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PREPARATION AND STUDY OF EPOXIDIZED NATURAL RUBBER

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Abstract

Epoxidized natural rubbers (ENRs) with different extents of epoxidation (B) were prepared under various reaction conditions. The effects of the amount of H_2O_2 and the reaction time on B are discussed. The glass transition temperature T_g, the thermal degradation temperature and the activation energy of thermal degradation of the ENRs increase with B. The results indicate that the thermal stability of the ENRs increases with B.

Keywords: ENR, kinetics, thermal degradation

Introduction

Natural rubber (NR) has a number of disadvantages: some of its engineering properties, such as its resistance to oils and solvents, air permeability and wet skid, are quite poor. These properties can be greatly improved by the modification of NR by means of epoxidation, using an organic peracid directly or produced in situ. In the 1980s, Gelling [1] and Ng and Gan [2] successfully carried out the epoxidation of NR with peracetic and performic acids under moderate reaction conditions. Many papers on preparations, vulcanizates, stabilities, aging behaviour and applications of epoxidized natural rubber (ENR) have subsequently been published [3–11]. As concerns the thermal analysis, only Chaki [5] has studied the thermal-oxidative degradation of ENRs with different extents of epoxidation (B), 50 mol% and 25 mol%, by thermogravimetry (TG). As yet, there is no detailed report on the thermal degradation of ENRs with different B values in nitrogen. The preparation and kinetics, stabilities and thermal degradation behaviour of ENRs with different B values are reported in this paper.

Experimental

Preparation of ENRs

A certain amount of concentrated NR latex with 60% (m/m) of dry rubber content was stabilized with a nonionic surfactant and diluted with a predetermined amount of distilled water. Formic acid and H_2O_2 solutions were added slowly to the latex with stirring. The reaction was carried out at a required reaction time and tem-

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perature. The temperature of the reaction system was reduced to room temperature with a cool water bath, and the required amount of aqueous ammonia was then added to adjust the pH up to 9. The ENR latex was subjected to analysis.

A certain amount of ENR latex was poured into a clean culture dish and was coagulated with alcohol. The serum in the upper layer was removed, and the coagulum was washed with alcohol and acetone 3 times. The coagulum was dried to constant mass under reduced pressure at 50°C after volatilization of the solvent.

Determination of B values of ENRs

The B values of ENR samples were determined on a Nicolet 5D-X infrared spectrometer [12].

Determination of glass transition temperatures (T_g) of ENRs

The T_g values of ENRs with different B values were determined on a Perkin Elmer DSC-2B differential scanning calorimeter. The T_g values of the ENRs were correlated with B.

Thermogravimetry (TG)

TG analysis was carried out on a Perkin Elmer TG S-2 thermobalance in a nitrogen atmosphere. The heating rate was 20°C min^{-1}.

Calculation of kinetic parameters of thermal degradation of ENRs

When the thermal degradation of a sample is carried out at a programmed heating rate, the thermal degradation rate can be expressed as follows:

$$\frac{\mathrm{d}c}{\mathrm{d}t} = kf(c)$$

where $c=100(W_o-W)/(W_o-W_u)$, W_o is the mass of sample, W is the mass of sample remaining at a certain time, W_u is the mass of undecomposed residue, k is the Arrhenius rate constant, expressed as $k=A\exp(-E/RT)$, E is the activation energy, A is the frequency factor, and T is the absolute temperature.

If it is assumed that the function $f(c)$ is not affected by the reaction temperature and time, then $f(c)=(1-c)^n$ (n is the reaction order). Thus, the equation $\mathrm{d}c/\mathrm{d}t=A\exp(-E/RT)(1-c)^n$ can be obtained. The constant heating rate $\beta=\mathrm{d}T/dt$, and therefore $\mathrm{d}c/\mathrm{d}T=(A/\beta)\exp(-E/RT)(1-c)^n$. By taking logarithms of the two sides of the equation, we get the following equation:

$$\ln\left(\frac{\mathrm{d}c}{\mathrm{d}T}\right) = \ln\left(\frac{A}{\beta}\right) + \ln e^{-E/RT} + n\ln(1-c)$$

which is equivalent to a linear model, i.e.

$$\ln\left(\frac{\mathrm{d}c}{\mathrm{d}T}\right) = C_o + C_1\ln(1-c) + C_2\frac{1}{T}$$

The linear model was regressed by computer and was verified by using a verification statistical F value. The TG data were interpolated and differentiated using a cubic spline function before regression [13]. The activation energy, the reaction order and the frequency factor were calculated from the regression coefficients.

Results and discussion

Kinetics of formation of ENRs

From the basic reaction equations and the mass action law, the reaction kinetics of the preparation of ENR can be deduced as follows:

$$\frac{1}{C_{ao}-C_{bo}}\ln\left[\frac{C_{bo}(C_{ao}-B)}{C_{ao}(C_{bo}-B)}\right]=k_5C_{co}t$$

where C_{ao}, C_{bo} and C_{co} are the initial molar concentrations of NR calculated in isoprene units, H_2O_2 and formic acid, respectively, t is the reaction time and k is the reaction constant.

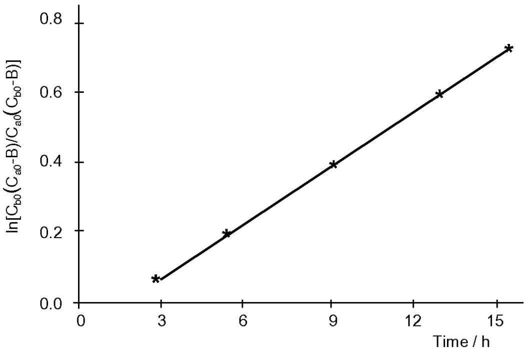

Fig. 1 Relation between the reaction time and B

The molar ratio values of the isoprene units of NR to H_2O_2 and formic acid was kept at 1.0:0.75:0.25 and the reaction temperature at 50°C. The product samples were taken at an interval of 3 h. The B values of the ENR samples were determined and $\ln[C_{bo}(C_{ao}-B)/C_{ao}(C_{bo}-B)]$ was calculated. From a plot of $\ln[C_{bo}(C_{ao}-B)/C_{ao}(C_{bo}-B)]$ *vs.* t (Fig. 1), it can be seen that B increases with elongation of the reaction time. The reaction time (t) is a linear function of $\ln[C_{bo}(C_{ao}-B)/C_{ao}(C_{bo}-B)]$, which indicates that the formation of ENR is a second-order reaction.

Storage stability of ENRs

The variations in the contents of epoxy bonds and double bonds were determined throughout a storage period interval. The results are shown in Table 1. It can be seen that ENR with high B has a relatively poor storage stability. The epoxy bonds are

Table 1 Storage stability of ENRs

Sample no.	0 month		3 months		6 months	
	B	*D*	*B*	*D*	*B*	*D*
1	5	92	4	92	5	92
2	16	81	16	80	16	80
3	28	66	28	66	27	68
4	34	60	33	60	34	59
5	46	49	43	49	43	49
6	56	36	52	37	52	37
7	65	28	61	27	57	27

Note: B and D are the mole percentages of epoxy bonds and double bonds

readily opened, which results in a decrease in the *B* value of the ENR. In contrast, ENR with a low *B* value has a good storage stability.

Effect of B on T_g values of ENRs

The ENR T_g values determined by DSC analysis and the shift in T_g relative to T_g of NR with the *B* values are shown in Fig. 2. With increase in *B*, T_g of the ENR increases linearly. The relation between *B* and T_g can be expressed as $T_g=kB+T_g^o$ (T_g^o is the T_g of NR).

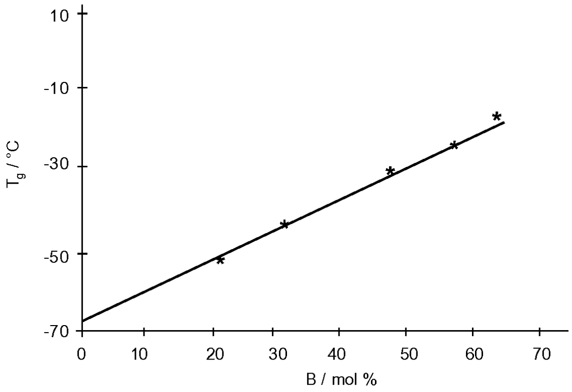

Fig. 2 Relation between T_g and *B*

Thermal degradation of ENRs

The thermal degradations of ENRs with different *B* values in nitrogen were studied by TG analysis. The TG and DTG curves are shown in Fig. 3. Initial temperatures of loss in mass (T_i), final temperatures of loss in mass (T_f) (calculated by the bitangent method) and temperatures at maximum rate of mass loss (T_p) are shown in Table 2.

Table 2 Temperatures of thermal degradation of ENRs

Sample no.	B/mol%	T_i/°C	T_p/°C	T_f/°C
1	0	355.5	382.7	408.4
2	5	358.4	386.1	421.6
3	16	363.7	389.4	426.8
4	28	366.3	392.3	432.1
5	34	367.6	394.6	432.1
6	56	366.3	411.5	447.9
7	65	371.0	400.4	442.6

It can be seen from Fig. 3 and Table 2 that the thermal degradations of the ENRs are one-step reactions, and T_i, T_p and T_f gradually rise with B. The reason for the rising T_i may be that the rings of the epoxy groups are opened at the beginning of heating, which brings about a crosslinking reaction and prevents the thermal degradation from carrying through.

The higher B is, the more obvious the crosslinking reaction is. It is the crosslinking reactions that makes T_i rise with increase in B. When this reaction ends, the thermal decomposition is mainly carried on by the endothermic reaction. The reason for the rises in T_p and T_f may be that the oxygen content of the ENRs increases with B. The percentages of high polar and oxygen-containing compounds in the thermal degradation products increase with B. The high polarities and volatilities of these compounds make the values of T_p and T_f increase.

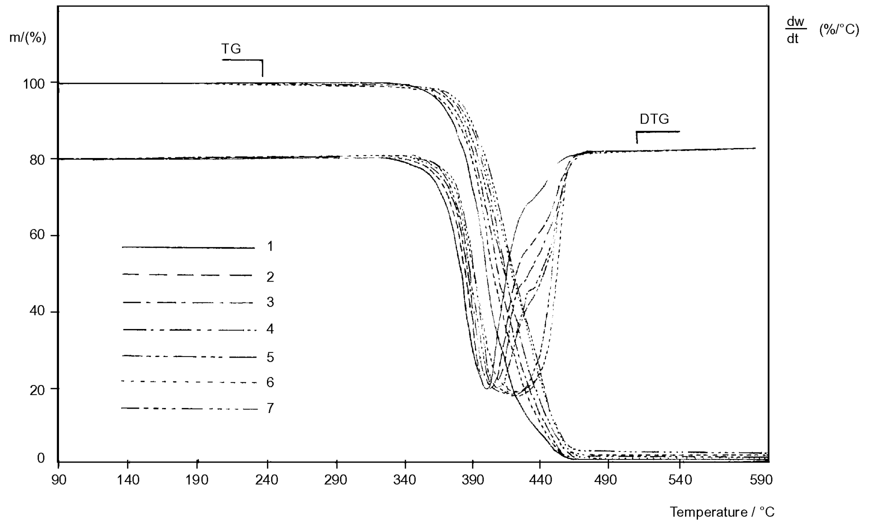

Fig. 3 TG and DTG curves of ENRs

Kinetics of thermal degradation of ENRs

The results of regression of the linear model are shown in Table 3. It can be seen that the calculated *F* values are greater than the critical values, which means that the hypothesis of the linear model is reasonable.

The calculated kinetic parameters of thermal degradation of the ENRs are shown in Table 4. It can be seen that all the thermal degradations of the ENRs are close to first-order reactions. Both the activation energy and frequency factors of the ENRs increase with *B*. This indicates that the thermal stability of the ENRs increases with *B*.

Conclusions

ENRs with different *B* values can be prepared by modifying the reaction conditions. The T_g values of the ENRs increase linearly with *B*.

The thermal degradation temperatures and the activation energies of the ENRs, calculated via binary linear regression, increase with *B*, which indicates that the thermal stabilities of the ENRs increase with *B*.

Table 3 Results of binary regression of linear models

No.	C_o	C_1	C_2	F	F_o
1	11.84	0.802	–10316.76	14.806	5.93
2	23.42	0.946	–18054.49	37.992	5.85
3	23.81	0.956	–18431.17	71.657	5.78
4	24.34	0.954	–18868.86	66.280	5.78
5	25.93	0.964	–19927.47	59.513	5.78
6	25.78	0.938	–20022.96	87.853	5.78
7	28.90	1.069	–21988.40	89.966	5.78

$C_o = \ln(A/\beta)$; $C_1 = n$; $C_2 = (-E/R)$

F is the verification statistical value; F_o is the critical value at the significance value: 0.01

Table 4 Kinetics of thermal degradation of ENRs

B/mol%	*A*	*n*	*E*/kJ mol^{-1}
0	$1.407 \cdot 10^{6}$	0.802	85.73
5	$1.478 \cdot 10^{11}$	0.946	150.03
16	$2.199 \cdot 10^{11}$	0.956	153.16
28	$3.720 \cdot 10^{11}$	0.954	156.80
34	$1.817 \cdot 10^{12}$	0.964	165.59
56	$1.571 \cdot 10^{12}$	0.938	166.39
65	$3.565 \cdot 10^{13}$	1.069	182.72

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