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# Effect of unsaturated polyester resin on the mechanical and ultrasonic properties of SBR and NBR

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#### Abstract

An unsaturated polyester resin is prepared by the ester interchange between *p*-carbethoxy phthalanilic acid and maleic anhydride with ethylene glycol in the ratio of (1:1:2.1 mol). The structure of this polyester was established by studying its IR and NMR spectra and the acid number was determined. The effect of 5 phr polyester on the mechanical and physical properties of two types of rubber namely styrene–butadiene rubber (SBR) and acrylonitrile–butadiene rubber (NBR) was studied. The ultrasonic velocity and attenuation have been investigated for both types of rubber with and without the polyester resin at 2 and 5 MHz in the temperature range between 180 and 346 K. For each type of rubber two relaxation peaks are observed in these temperature and frequency ranges, a main peak and a secondary one. The addition of the polyester resin is found to affect the position and height of the main peak in SBR but not in NBR. It was found that the apparent activation energy of the main relaxation process is temperature dependent and increases with the addition of the polyester resin in both types of rubber. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Styrene-butadiene rubber; Acrylonitrile-butadiene rubber; Polyester

#### 1. Introduction

Raw rubber, either polar (NBR) or non-polar (SBR), has poor physico-chemical properties. To improve these properties, some ingredients such as accelerators, activators, antioxidants, and softeners should be added to the raw rubber in small quantities. These small quantities could affect the physical and mechanical properties of the mix [1]. The main problems encountered in obtaining useful results are to find the suitable components and using the right technique. Unsaturated polyesters and different mixing techniques have been tried before [2-5]. In previous publications [6-8] the polyesterification between p-carbethoxy succinanilic acid either alone or in the presence of maleic anhydride with different glycols had been studied. The present work aims to study the effect of the half ester prepared from the corresponding aromatic acid (p-carbethoxy phthalanilic acid) and maleic anhydride with ethylene glycol on both physical and mechanical properties of the styrene-butadiene rubber (SBR) and acrylonitrile-butadiene rubber (NBR).

Ultrasonic measurements in the megahertz range have been considered to be an important tool for the investigation of different molecular mechanisms in polymers and polymeric composites [9–13]. In order to explore how the polyester molecules affect these mechanisms in SBR and NBR, the ultrasonic velocity and attenuation are measured at 2 and 5 MHz in the temperature range between 180 and 346 K, the range through which the two types of rubber pass their glass– rubber transition. Measurements of the ultrasonic properties in these systems at higher frequencies were precluded because of the extremely high ultrasonic absorption.

# 2. Materials and experimental technique

#### 2.1. Materials

The materials used in the present study are

 The prepared unsaturated polyester (UPE) is based on p-carbethoxy phthalanilic acid and maleic anhydride with ethylene glycol. The halfester p-carbethoxy phthalanilic acid was first prepared by dissolving benzocaine (p-carbethoxy aniline) (1 mol) and phthalic anhydride (1.01 mol) in acetone. The mixture was warmed for 5 min and was left at room temperature overnight with frequent shaking. Colorless crystals were obtained and recrystallized from ethanol (yield 68%, m.p. 447– 448 K). The linear copolyester was prepared by the

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Table 1

Formulation of samples, rheometric characteristics, physico-mechanical properties and differential scanning calorimetery

Sample	S1	S2	N1	N2					
Formulation									
Ingredients									
SBR	100	100	_	_					
NBR	_	_	100	100					
UPE	_	5	_	5					
Peroxide	4	4	4	4					
Rheometric characteristic	ts at 415 $\pm$	1 K							
$M_{\rm L}$ (dN m)	12	12	6	6					
$M_{\rm H}$ (dN m)	100	101	68	76					
$T_{c90}$ (min)	34	37.5	37	35.5					
$T_{s2}$ (min)	2	2.2	3.5	2.5					
CRI (min <sup>-1</sup> )	3.125	2.83	2.99	3.03					
Physico-mechanical prop	erties								
Tensile strength (MPa)	1.04	1.14	1.4	1.95					
Elongation at break (%)	87	130	210	360					
Swelling in toluene (%)	147.68	174.3	130.76	110.7					
Differential scanning cald	orimetery								
Sample	S1	<b>S</b> 2	N1	N2	UPE				
$T_{g}$ (K)	224	234	251	251	250				

condensation of *p*-carbethoxy phthalanilic acid (1 mol), maleic anhydride (1 mol) and ethylene glycol (2.05 mol). The mixture was heated at 443–453 K for 2 h. The temperature was increased gradually at a rate of 10 K/h until it reaches 483 K. The reaction mixture was allowed to stand at this temperature for 2 h. The total reaction time is 7 h. The polyester was purified by dissolving in chloroform and precipitated in petroleum ether 40–60 to give a brown viscous resin with acid number 7.65 mg KOH/gm sample.

2. Styrene-butadiene rubber (SBR 1502) with specific



Fig. 1. Schematic diagram of experimental ultrasonic technique.

gravity of  $0.945 \pm 0.005$  and Moony viscosity (ML 4) of about 52 at 373 K.

3. Acrylonitrile-butadiene rubber (NBR) (Krynac 34-52), acrylonitrile content of 33%, specific gravity of 0.990  $\pm$  0.005 and Moony viscosity (ML 4) of about 45 at 373 K.

Keeping all conditions of mixing the same, the prepared samples were mixed with 4 phr dicumyl peroxide. The rubber mixes with and without 5 phr of the prepared UPE were mixed on a two roll laboratory mill of outside diameter 470 mm and working distance 300 mm, speed of slow roll 24 rpm and gear ratio 1:1.4. After completing the mixing, the rubber mixes were subjected to sheeting on the mill. The determination of the rheometeric characteristics, maximum torque  $M_{\rm H}$ , minimum torque  $M_{\rm L}$ , Scorch time  $t_{\rm s2}$ , optimum cure time  $t_{c90}$  and cure rate index (CRI), were done using a Monsanto oscillating disc rheometer 100 according to ASTM D 1646 (1996). The vulcanization was carried out in a heated flatten press under a pressure of about 40 Kg/cm<sup>2</sup> and a temperature of  $415 \pm 1$  K. Circular disks of thickness 3 mm were obtained. The rubber formulations as well as their rheometric characteristic are given in Table 1. All used solvents and chemical reagents were of pure grade.

# 2.2. Techniques of characterization (FTIR, NMR, DSC, mechanical and swelling)

The infrared spectra were recorded on a JASCOFT/IR 300 E Fourier Transform Infrared (FTIR) spectrometer. The nuclear magnetic resonance spectrum was run at 260 MHz on a Jeol-Ex-270 NMR spectrometer. Differential scanning calorimetery (DSC) is done by Shimadzu DSC-50 for accurate determination of glass transition temperatures  $T_g$ . The specimen was fast cooled to 163 K and DSC was recorded on heating up to 373 K at a rate of 5 K/min. The values of  $T_g$  were reproducible within ±1 K and are shown in Table 1. The mechanical properties were measured at room temperature using a tensile testing machine (Zwick 1101) according to ASTM D 412 (1998). Swelling in toluene was carried out for 24 h at room temperature [14].

# 2.3. Ultrasonic technique

Ultrasonic measurements were performed using an ultrasonic flaw detector of type Krautkrämer-Branson USD10. The adopted technique is the pulse–echo immersion technique [15]. Ultrasonic transducer of frequency 2 or 5 MHz was bonded to an immersion tank of volume  $4.6 \times 4.4 \times$  $5.2 \text{ cm}^3$ . The immersion liquid is chosen to be ethyl alcohol because of its low melting temperature (158 K). In addition, ethyl alcohol has an ultrasonic attenuation of the order of 1 dB/cm, which is negligibly small when compared to that of rubber (20–150 dB/cm). The cooling–heating system is shown in Fig. 1. Firstly, the ultrasonic velocity and attenuation in alcohol were measured in a separate experiment from 180 to 346 K, which is the investigated temperature range. The velocity in alcohol (in m/s) is found to vary with



Fig. 2. IR spectrum for the prepared polyester resin.

the absolute temperature T according to linear relations of the form

$$V_{\rm a} = -3.56T + 2230 \tag{1}$$

$$V_{\rm a} = -3.82T + 2363 \tag{2}$$

at 2 and 5 MHz, respectively. No attenuation peaks were observed in alcohol in these temperature and frequency ranges. For velocity and attenuation measurements in rubber samples using immersion technique, the sample was immersed in alcohol and were both cooled down to 180 K at a rate of 1 K/min. The measurements were recorded while both alcohol and the immersed samples were heated up to 346 K at the same rate. Two useful equations were used to calculate the velocity and the attenuation [15]:

$$V_{\rm r} = 2LV_{\rm a}/[2L - V_{\rm a}(t_1 - t_2)]$$
(3a)

$$\exp\left(-2\alpha_{\rm r}L\right) = R \exp\left(-2\alpha_{\rm a}L\right) \left[ \left(\frac{\rho_{\rm a}V_{\rm a}}{4\rho_{\rm r}V_{\rm r}}\right) + \left(\frac{\rho_{\rm r}V_{\rm r}}{4\rho_{\rm a}V_{\rm a}}\right) + \frac{1}{2} \right]$$
(3b)

where the subscripts 'a' and 'r' stand for alcohol and rubber, respectively, V is the ultrasonic velocity, L is the specimen thickness,  $t_1$  and  $t_2$  are the times of flight of ultrasonic waves in a round trip with the specimen removed and immersed, respectively,  $\alpha$  is the attenuation coefficient,  $\rho$  is the density and R is the ratio of the received amplitudes when the specimen is removed and immersed. The density of rubber can be considered constant since the last bracket in Eq. (3b) is close to unity and is not affected by the, almost, non-varying density of rubber. The densities were taken as 945 and 990 kg/m<sup>3</sup> for SBR and NBR, respectively. On the other hand the density of alcohol varies considerably with temperature [16] and this variation was taken into consideration when substituting in Eq. (3b). The accuracy of measuring the velocity is 1.5 m/s which corresponds to percentage error of 0.1%. The error in measuring the attenuation in rubber does not exceed 5%.

#### 3. Results and discussions

#### 3.1. Characterization of unsaturated polyester resin

The prepared unsaturated polyester resin (UPE) is a brown hard resin, which is stable after long storage period and is soluble in most organic solvents except in ethyl alcohol, benzene and petroleum ether. The linear structure of this polyester was deduced from IR and NMR spectra. The IR spectrum of the prepared resin (Fig. 2) shows a strong broad band centred at 3400–3500 cm<sup>-1</sup> characteristic of the stretching frequency of –OH and –NH groups. The intense broad bands at 1720 cm<sup>-1</sup> is quite characteristic of the stretching frequency of the carbonyl group (>C=O) of the aliphatic acid and aromatic ester. The absorption at 1520 cm<sup>-1</sup> corresponds to amide carbonyl group, while the strong bands at 660, 720, 770, and 826 cm<sup>-1</sup> are quite indicative of the presence of *cis*-olefin and aromatic residues in the polyester chain [17].

The NMR spectrum (Fig. 3) indicates the presence of an AB system for the aromatic protons of phthalic anhydride residue  $\sim$  as two ill-defined distorted doublet at  $\delta = 7.7$  and  $\delta = 8$  ppm. The signal at  $\delta = 6.8$  ppm is characteristic of the olefinic protons in maleic acid residue –CH=CH–. Also, the presence of a group of signals between  $\delta = 3.8 - 4.5$  ppm seems to be due to the methylene



Fig. 3. NMR spectrum for the prepared polyester resin.

protons in ethylene glycol residue  $[-O-CH_2-CH_2-O-]$ . The three protons of the methyl group in the half-ester residue appear as a triplet at  $\delta = 1.4$  ppm [17].

# 3.2. Physico-mechanical data

The mechanical properties were determined for the prepared vulcanizates and are listed in Table 1. It is clear from the obtained data that the addition of 5 phr polyester improves the mechanical properties of both types of rubber (S1, N1) which is shown by the increase in both tensile strength and elongation at break. This may be explained by the fact that the unsaturation sites of UPE resin can react with the unsaturation sites of rubber mixes thus increasing the degree of cross-linking. A small percentage of unsaturated groups remain unreacted and imparting some flexibility to the cured rubber [18]. On the other hand, the presence of polyester increases the equilibrium swelling of SBR in toluene which can be attributed to the polar nature of UPE, while it decreases the swelling of NBR in toluene due to the increase in the degree of cross-linking.

# 3.3. Ultrasonic results

# 3.3.1. The main relaxation peak and velocity behavior in blank samples S1 and N1

The variation of ultrasonic velocity V and ultrasonic attenuation per wavelength  $\alpha\lambda$  with temperature are shown in Figs. 4 and 5 for S1 and N1, respectively, at the

two experimental frequencies 2 and 5 MHz. For both types of rubber the experimental points representing the velocity show a sudden change in the slope  $(\Delta V/\Delta T)$ , a kink, followed by a sharp drop after which the velocity reaches half its starting value at 180 K. Table 2 shows the values of the temperature coefficient of the ultrasonic velocity  $(-1/V)(\Delta V/\Delta T)$  before and after the velocity kink in both types of rubber. This abrupt change in  $(-1/V)(\Delta V/\Delta T)$  and the sharp drop in the velocity are considered as characteristics of the glass-rubber transition in any polymer or high polymer [19]. The temperatures at which the velocity kinks appear to be frequency dependent. If we assume an Arrhenius relation between the experimental frequency and the kink temperature of the form:

$$f = f_0 \exp\left(-E_a/RT\right) \tag{4}$$

it is possible to calculate the apparent activation energy  $E_{\rm a}$ . This can be safely applied since the change in temperature with frequency is limited and Arrhenius relation holds in any small temperature interval. The values of the velocity kink temperatures, the change in temperature coefficients of velocity at the two experimental frequencies, and the apparent activation energies calculated from Eq. (4) are shown in Table 2.

The experimental points, showing the variation of  $\alpha\lambda$  with temperature, exhibit a main peak and a secondary shoulder attached to the main peak at lower temperatures. The height and clarity of the main peak, beside its position



Fig. 4. Ultrasonic velocity at 2 MHz ( $\bullet$ ) and 5 MHz ( $\blacktriangle$ ) and ultrasonic attenuation per wavelength at 2 MHz ( $\times$ ) and 5 MHz (+) in S1. The solid line represents the fitting of Eq. (5).



Fig. 5. Ultrasonic velocity at 2 MHz ( $\bullet$ ) and 5 MHz ( $\blacktriangle$ ) and ultrasonic attenuation per wavelength at 2 MHz ( $\times$ ) and 5 MHz (+) in N1. The solid line represents the fitting of Eq. (5).

Sample	Frequency (MHz)	Velocity data				Attenuation per wavelength				
		T <sub>kink</sub> (K)	$10^{3}(-1/V)(\Delta V/\Delta T) (\mathrm{K}^{-1})$			Main peak			Secondary peak	
			$T < T_{\rm kink}$	$T > T_{\rm kink}$	<i>E</i> <sub>a</sub> (kcal/mol)	$T_{\max}$ (K)	т	E <sub>a</sub> (kcal/mol)	$T_{\max}$ (K)	E <sub>a</sub> (kcal/mol)
S1	2	228	1.71	6.33	16.3	268	0.42	19.3	217	11.2
	5	234	2.24	6.12		275	0.37		225	
N1	2	241	6.96	58.8	21.7	286	0.37	25.5	219.5	11.4
	5	246	9.11	60.3		292	0.27		227.5	

Table 2 Ultrasonic velocity and attenuation data in S1 and N1

above the glass transition temperature, suggests that the peak is due to the unfreezing of segmental elements of a polymer chain back-bone, which move on a large scale in a cooperative motion. This suggestion is supported by dynamic mechanical analysis carried out at 11 Hz on block and random styrene-butadiene copolymers by Sarde-lis et al. [20], who observed a single main relaxation peak that appears in the temperature range from 230 K for uncrosslinked slightly randomized samples to 290 K for crosslinked highly randomized samples. On the contrary, the styrene-butadiene block copolymer shows two separate main peaks in tan  $\delta$  versus *T* curves [20]. The low temperature peak corresponds to unfreezing of polybutadiene

segments above its glass transition temperature. The peak temperature ranges from 195 to 218 K depending on the butadiene content and the degree of crosslinking. The high temperature peak is due to glass transition of styrene and appears at 393 K. The ultrasonic measurements of Adachi et al. [21] on styrene–butadiene block copolymer at 5.5 MHz showed two separate peaks one at 230 K for polybutadiene and the other at 430 K for polystyrene. Williams et al. [22] reported, for different types of acrylonitrile–butadiene random copolymers, that the main peak appears at temperatures between 246 and 293 K (in the kHz range).

In order to separate the two experimental peaks and to determine accurately their temperatures, either at 2 MHz or



Fig. 6. Ultrasonic velocity at 2 MHz ( $\bullet$ ) and 5 MHz ( $\blacktriangle$ ) and ultrasonic attenuation per wavelength at 2 MHz ( $\times$ ) and 5 MHz (+) in S2. The solid line represents the fitting of Eq. (5).



Fig. 7. Ultrasonic velocity at 2 MHz ( $\bullet$ ) and 5 MHz ( $\blacktriangle$ ) and ultrasonic attenuation per wavelength at 2 MHz ( $\times$ ) and 5 MHz (+) in N2. The solid line represents the fitting of Eq. (5).

at 5 MHz, the experimental points of  $\alpha\lambda$  were fitted to an empirical model

$$\alpha \lambda = (\alpha \lambda)_{\text{max}} \operatorname{sech} m \left[ \frac{E_{a}}{R} \left( \frac{1}{T_{\text{max}}} - \frac{1}{T} \right) \right]$$
 (5)

proposed by Fuoss and Kirkwood [23]. Here  $(\alpha \lambda)_{max}$  is the maximum value of the attenuation per wavelength, *m* is the Fuoss–Kirkwood coefficient representing the peak width,  $E_a$  is the activation energy, R is the gas constant and  $T_{max}$  is the temperature of the peak.

A rough estimation of the apparent activation energy was done first from the experimental peak temperatures at the two frequencies using Eq. (4). A computer program was used for obtaining numerical values of  $T_{\text{max}}$  and m, which give the best fitting. The details of the procedure were explained elsewhere [24]. The fitting is shown as a solid line in Figs. 4 and 5. Evidently, it fits satisfactorily the high temperature side of the peak, while the shoulder appearing at lower temperatures causes a considerable deviation of experimental points from the fitting curve. The temperatures of the main peaks together with the apparent activation energies, calculated from Eq. (4) are listed in Table 2. The value of  $E_a$  for S1 (19.3 kcal/mol) agrees well with activation energy calculated from stress relaxation experiments on styrene-butadiene block copolymer of 83.7 kJ/mol (20 kcal/mol) [25]. Unfortunately, no similar information could be obtained for comparison in NBR. On the other hand, the activation energies calculated from the

shift in velocity data and  $\alpha\lambda$  fitting curves differ by about 15%. The reason of this difference is that the temperatures at which the velocity kinks occur were roughly estimated because of the curvature in the velocity data.

#### 3.3.2. Effect of polyester

Figs. 6 and 7 show the variation of ultrasonic velocity V and ultrasonic attenuation per wavelength  $\alpha \lambda$  with temperature for S2 and N2, respectively, at the two experimental frequencies 2 and 5 MHz. The blending of SBR with polyester causes the following variations:

(a) Rise in the main peak temperature as indicated in Table 3. This is expected since the glass transition temperature for polyester is higher than that of SBR, as determined from DSC measurements (see Table 1).

(b) Rise in the apparent activation energy of the main process (Table 3), since the polyester molecule can attach to the butadiene molecules in the chain backbone causing more cross-links and consequently more energy is needed to move chain segments of the polymer.

(c) Slight rise in the main peak height and width (Fig. 6). This means that the area under the main peak is increased and more energy is absorbed by the blend [26], in accordance with the explanation of item (b).

(d) General increase in the velocity values, which is accounted for by the stronger bonds between neighboring chains, caused by the polyester molecules.

Sample	Frequency	Attenuation per wavelength						
		Main peak	Main peak			Secondary peak		
		T <sub>max</sub> (K)	т	E <sub>a</sub> (kcal/mol)	$T_{\max}$ (K)	$E_{\rm a}$ (kcal /mol)		
S2	2	279	0.31	24.3	219	13		
	5	285	0.29	2.10	226			
N2	2	285	0.28	30.3	222	15.5		
	5	290	0.23	50.5	228	15.5		

Table 3Ultrasonic attenuation data in S2 and N2

On the other hand NBR behaves in a rather different manner from the following aspects:

(a) The main peak temperature is very slightly reduced (Table 3). This may be due to the fact that the glass transition temperature of polyester is slightly less than that of NBR (see Table 1).

(b) The activation energy of the main process is increased. Apparently the polyester molecule can attach to the butadiene molecules in a manner similar to what happens in SBR and the degree of crosslinking has increased by addition of polyester.

(c) The main peak height is slightly decreased while its width is increased. This leads to an increase in the area under the peak and in absorbed energy.

(d) An increase in the degree of crosslinking is accompanied by increase in velocity by addition of polyester.

# 3.3.3. The secondary relaxation peak

When the fitting curve of the main peak, represented as solid line in Figs. 4–7, is subtracted from the experimental points, we get points that represent the secondary peak. Figs. 8 and 9 show the secondary peaks in blank specimens and those containing 5 phr polyester. The peak shifts to higher temperatures as the experimental frequency is increased. Table 2 shows the temperatures of the secondary peak at 2 and 5 MHz and the apparent activation energies  $E_a$  calculated from Eq. (4) for S1 and N1. The peaks exhibit different



Fig. 8. Ultrasonic attenuation per wavelength at 2 MHz (--) and 5 MHz (--) in S1 ( $\bullet$ ,  $\blacksquare$ ) and in S2 ( $\blacktriangle$ , ×).



Fig. 9. Ultrasonic attenuation per wavelength at 2 MHz (--) and 5 MHz (--) in N1 ( $\bullet$ ,  $\blacksquare$ ) and in N2 ( $\blacktriangle$ , ×).



Fig. 10. Normalized ultrasonic attenuation per wavelength at 2 MHz ( × ) and 5 MHz ( + ) in S1 (- - -) and in S2 (--).



Fig. 11. Normalized ultrasonic attenuation per wavelength at 2 MHz (×) and 5 MHz (+) in N1 (---) and in N2 (--).

values of  $E_a$  in SBR and in NBR and are broad enough to assume that, in each type of rubber, different mechanisms take place simultaneously in this temperature region. For S1 the value of  $E_a$  (11.2 kcal/mol) suggests that this peak may be connected to side rocking of the phenyl groups of styrene which was observed in dynamic mechanical analysis at temperatures between 183 and 193 K at frequencies of 200-300 Hz [27]. The activation energy of this process was found to be 7.5 kcal/mol [19], which satisfactorily agrees the obtained value. In addition, small segments of butadiene in the backbone, formed of 3 or 4 monomers, can contribute to the relaxation mechanism at these temperatures since they are free to undergo limited motion above their glass transition temperature [20]. On the other hand for N1 the value of  $E_a = 11.4$  kcal/mol is in good agreement with 9.5 kcal/mol associated with a low temperature process (T = 213 K) observed in dielectric loss measurements on styrene-acrylonitrile copolymer at 1 kHz [28]. The process was related to limited motions of acrylonitrile dipoles in the glassy state. However the reason for this slight difference may be the different tools used in the investigations (dielectric and ultrasonic) and the effect of neighboring molecules, which are butadiene in our case instead of styrene as in Ref. [28]. On the other hand, the small-scale segmental motion of butadiene should be taken into consideration, similar to that occurring in SBR. There is rise in the activation energy of the secondary process (see Tables 2 and 3), due to polyester blending, which is also expected since the small butadiene

segments, responsible in part for the secondary process, are now restricted to move due to polyester attachments.

#### 3.3.4. Apparent activation energy in SBR and NBR

In order to explore how the activation energy depends on temperature; the fitting curves in Figs. 4–7 were normalized to unity. The normalized curves of S1 and S2 are shown in Fig. 10 and those of N1 and N2 are shown in Fig. 11. It is evident that the normalized curves at 2 and 5 MHz have different widths (Tables 2 and 3). The shift of the fitting curve, due to change in frequency, varies with temperature. This is not surprising since the sudden fall of ultrasonic velocity and the accompanying main peak of ultrasonic attenuation, in blank specimens and in specimens containing 5 phr polyester, are attributed to unfreezing of segmental micro-Brownian motion at certain range of temperature corresponding to the experimental frequencies adopted. The activation energy governing this process is thus temperature dependent [29]. Using high-resolution plotting computer software the shift of the fitting curves could be estimated almost every 1 K and the apparent activation energy could be calculated at each temperature using Eq. (4). The variation of activation energy with temperature is shown in Fig. 12 for both types of rubber. There is no doubt that in both types of rubber the introduction of 5 phr polyester causes increase in the activation energy of the main process. In SBR this increase amounts to 36% at low temperatures and 43% at high temperatures. In NBR it



Fig. 12. Apparent activation energy in S1 ( $\bullet$ ), S2 ( $\blacktriangle$ ), N1 ( $\blacksquare$ ) and N2 ( $\times$ ).

amounts to 22% at low temperatures and 38% at high temperatures.

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#### 4. Conclusion

The activation energy of the glass-rubber transition in SBR and NBR and the dynamic glass transition temperatures were determined from ultrasonic measurements of velocity and attenuation at frequencies of 2 and 5 MHz. The blending of the two types of rubber with 5 phr polyester increases the glass transition peak temperature and the activation energy in SBR. Polyester increases the activation energy in NBR while it has no effect on the glass transition peak temperature of NBR. These observations appear to be in harmony with DSC, mechanical and swelling data that show improvement in rubber characteristics by polyester additives. The attachment of the polyester molecules to the butadiene molecules in SBR and NBR may encourage studying the effect of polyester on blends of SBR and NBR and its effect on improvement of the blend properties.

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