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Epoxidized natural rubber/dicarboxylic acid self-vulcanized blends

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ABSTRACT

Curing behaviour as well as mechanical properties of binary blends of epoxidized natural rubber (ENR) and dodecanedioic acid (DA) were investigated for development of self-vulcanizable elastomer blends. Cross-linking reaction at 180 °C of reactive functional rubber containing 25 and 10 mol% epoxide groups was followed by rheology. The properties of the cured materials were studied by dynamic mechanical analysis, stress–strain experiments, and DSC measurements. It was shown that a specific ratio ENR/DA gave rise to optimum mechanical properties. This ratio decreases together with the epoxidation level of the rubber. DSC measurements revealed that the glass transition temperature of the cured material increases nonlinearly at high concentrations of cross-linking agent. By comparing cross-linking with DA and reaction with monofunctional lauric acid, this behaviour was attributed to polar interactions due to free carboxylic groups of pending diacid grafts.

1. Introduction

Epoxidized natural rubber (ENR) is a material of great interest, exhibiting a double functionality for cross-linking (double bonds and epoxy sites), while retaining most of the properties of natural rubber [1,2]. By epoxidation of NR (natural rubber) in solution or at the latex stage, ENR of any degree of epoxidation can be prepared [3]. The resulting ENRs exhibit a random distribution of the epoxy groups along the polymer backbone [4].

A gradual change in the properties of these materials occurs with increasing epoxidation level [5,6]. Most of the studies were, however, confined to ENR25 and ENR50 (25 and 50 mol% epoxidation, respectively) which are the commercially available grades. As the level of epoxidation increases, the glass transition temperature T_g goes up linearly, resulting in decreased resilience. Due to the polar nature of the oxirane groups, the epoxidized NR exhibits various useful properties, *e.g.*, low gas permeability [7], oil resistance [8], as well as enhanced compatibility with polymers bearing polar groups like polyamide [9] or PVC [10]. Besides, unlike other synthetic copolymers based on *cis*-1,4-polyisoprene, ENR is still able to undergo strain crystallization, maintaining high tensile properties and hence resistance to crack propagation up to 50 mol% epoxidation [11]. The epoxidation process which is stereospecific preserves the *cis*-1,4-configuration of the polymer and the oxygen atom is small enough to fit into the crystal lattice with only minor geometrical rearrangements. However, the percent crystallinity under strain reduces significantly beyond 50 mol% epoxidation [11]. In addition, a degree of reinforcement comparable to carbon black may be obtained with silica without the use of a coupling agent [5,6]. These materials have thus potential applications including coloured vulcanizates.

Sulphur [12] or peroxides [13] formulations, which require many assisting reagents in addition to the cross-linker, can be employed to cure ENR. Sulphur reacts preferentially with the double bonds rather than with the epoxide groups. However, vulcanization by sulphur is more effective than in the case of NR. Model molecules showed that this effect was associated to two main causes. First, epoxide groups contiguous to double bonds might have an activator role. Second, sulphur reaction with double bonds is a radical addition mechanism, which is slowed down by side reactions between adjacent double bonds. Since epoxidized NR contains some isolated double bonds, this effect is reduced [12]. Sulphur vulcanizates of ENR show poor ageing, because thermal decomposition of oxidized sulphides delivers acids which, over time, catalyze ring opening reactions with the formation of ether cross-links, and a subsequent increase in the stiffness of the vulcanizates [12].

As a reactive functional polymer, ENR may alternatively be cross-linked *via* ring opening of the epoxide groups [14]. ENR can be crosslinked by amine compounds [15] or aminosilanes and moisture curing [16]. Several studies have shown that carboxylic monoacids [17], *e.g.*, benzoic acid [18,19], naphtylacetic acid [20], methacrylic acid [21] react with ENR to form β-hydroxy-esters along the chain, but only a few studies were concerned with the

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reaction of ENR with di- or multifunctional acids [13,22–24]. These studies have focused on the behaviour of ENR50.

Herein we report on simple binary blends of dicarboxylic acid and ENR, and subsequent curing at 180 °C. Low levels of epoxidation (10 and 25 mol%) were preferred in an attempt to preserve most of the properties of natural rubber and to minimize the ecological cost of peroxidation. The mechanical properties of the cured materials have been investigated to design a simple self-vulcanized blend having optimum stress–strain behaviour.

2. Experimental

2.1. Materials

ENR10, ENR25 and ENR50, containing, respectively, 10, 25 and 50 mol% epoxide groups, were supplied by the Tun Abdul Razak Research Centre (Malaysia). Dodecanedioic acid (DA) (99%, Acros) and lauric acid (LA) (98%, Aldrich) were used without further purification. Sulphur, stearic acid, zinc oxide and mercaptobenzothiazole, used in sulphur formulations, were provided by Univar, Umicore, and Flexsys, respectively.

2.2. Sample preparation

Blends of rubber and acid were made in a Haake Polydrive mixer equipped with cam rotors. Dodecanedioic acid (mp: 128–130 °C) was mixed with rubber at 40 °C for about 12 min. During mixing the temperature goes up to about 70 °C. Blends with lauric acid (mp: 44–46 °C) were performed at 20 °C under circulation of cooling water, to avoid melting of the acid during the process. Materials were cured for 3 h in a CARVER press at 180 °C under 8-ton pressure.

2.3. Measurements

2.3.1. Curing

Cross-linking process was followed by rheology using a TA Instruments ARES rheometer, in plate–plate geometry (25 mm diameter) (1 Hz frequency, 0.1% strain). To ensure a good contact between the material and the plates, an axial force of 15 N was first applied to the sample. The temperature was raised from 25 °C to 180 °C at 5 °C/min, and then the sample was left under shearing for curing. To validate the results, curing was also studied by following the torque evolution in a Moving Die Rheometer (Monsanto MDR) (1.66 Hz frequency, ±0.5° oscillation amplitude). The sample mass used for each testing was about 5 g. When comparing data measured with the two rheometers, the origin of time was taken at 180 °C at the minimum of the elastic modulus G' in both cases. Hence, the results are not dependent on the difference of heat treatment underwent by the samples (ramp of temperature from 25 to 180 °C in the ARES, sample introduced in the rheometer preheated at 180 °C in the MDR).

Table 1
Mix compositions with different epoxide/diacid ratios: DA = dodecanedioic acid; phr = parts per hundred parts of rubber by weight; p = epoxide sites for 1 diacid molecule; M/DA = total monomer units/diacid.

DA (phr)	p_{ENR10}	p_{ENR25}	M/DA
0.8	40	100	400
1.6	20	50	200
3.2	10	25	100
8	4	10	40
16	2	5	20

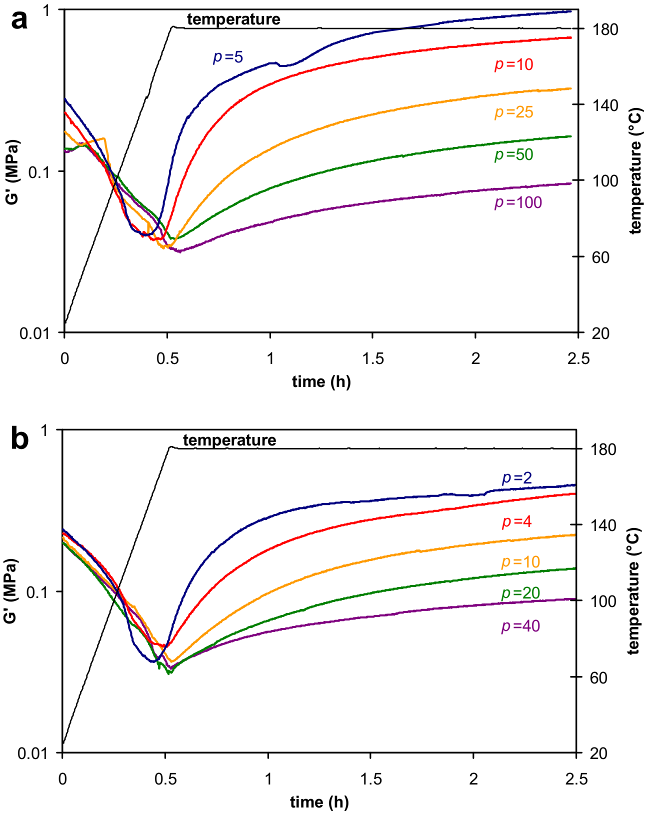

Fig. 1. Cross-linking of ENR25 (a) or ENR10 (b) with DA in the ARES rheometer. $T_{\max} = 180$ °C.

2.3.2. Mechanical properties

Temperature evolution of Young modulus was measured on cured samples using a TA Instruments Dynamical Mechanical Analyzer (DMA), in film tension configuration. Samples cut in a cured rubber sheet (1.5 mm thickness) were submitted to a 1-°C/min temperature ramp from 25 °C to 180 °C (1 Hz, 0.1% strain).

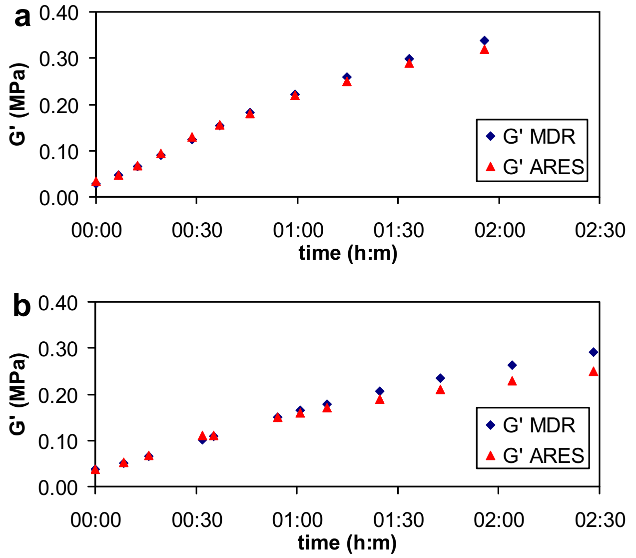

Fig. 2. Comparison of results obtained in the ARES rheometer (triangles) and in the MDR rheometer (diamonds) for blends of ENR25 ($p = 25$) (a) or ENR10 ($p = 10$) (b) with DA. $T = 180$ °C.

Table 2a
Effect of the epoxide/diacid ratio on the crosslinking reaction of ENR25 with DA.

ENR25 + DA	$mDA_p/mDA_{p=25}$	v_0 (10^{-3} MPa min^{-1})	$v_{0p}/v_{0p=25}$	G' (MPa)	$G'_p/G'_{p=25}$	E' (MPa)	E'/G'
$p = 100$	0.25	0.7	0.18	0.083	0.26	0.22	2.7
$p = 50$	0.5	1.5	0.4	0.16	0.5	0.54	3.4
$p = 25$	*1*	*3.7*	*1*	*0.32*	*1*	*1.19*	*3.7*
$p = 10$	2.5	11	3	0.67	2.1	2.72	4.1
$p = 5$	5	17	4.6	0.97	3.0	4.19	4.4

Table 2b
Effect of the epoxide/diacid ratio on the crosslinking reaction of ENR10 with DA.

ENR 10 + DA	$mDA_p/mDA_{p=10}$	v_0(10^{-3} MPa min^{-1})	$v_{0p}/v_{0p=10}$	G' (MPa)	$G'_p/G'_{p=10}$
$p = 40$	0.25	0.8	0.39	0.09	0.4
$p = 20$	0.5	1.2	0.55	0.14	0.6
$p = 10$	*1*	*2.15*	*1*	*0.22*	*1*
$p = 4$	2.5	4.85	2.25	0.40	1.8
$p = 2$	5	10	4.69	0.45	2.1

v_0, initial rate; G', elastic modulus measured at 180 °C (2.5 h) in the ARES rheometer; E', Young modulus measured at 180 °C in the DMA on cured samples (3 h at 180 °C).

Strain–stress behaviour was established using an Instron machine with a crosshead speed of 500 mm/min, until break. Dumbbells of 10 mm of effective length and 2 mm of width (or 25 mm length and 4 mm width for low-deformation samples) were cut in a 1.5-mm thick cured rubber sheet. For each sample, five specimens were tested. Strain was followed using a video extensometer.

Hardness Shore A and resilience of the cured rubbers were measured according to the standards ISO 7619-1 and ISO 4662, respectively.

2.3.3. Differential scanning calorimetry

DSC measurements were performed using a Q1000 series TA Instrument under nitrogen flow. Samples (10 mg) encapsulated in hermetic pans were first submitted to a temperature ramp from 0 °C to 140 °C to equilibrate the system, and then samples underwent a cycle from 140 °C to −100 °C and from −100 °C to 180 °C, at a rate of 10 °C/min.

3. Results and discussion

Blend ratios of ENR25/DA and ENR10/DA binary mixtures are compiled in Table 1. The ratio epoxide/diacid is referred to as p = number of epoxide sites for 1 diacid molecule: the higher the number p, the lower the concentration in DA. For instance, $p = 25$ for ENR25 corresponds to 25 epoxide units for 1 diacid, *i.e.*, 1 diacid for 100 total monomer units of the polymer backbone (M/DA = 100). The epoxide groups being always in excess compared to the diacid, it follows that $p = 25$ for ENR25 and $p = 10$ for ENR10 should lead to the same quantity of cross-links if all the acid had reacted.

3.1. Curing behaviour

Fig. 1 shows the evolution of elastic modulus for blends of ENR25 (a), or ENR10 (b), with DA, when heating at 180 °C in the ARES rheometer. During the temperature ramp, G' first decreases because of softening of ENR. At 180 °C, the increase of G' shows that the cross-linking reaction becomes effective. The increasing slope of G' with decreasing p indicates that the reaction proceeds faster with increasing amount of diacid. The final elastic modulus increases with decreasing p, which indicates a higher cross-linking density with increasing quantity of diacid.

Rubber cross-linking is usually followed in rheometers having a closed cavity like the MDR. We made measurements in a MDR as well, to check the validity of the results obtained in the ARES rheometer. Fig. 2 shows the comparison between elastic modulus measured in the ARES, and elastic modulus G' calculated from the torque S' measured in the MDR:

$$G' \approx \frac{3S'}{2\pi R^3 \gamma}$$

with R the radius of the geometry and γ the strain applied, for blends of DA and ENR25 (a) or ENR10 (b). These data show that ARES rheometer is suitable to follow the cross-linking reaction in the present system.

In Tables 2a and 2b are summarized the initial rate of reaction v_0 and the maximum of elastic modulus G' (at 2.5 h) for all compositions. To make easier the comparison between experiments, all values of v_0 and G' were normalized by the value at a ratio corresponding to 1 diacid for 100 monomers (in italic in the tables). The initial rate v_0 was estimated by the tangent at the G' curve when the elastic modulus starts increasing. The kinetics of ENR10/DA reaction is slower that the one of ENR25/DA for the same proportion of DA (same M/DA, Table 1), probably because of a lower meeting probability between carboxylic acid functions and epoxide sites in the ENR10 case. However, cured ENR10 exhibits promising mechanical properties (*vide infra*).

The elastic modulus G' is proportional to the cross-link density of the network being formed by chemical bonds and physical entanglements. Its change during the time of curing may be associated to the ring-opening reaction. If it is assumed that the change

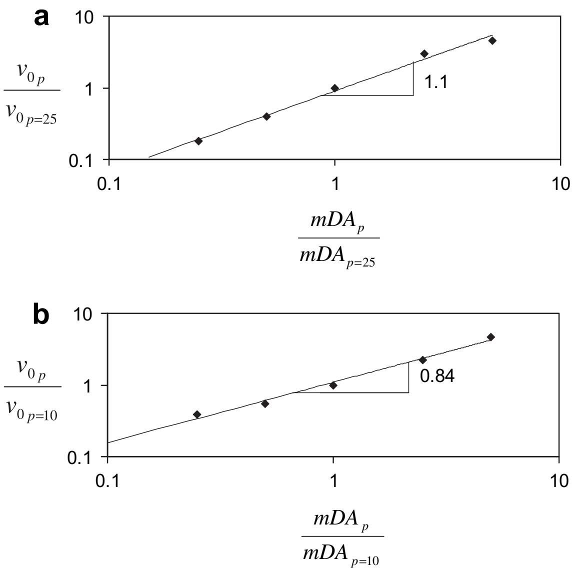

Fig. 3. Effect of the amount of diacid on the initial rate of the crosslinking reaction of ENR25 (a) or ENR10 (b) with DA.

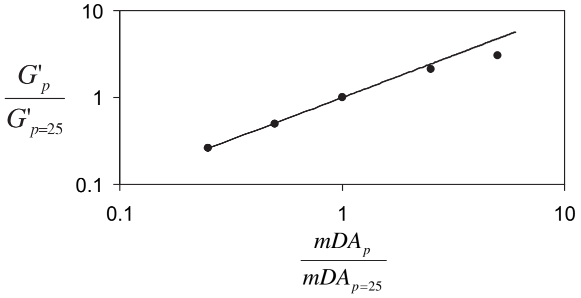

Fig. 4. Variation of the normalized value of G' versus the normalized amount of crosslinking agent in ENR25/DA blends.

of G' is directly proportional to the extent of the reaction with the diacid, then the rate of reaction may be written as:

$$\frac{dG'}{dt} \propto -\frac{d[\mathrm{DA}]}{dt} = Ck[\mathrm{DA}]^m[\mathrm{ENR}]^n$$

where C is a proportionality constant, k the rate constant, [DA] and [ENR] the concentrations in diacid and epoxy, m and n the respective orders of reaction. For a given ENR (*i.e.*, [ENR] = constant), the initial change of G' with time increases with the amount of diacid, as indicated by the increasing slope of G' versus decreasing p in Fig. 1. The plot of initial rate v_0 versus diacid concentration (Fig. 3) suggests that the reaction is approximately first order with respect to the diacid ($m \approx 1$). This value is in agreement with kinetic studies of the reaction of ENR50 and benzoic acid as determined *via* isothermal differential scanning calorimetry [18,19].

At low amount of DA, the maximum value of G' is linearly related to the increase of diacid mass. For the highest proportions of diacid, however, a deviation from the linearity is observed (Fig. 4). In these latter cases, the diacid/epoxide reaction becomes less effective. Several causes may be invoked: close vicinity of the crosslinking points, mono-reacted diacids (pending chains), unreacted residual diacids, or increased density of the network reducing the diffusion of DA. The same effect on G' is observed in the case of ENR10/DA blends.

3.2. Mechanical properties

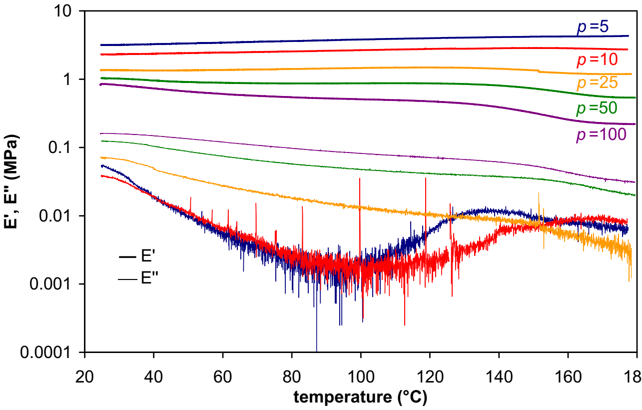

Fig. 5. Effect of the epoxide/diacid ratio on Young modulus of ENR25 + DA cured samples (3 h at 180 °C). E' and E'' are the elastic and viscous moduli, respectively.

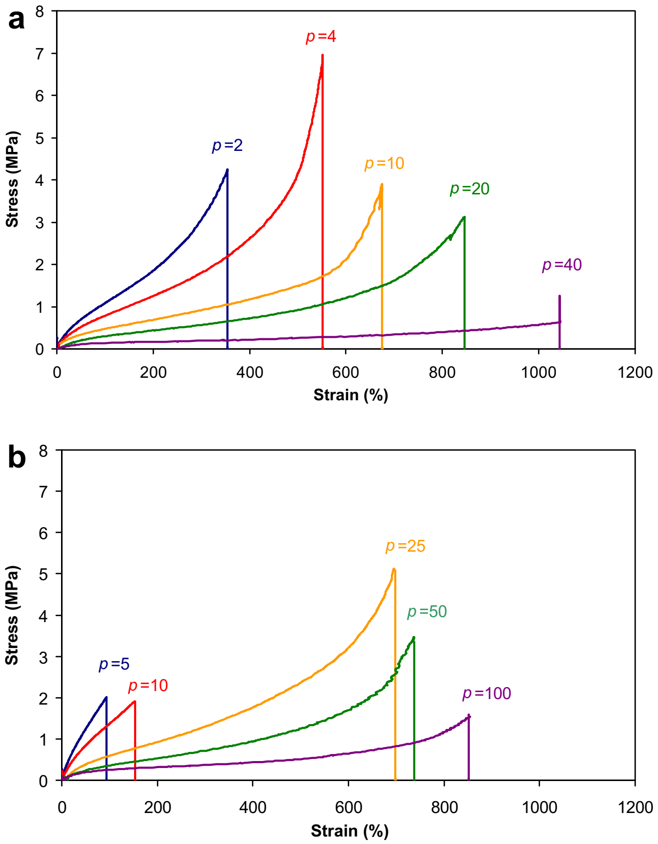

Fig. 6. Strain–stress measurements after curing for 3 h at 180 °C in press: (a) ENR10 + DA, (b) ENR25 + DA.

Mechanical properties of samples cured for 3 h at 180 °C were examined by Dynamical Mechanical Analysis and stress–strain measurements. DMA confirms that with increasing DA concentration (decreasing p), the elastic modulus E' rises whereas the viscous modulus E'' decreases (Fig. 5). For $p = 5$ and $p = 10$ systems, an increase of the viscous modulus is observed around 120–130 °C, which may be due to additional relaxations (see Section 3.3). In Table 2a are compared values obtained for E' at 180 °C and for the maximum of G' measured in the ARES rheometer at the same temperature. Theory predicts:

$$G = \frac{E}{2(\upsilon + 1)}$$

with υ the Poisson coefficient [25]. For natural rubber, $\upsilon = 0.5$ [26], hence $E = 3G$. Experimentally, we found E'/G' close to 3 (Table 2a). This ratio is slightly higher for high concentrations in DA. This could be due to the fact that cross-linking reaction is more advanced for cured samples observed in DMA (3 h in the press, instead of 2.5 h including ramp temperature in the rheometer).

On Fig. 6 are presented the strain–stress measurements on samples cured for 3 h in the press at 180 °C. The elongation at break is in average higher with ENR10 than with ENR25, probably because

Table 3
Effect of the epoxidation level on mechanical characteristics of materials cured with dodecanedioic acid DA.

	ENR50 + DA ($p = 50$)	ENR25 + DA ($p = 25$)	ENR10 + DA ($p = 10$)
Hardness Shore A	38	35	29
Resilience (%)	10	60	75
Elongation break (%)	400	690	660

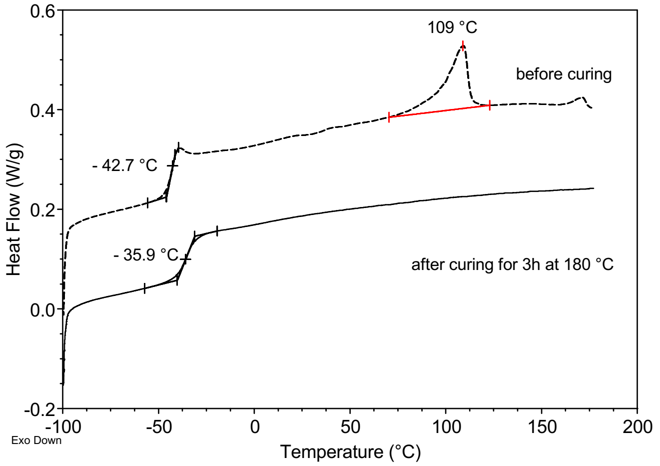

Fig. 7. DSC curves of ENR25 + DA ($p = 10$) before (dashed) and after (full) curing for 3 h at 180 °C.

of higher strain-induced crystallization. For ENR25, the ratio $p = 25$ is the optimum tested as it presents the highest tensile strength and a satisfactory elongation at break. When more diacid is incorporated to the rubber, the resulted material becomes brittle. It breaks at low deformation rate, and the curve does not show hyper-elastic behaviour. With less crosslinking agent, the tensile strength decreases and some creep may take place. ENR10 exhibits an optimal behaviour at $p = 4$. Compared to ENR25, this optimum corresponds to a higher amount of diacid per 100 monomers of rubber. Since the crosslinking reaction is slower for ENR10 which contains fewer epoxy sites than ENR25, more crosslinking agent is needed for ENR10 to reach the same modulus as ENR25.

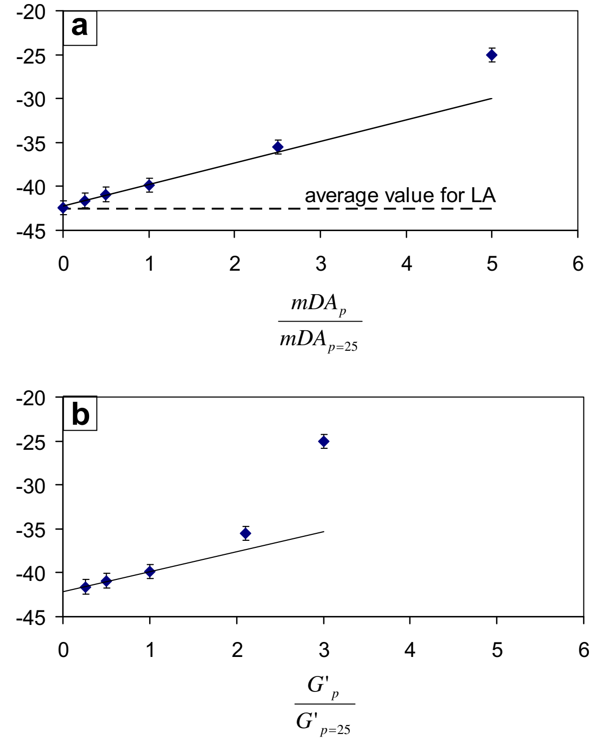

Fig. 8. Variation of T_g after curing ENR25 for 3 h at 180 °C: (a) versus the normalized amount of DA, (b) versus the normalized shear modulus G' at its maximum. Dashed line in (a) indicates the average T_g value for different amounts of LA after curing (Table 4).

Table 4
Evolution of T_g with the amount of LA, before and after curing for 3 h at 180 °C.

LA (phr)	p'_{LA}	p_{DA}	T_g (°C) before curing	T_g (°C) after curing
0			−42.4	–
1.1	62.5	125	−43.2	−42.8
2.2	31.5	62.5	−44.4	−42.4
5.6	12.5	25	−45.2	−42.7
13.9	5	10	−44.6	−42.1
27.8	2.5	5	−44.2	−42.3

In Table 3 are compared mechanical properties of ENR25 and ENR10. ENR50, the epoxide grade, the most studied in literature, was also investigated here for comparison. For the three blends, the same amount of DA was introduced. The hardness Shore A decreases with decreasing epoxide level, in agreement with the measured modulus E'. In parallel the resilience increases. Values obtained for ENR10 are even comparable to values for sulphur-vulcanized natural rubber ($65 < \%\text{resilience} < 85$ [27,28]). This may be rationalized by the glass transition temperature of the materials, which decreases together with the epoxide level of the rubber ($T_g = -20$ °C, −42 °C, −55 °C, for ENR50, ENR25, ENR10, respectively).

3.3. Thermal behaviour

Evolution of the glass transition temperature of the materials with concentration in DA was evaluated, as well as its relationship with the crosslinking density. DSC measurements were performed on ENR25/DA blends, before and after curing for 3 h at 180 °C. An example for $p = 10$ is shown in Fig. 7. For all samples, the glass transition temperature of the elastomer before curing is not affected by the presence of unreacted DA ($T_g \approx -42$ °C for all samples, as for raw ENR25). This may be due to the fact that ENR25 glass transition temperature and DA melting point are well separated. The melting temperature of DA in the blend (≈109 °C) is lower than the one of pure DA (129 °C). A decrease is also observed in the DA melting enthalpy ($\Delta H = 142$ J/g versus 245 J/g for pure DA). This indicates that about only 60% of the total DA crystallizes in the polymer matrix, possibly because of the dilution of DA in the elastomer. For concentrations lower than $p = 10$, DA melting is even hard to observe. After 3 h of curing at 180 °C (Fig. 7), the melting peak is no longer visible, meaning that most of the DA was consumed or at least that there is not enough free diacid to be detected. For all samples, cured materials exhibit a higher T_g than

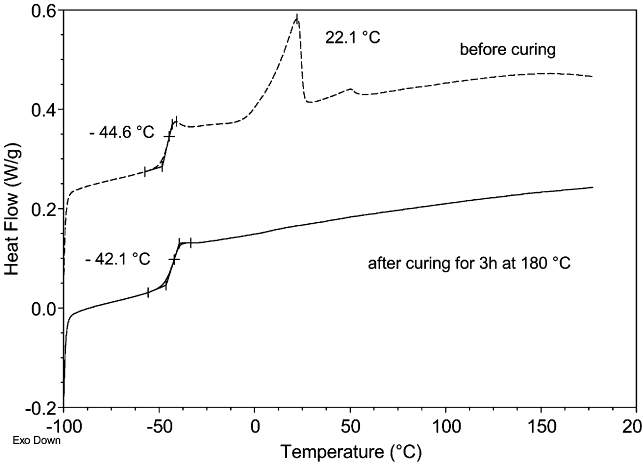

Fig. 9. DSC curves of ENR25 + LA ($p = 10$) before (dashed) and after (full) curing for 3 h at 180 °C.

Table 5
Blend compositions of ENR25 + S and ENR10 + S. phr=parts per hundred parts of rubber by weight; MBT=mercaptobenzothiazole.

phr	S + ENR25 or ENR10
ENR	100
ZnO	6
Stearic acid	0.5
MBT	0.5
Sulphur	3.5

raw ENR25, meaning that reaction with diacids decreases the mobility of elastomer matrix. This phenomenon can be explained by cross-links formation, as well as by main-chain modifications due to the ring-opening of the oxirane groups. For low concentrations in DA, T_g increases proportionally to the mass of cross-linking agent. At high concentrations ($p = 10$ and $p = 5$), the linearity is lost (Fig. 8(a)): T_g shifts to higher temperatures.

Fox and Loshaek have established a variation law for glass transition temperature with mass between cross-links, M_r:

$$T_{g(\text{network})} = T_{g(\text{linear})} + \frac{k}{M_r}$$

where $T_{g\ (\text{network})}$ and $T_{g\ (\text{linear})}$ are the glass transition temperatures of the cured material and uncured material, respectively, and k a factor depending on the network rigidity [29]. As the shear modulus G is inversely proportional to M_r, T_g should vary linearly with G' if the network formation was the only phenomenon responsible for its increase. In Fig. 8(b) are reported the T_g values *versus* the ratio $G'_p/G'_{p=25}$ (from Table 2a). The figure shows that T_g increases nonlinearly with G' at high concentrations in DA.

This deviation may be due to mono- or unreacted diacids, pendant chains, or main-chain modifications caused by the hydroxyl groups present after epoxide ring-opening. To investigate this, DSC measurements were performed on mixtures of ENR25 and lauric acid (LA). Lauric acid is a 12-carbon chain monofunctional acid, which cannot induce cross-linking reactions. The mixture compositions are compiled in Table 4: p' is the number of epoxide sites for one molecule of monoacid, p is the same ratio for the diacid. Because of the double functionality of DA, $p = 2p'$.

On Fig. 9 are presented the DSC curves for ENR25 + LA blends before and after curing for 3 h at 180 °C. The ratio epoxide/acid ($p' = 5$) is here the same as for the ENR25 + DA blend presented on Fig. 7 ($p = 10$). Before curing, LA melting peak is observed around 22 °C, lower than the one of pure LA (44–46 °C). In presence of lauric acid, the T_g of the rubber is slightly lower (≈ 2 °C) than the one of pure ENR25 (Table 5). After curing for 3 h at 180 °C, the LA melting peak disappears, indicating that lauric acid is grafted on ENR25. For all the proportions tested, the T_g of grafted elastomers remained unchanged in comparison with pure ENR25 (≈ -42.5 °C). This shows that the ring-opening of epoxide sites, resulting in hydroxyl and ester formation, does not induce an increase of T_g. Therefore main-chain modifications cannot explain the deviation of T_g to higher temperatures for high proportions in DA. This result is significantly different from the one obtained earlier in the reaction of ENR50 with benzoic acid [18]. In that case, T_g of the reacted blend was shown to increase linearly with benzoic acid loading (3.7 Kmol^{-1}, $\Delta T_g = +25$ °C for 12.5 phr). This effect was attributed to the polar hydroxyl group present on the main-chain after ring-opening, introducing inter- and intramolecular hydrogen bonding. The same effect is not observed with lauric acid, may be because linear lauric acid is less bulky than benzoic acid and does not intervene in the main-chain mobility.

Since the increase of T_g is not due to main-chain modifications, our hypothesis to explain the deviation from linearity is that the samples containing high amounts of DA present more pending chains. This may induce polar interactions with other carboxylic groups (from pendant chains) or epoxide sites (Fig. 10), contributing to reduce the mobility, together with the cross-link formation. It is well known that polar interactions may influence significantly the physical properties of elastomers. Physical cross-links based on ionic interaction or hydrogen bonding have been shown to improve the tensile properties of thermoplastic elastomers [30,31]. Interaction between pendant carboxylic acid groups and Zn^{2+} ions leading to the formation of ionic clusters has been invoked in the self-reinforcement of ZnO-cured elastomeric ionomers [32–34]. DMA measurements (Fig. 5) were in agreement with the assumption of polar interactions in our system, as the increase of the viscous modulus E'' for samples $p = 5$ and $p = 10$ at high temperatures could be associated to secondary relaxations of aggregates formed by hydrogen bonds.

3.4. Comparison with sulphur vulcanization

A classical vulcanization by sulphur (S) was performed to compare with crosslinking by diacids. In Table 5 is given the standard recipe for sulphur-vulcanization used here.

When ENR/S blends undergo the same thermal treatment as ENR/DA blends (3 h at 180 °C), mechanical properties of the resulted materials are very comparable (Fig. 11). Classical sulphur cures performed a few minutes at 140–160 °C are generally known to produce high tensile strength materials, though. Here the long thermal treatment at 180 °C leads to degradation of the properties of the sulphur vulcanized rubber.

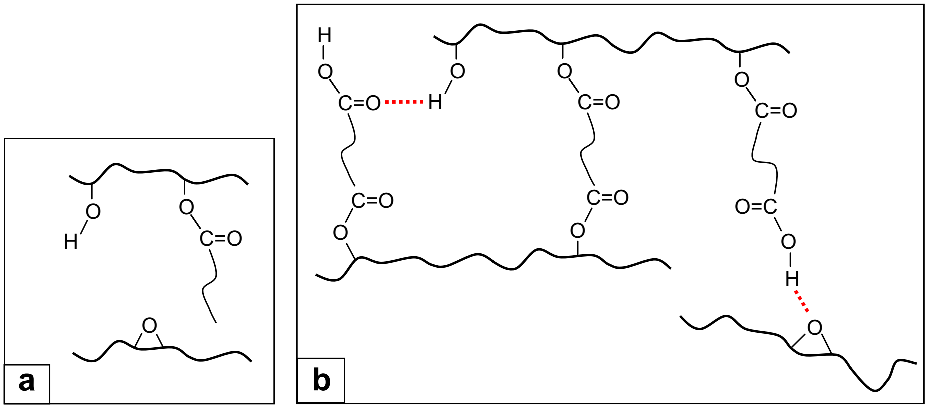

Fig. 10. (a) Graft LA; (b) graft DA: different secondary interactions induced by free carboxylic groups.

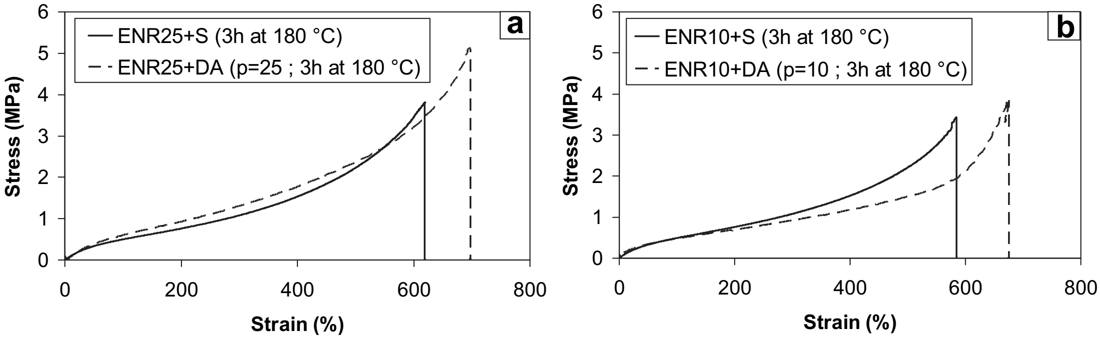

Fig. 11. Strain–stress measurements after curing for 3 h at 180 °C. Comparison between materials crosslinked by sulphur (S) or by DA: (a) ENR25, (b) ENR10.

If the reaction of cross-linking with the diacids could be achieved faster, better mechanical properties of the ENR/diacid systems would be expected. Moreover the chemical stability of the carbon–carbon covalent bond may produce materials with superior properties of ageing, compared with classical vulcanization. The reaction between ENR and diacid has thus to be accelerated to weaken the detrimental effect of heat treatment and to subsequently improve the mechanical properties of the vulcanizates. Catalysis of the reaction of ENR with dicarboxylic acids is currently under progress in our group.

4. Conclusion

Curing behaviour as well as mechanical properties of binary blends of epoxidized natural rubber (ENR) and dodecanedioic acid (DA) were investigated. By varying the amount of diacid, we studied the effect of the cross-linker concentration on the reaction kinetics, and the effect of the cross-linking density on the mechanical properties. It was shown that the reaction kinetics was first order regarding to DA, and that cross-linking was more efficient for rubbers with high epoxide functionality. Optimum mechanical properties were reached for a particular ratio ENR/DA. This ratio decreases with epoxidation level of the elastomer. The T_g of the cured systems increased non-linearly with the amount of DA. A comparison with blends of ENR and monofunctional lauric acid showed that this behaviour may be associated to polar interactions due to unreacted carboxylic groups of pending diacid grafts.

ENR is a reactive functional rubber derived from natural product. Dicarboxylic acids are environmentally friendly since some of them are even used as food ingredients like flavorant or gelling aids (adipic acid). Hence ENR crosslinked by diacids without any toxic additive like especially zinc oxide may provide a wide range of potential applications as green rubber, including non-black vulcanizates.

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