-
Polyoil 130	83	71	25	23	30	44	98	115	117	157	125	135
Lithene 5000	87	45	-	20	27	-	89	104	-	164	127	-
Lithene PH	28	11	-	24	33	-	108	127	-	185	140	-
20048-4	25	7	-	29	37	-	129	141	-	185	136	-
38369-4												

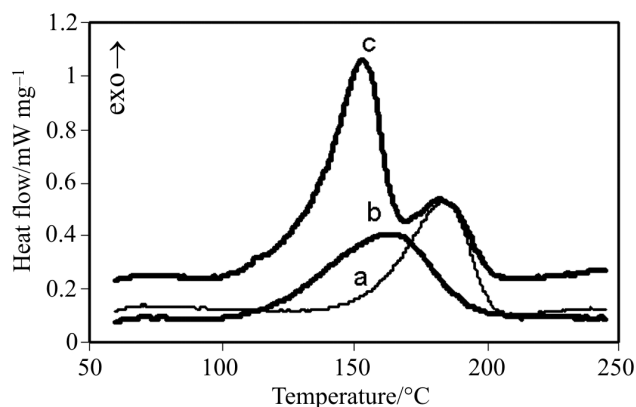


Fig. 3 DSC curves of Lithene PH with: a – 2% DCP, b – 10% MA, c – 10% MA and 2% DCP

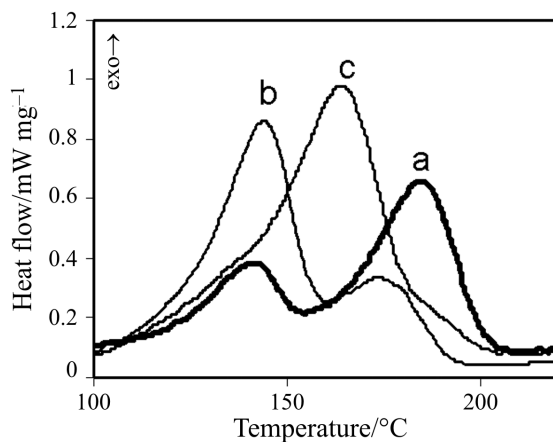


Fig. 4 DSC curves of Lithene PH with 2% DCP and: a – 5% MA, b – 10% MA, c – 15% MA

Therefore, the comparison of ΔH values only is reported in Table 4. The data were obtained by integration of the cumulative thermal effect (maleinization plus crosslinking) and then by subtraction of the integration value corresponding to the crosslinking peak. As in the case of thermal maleinization, Lithenes show higher thermal effects, whereas the butadienediol follows behind. The ΔH values for radical maleinization are higher than the corresponding values of pure thermal reaction reported in Table 2 and the increase is even relatively stronger for Polyoils. In any case the reaction enthalpy increases with maleic anhydride content.

Table 4 Comparison between ΔH values in polybutadiene maleinization with 2% DCP

Polybutadiene	$\Delta H/J\ g^{-1}$				ΔH maleinization/ $J\ g^{-1}$		
	Maleic anhydride/%	0	5	10	5	10	15
Polyoil 110	33	-	112	-	-	80	-
Polyoil 130	24	64	69	89	40	45	64
Lithene 5000	108	163	204	218	55	96	110
Lithene PH	70	134	172	198	64	102	129
20048-4	49	-	89	-	-	41	-
38369-4	37	-	91	-	-	54	-
Polybutadienediol	43	-	153	-	-	110	-

Conclusions

The kinetic study of the maleinization reaction of liquid polybutadienes using DSC has confirmed the influence of *m.w.* and polybutadiene microstructure on the reaction progress. Thermal maleinization, however, carried out in the presence of copper naphthenate proved that in some cases crosslinking reactions also occur, but this additive can allow the polybutadienes to be maleinized at lower temperature without crosslinking.

Moreover, the maleinization in the presence of a radical initiator as DCP yielded higher enthalpy values than pure thermal reaction increasing with maleic anhydride content, but the exothermal peaks due to maleinization and crosslinking are partially overlapped. Therefore the use of a radical initiator seems to be unreliable for the preparation of maleinized polybutadiene resins.

These results prove that the calorimetric analysis is a powerful method to investigate the course of the graft polymerization of maleic anhydride onto liquid polybutadienes allowing to discriminate among the competing reactions of graft polymerization and polymer crosslinking.

References

- 1 A. R. Luxton, *Rubber Chem. Technol.*, 54 (1981) 596.
- 2 B. C. Trivedi and B. M. Culbertson, *Maleic Anhydride*, Plenum Press, New York 1982.
- 3 H. M. R. Hoffman, *Angew. Chem. Intern. Ed. Engl.*, 8 (1969) 556.
- 4 F. R. Benn, J. Dwyer and I. Chappell, *J. Chem. Soc. Perkin Trans. 2*, (1977) 533.
- 5 J. Sheng, X. Lu and K. Yao, *J. Macromol. Sci. Chem.*, 27 (1990) 167.
- 6 J. Luchtenberg and H. Ritter, *Macromol. Chem. Phys.*, 195 (1994) 1623.
- 7 J. Luchtenberg and H. Ritter, *Macromol. R. C.*, 15 (1994) 81.
- 8 H. D. W. Zagefka, *Adv. Org. Coat. Sci. Technol. Ser.*, 12 (1990) 58.
- 9 Y. Nakayama, *Prog. Org. Coat.*, 33 (1998) 108.
- 10 A. I. Aigbodion, F. E. Okieimen, E. O. Obazee and I. O. Bakare, *Prog. Org. Coat.*, 46 (2003) 28.
- 11 I. Gancarz and W. Laskawski, *J. Polym. Sci. Polym. Chem. Ed.*, 17 (1979) 683.

- 12 F. Ferrero, M. Panetti and G. B. Saracco, *Chimica e Industria*, 66 (1984) 3.
- 13 M. Ghaemy and M.H. Riahy, *Eur. Polym. J.*, 32 (1996) 1207.
- 14 E. J. Choi, J. C. Seo, B. K. Choi and J. K. Lee, *Polym. Bull.*, 48 (2002) 111.
- 15 D. Rosu, C. N. Cascaval, F. Mustata and C. Ciobanu, *Thermochim. Acta*, 383 (2002) 119.
- 16 C. Esposito Corcione, A. Greco and A. Maffezzoli, *J. Therm. Anal. Cal.*, 72 (2003) 687.
- 17 J. L. Martin, *Polymer*, 40 (1999) 3451.
- 18 J. M. Kenny, G. Pisaniello, F. Farina and S. Puzziello, *Thermochim. Acta*, 269/270 (1995) 201.
- 19 G. Vazquez, J. Gonzalez-Alvarez, F. Lopez-Suevos, S. Freire and G. Antorrena, *J. Therm. Anal. Cal.*, 70 (2002) 19.
- 20 D. Morero, A. Santambrogio, L. Porri and F. Ciampelli, *Chimica e Industria*, 41 (1959) 758.
- 21 G. Widmann and R. Riesen, *Thermal Analysis*, Hüthling Verlag, Heidelberg 1987.