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The Effect of Epoxidized Sunflower Oil on the Miscibility of Plasticized PVC/NBR Blends

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Blends of plasticized poly(vinyl chloride) (PVC) with several ratios of nitrile rubber (NBR) were studied. The effects of epoxidized sunflower oil (ESO) in combination with di-(2-ethylhexyl)phthalate (DEHP) in the PVC blends on the tensile strength, elongation, hardness, and dynamical mechanical analysis (DMA) were studied. The modulus and hardness results revealed that the addition of ESO to the blend favors the miscibility of PVC and NBR. The PVC/NBR/(DEHP-ESO) blends behave as a compatible system as is evident from the single T_g observed in DMA. The moderate level broadening of the T_g zone in blends is due to the presence of ESO in the plasticizer system. Blends of plasticized PVC and nitrile rubber showed promising properties. The ESO is suitable to partially replace DEHP in PVC/NBR blends.

Keywords dynamical mechanical analysis, mechanical properties, miscibility, PVC/NBR

INTRODUCTION

Nowadays, considerable research interest is focused on new polymeric materials obtained by blending two or more polymers. The major feature of such blends is that the intermediate properties are in some cases better than those exhibited by either component. In order to make PVC soft or flexible, plasticizers are added as per the degree of flexibility required. The unique ability to accept large amounts of plasticizer makes PVC one of the most versatile

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polymers. Di-(2-ethylhexyl)phthalate (DEHP) is commonly used in PVC as a plasticizer. There has been increasing concern regarding the impact of DEHP exposure on human health and the environment [1,2]. Nitrile rubbers (NBR) are copolymers of acrylonitrile and butadiene. They are compatible with PVC, and nitrile rubbers have been used to make alloys with PVC [3,4]. Blends of NBR with plasticized PVC are described as thermoplastic elastomers, because they combine ease of melt processing with flexibility and rubber elasticity [5]. Our study investigates the suitability of epoxidized sunflower oil (ESO) as a PVC plasticizer. Sunflower oil, the derivative of a renewable natural vegetable oil, may be more environmentally friendly than DEHP. Epoxidation is the addition of an oxygen atom to a carbon-carbon double bond to form a 3-membered ring with epoxide (or oxirane) functionality. This investigation deals with the study of the miscibility induced in PVC/NBR blends by epoxidized sunflower oil (ESO) in combination with DEHP. It investigates how the ratio of PVC/NBR/plasticizer (DEHP alone or in the presence of ESO) in the formulation affects the properties of the material produced.

EXPERIMENTAL

Materials

Suspension PVC (4000 M, Skikda, Algeria), (K value 65–67) was used. Nitrile butadiene rubber (NBR) (BUNA NB 196 HF), acrylonitrile content: 33%, and with Mooney viscosity ML (1 + 4)100°C = 55–75 was obtained from Czech Republic. Other additives, di-(2-ethylhexyl)phthalate (DEHP) from Sigma Aldrich, epoxidized sunflower oil (ESO) with 6.5% oxirane oxygen, prepared in our laboratory, and Ba/Cd/Zn were used as coplasticizer and stabilizer, respectively.

Blending

Various blend formulations: PVC/NBR, PVC/DEHP binary blends and PVC/NBR/DEHP or PVC/NBR/(DEHP-ESO) ternary blends, were prepared. The levels of PVC/NBR are expressed in terms of weight percentages, and add up to 100%. The DEHP and ESO are expressed in phr to PVC. The stabilizer was at a fixed level of 2 phr to the amount of PVC. The blend compositions are shown in Table 1.

Processing

The blends were processed into sheets on a two-roll mill with the rolls set at a temperature of 170°C, roll speed of 10 m/min, and a friction ratio of 1.25. The sheets were compression-molded to make plaques, which were required for some of the tests. The operating temperature was 170°C for 5 min with hydraulic pressure of 20 tons.

Table 1: Notation of PVC blends compositions.

Formulation PVC/NBR/DEHP	Notation	PVC	NBR	DEHP (phr)	
100/33/00	FNBR-33	100	33	00	
100/00/33	FDEHP-33	100	00	33	
100/00/50	FDEHP-50	100	00	50	
90/10/50	A1	90	10	50	
75/25/50	A2	75	25	50	
50/50/50	A3	50	50	50	
25/75/50	A4	25	75	50	
10/90/50	A5	10	90	50	
67/33/50	B1	67	33	50	
75/25/33	B2	75	25	33	
82/18/21	B3	82	18	21	

Formulation PVC/NBR/DEHP/ESO	Notation	PVC	NBR	DEHP (phr)	ESO (phr)
75/25/25/08	C1	75	25	25	8
75/25/16.5/16.5	C2	75	25	16.5	16.5
75/25/08/25	C3	75	25	8	25

Stress-Strain Testing

Tensile properties were measured on MTS instruments. Tests were carried out at $23 \pm 1^\circ\text{C}$, with a crosshead speed of 20 mm/min.

Shore A and Shore D Hardness

Hardness Shore A and Shore D were performed on ATS-FAAR type A and D testers.

Characterization by Dynamical Mechanical Analysis

All experimental data were collected on a TA Instruments DMA 2980 machine, using the tension film clamping arrangement. Specimens were excited using a $20\ \mu\text{m}$ dynamic displacement, and a small preload (0.2 N) to insure that the specimens were always in tension. The measurements were made over a temperature range from -100 to 120°C , at 1 Hz.

RESULTS AND DISCUSSION

Mechanical Properties

The most widely tested properties include tensile strength at break, elongation at break and Young's modulus, that can be obtained from the stress-strain curve, are shown in Figures 1–3 respectively. Figure 1 shows the tensile strength

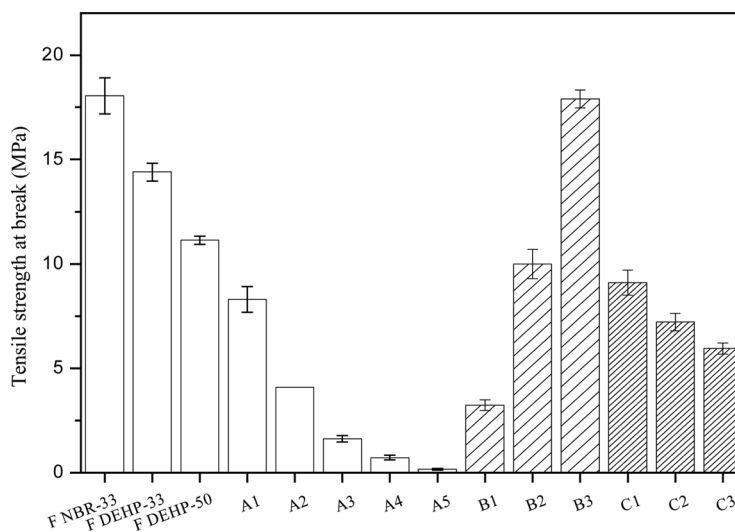


Figure 1: Effect of DEHP, NBR, and its combination with ESO on tensile strength at break of PVC blends.

plotted for each sample measured. It is seen that as the amounts of both DEHP and NBR in the formulation increase, there is a reduction in tensile strength. The tensile strength at break decreases with the amount of NBR (sample A1 to A5) in the blends. Similar behavior was observed with the increase of DEHP in PVC (sample FDEHP-33 and FDEHP-50). However, samples plasticized with NBR alone show a much smaller reduction of tensile strength than those

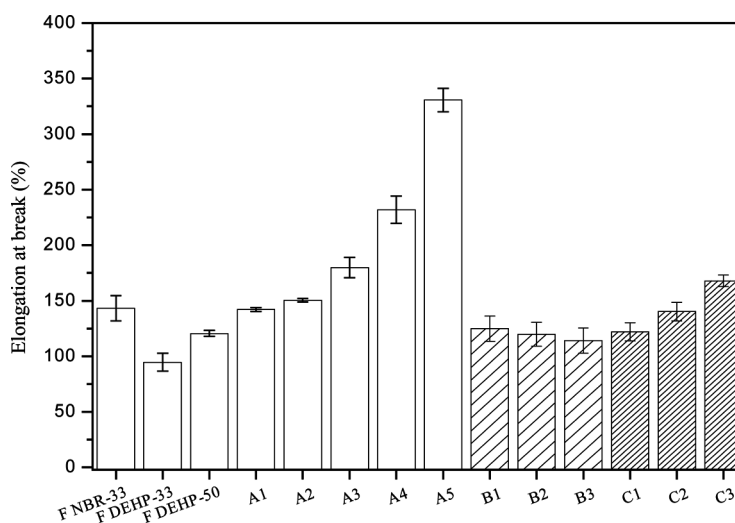


Figure 2: Effect of DEHP, NBR, and its combination with ESO on elongation at break of PVC blends.

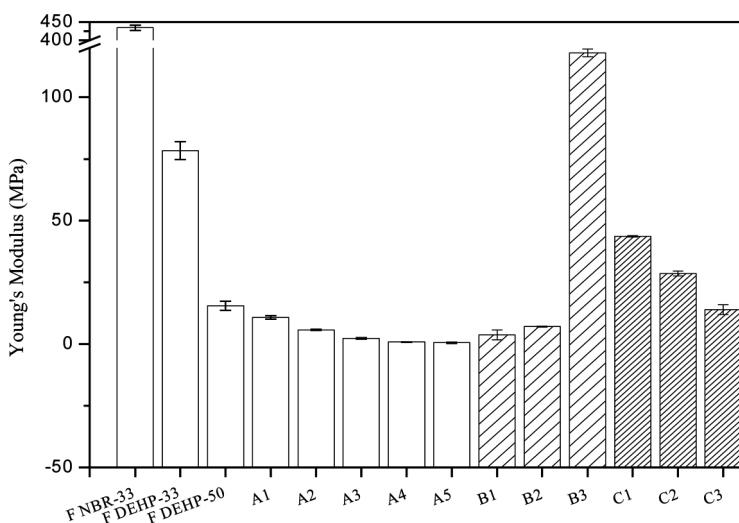


Figure 3: Effect of DEHP, NBR, and its combination with ESO on Young's modulus of PVC blends.

plasticized with DEHP or a mixture of DEHP and NBR. It is seen that tensile strength is reduced when PVC is replaced by either NBR or DEHP, but the effect is considerably greater with DEHP.

The blends B1, B2, and B3, with a simultaneous decrease of NBR and DEHP amount in them, show a gradual increase in tensile strength at break due to the loss in blend softness. By comparing sample B2 to sample C1, C2, and C3 (with the same composition of PVC/NBR (75/25)), the effect of DEHP/ESO ratio on tensile strength at break can be seen to be decreasing with the addition of ESO, proof of the plasticization effect.

Results of elongation at break are plotted in Figure 2. As expected, the elongation at break increases with the concentration of NBR in the blend (samples A1 to A5), also the same phenomenon was observed with increasing DEHP in PVC. There is a decrease in the elongation at break when both the DEHP and NBR amount decrease in the blends B1, B2, and B3. The evolution of this property is observed with DEHP/ESO ratio. This figure shows that there is a decrease when the ESO amount increased. Figure 3 shows a decrease in modulus with the amount of NBR in PVC blends (samples A1 to A5), also the same tendency with DEHP (FDEHP33, FDEHP50) due to their plasticizer effect. By comparing sample B2 to C2 it is clear that ESO is able to replace DEHP until 50%.

According to the results of mechanical properties, as suggested by Margaritis et al. [6] and Hernandez et al. [7], it can be seen that the addition of some plasticizers to PVC such as NBR, DEHP and ESO gives rise to a change in the softness of the product, to a decrease in the tensile strength and in the modulus

as well as an increase in the elongation at break, depending on the nature and the amount of plasticizer. The results show that both DEHP and NBR have similar general behavior: they decrease tensile strength and Young's modulus and increase the elongation at break, but the plasticizing effect of NBR is greater than that of DEHP at the same concentration (sample FNBR33, FDEHP33) due to their chemical structure. Hence the action of NBR is different. The addition of NBR does not disrupt the PVC interchain interaction but, the NBR chains form a physical network between PVC chains, causing chain slippage and consequently high elongation at break of blend. ESO plasticizer, when added in combination of DEHP in the composition 75/25 of PVC/NBR blends for partial replacement of DEHP, acts as plasticizer component, because it decreases tensile strength and increases elongation at break. This action mode of ESO is attributed also to the increased polarity of ESO due to the presence of the epoxy groups, which increases the cohesive energy density (intensity of intermolecular attraction), such that with higher polarity, blends tend to hold themselves together more tightly [8]. Also, this epoxy ring might react with labile hydrogen sites in the PVC to form an ether linkage [9].

The results of shore A and shore D hardness are plotted in Figure 4(a) and (b), respectively. As expected, it can be seen that increasing the level of DEHP (samples DEHP-33 and DEHP-50) caused a reduction in hardness. The addition of increasing the amounts of NBR (samples A1 to A5) also gave a reduction in hardness, but much less than that achieved with DEHP (comparing A2 to B2). This histogram again clearly shows that NBR have a plasticizing effect on PVC, but is far inferior in this respect to DEHP. It confirms that, in the absence of DEHP, it is necessary to add in excess of 33% of NBR to achieve any reduction in hardness. Hence, it can be concluded that NBR cannot be used to plasticize PVC formulations in the absence of a low molecular weight plasticizer. Also increasing the concentration of DEHP from 33% to 50% in PVC (sample FDEHP-33, FDEHP-50) produced some reduction in the hardness of blends. The plasticizing effect of DEHP is higher than NBR [10]. The reduction in the amounts of both NBR and DEHP in blends (sample B1, B2, and B3) shows an increase in shore A and shore D hardness, due also to increased PVC concentration. Both values of hardness decrease with the amount of ESO in DEHP/ESO ratio. This decrease could be attributed to the polar nature of ESO component, and the presence of ether linkages.

Dynamical Mechanical Analysis (DMA) Properties

DMA was used to investigate the miscibility of the blends. Generally, for an immiscible blend, the $\tan \delta$ curve shows two damping peaks corresponding to T_g 's of the individual polymers. For a highly miscible blend, the curve show only a single peak in between the transition temperature of the component

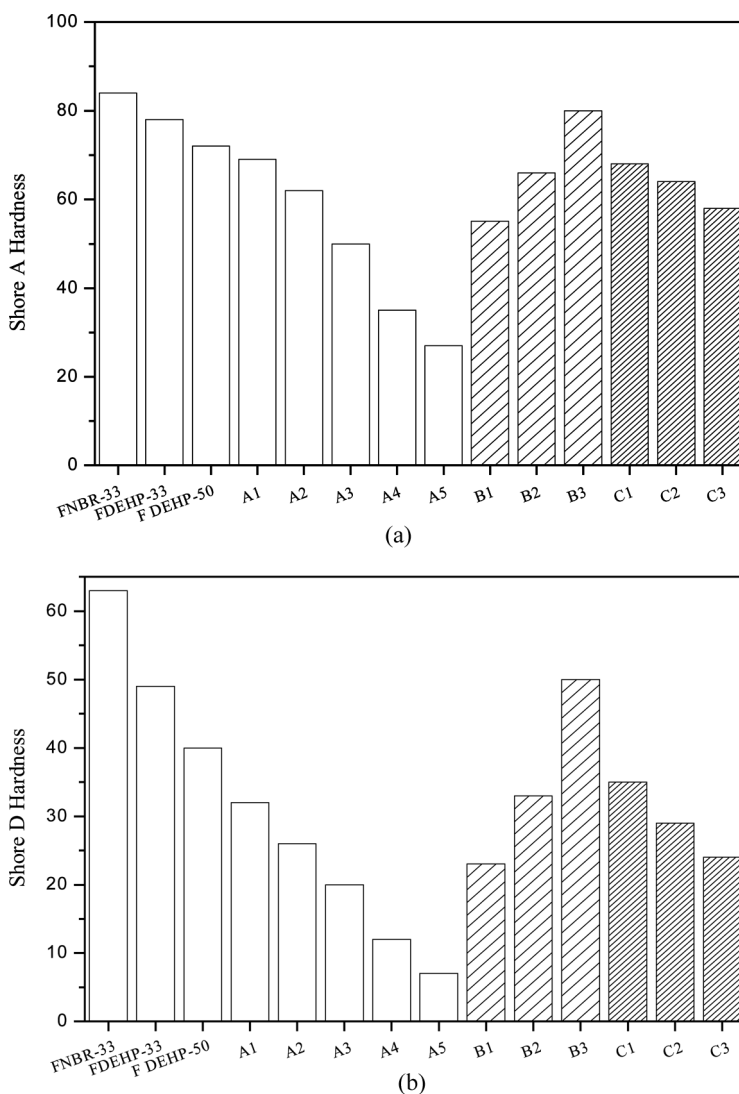


Figure 4: Effect of DEHP, NBR, and its combination with ESO on Shore A Hardness (a) and Shore D Hardness (b) of PVC blends.

polymers [11]. Dynamic storage modulus (E'), loss modulus (E'') and damping factor $\tan \delta$ of our blends are shown respectively in Figures 5–7.

Figure 5 shows that the storage modulus (E') decreases slightly at the T_g zone as more NBR is added in the blend (sample A1 to A5). However, increasing the amount of DEHP from 33% to 50% in PVC leads to a significant decrease in the dynamic storage modulus. The sample with large amounts of NBR shows a storage modulus higher than those with DEHP due to the plasticization effect of DEHP which is superior to NBR [12].

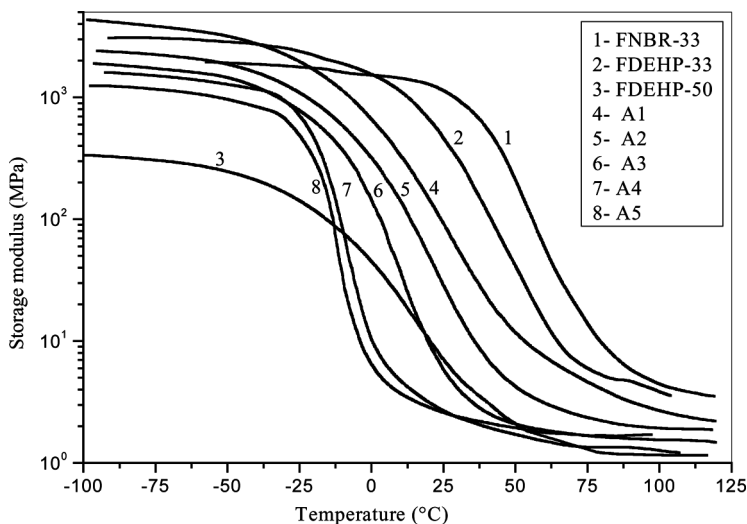


Figure 5: Storage modulus of (PVC/NBR/DEHP) blends.

The area under the loss modulus curves (see Figure 6) decreases when the amount of NBR increases in the blend. The area under the loss modulus curve of FDEHP-33 sample is larger than that of FDEHP-50 sample, because in plasticized PVC, the monomer plasticizer swells amorphous regions, separating PVC molecules in these regions and thus increasing the main chain mobility. This leads to a decreased area under the loss modulus curve. Furthermore, it is known that if a plasticizer is miscible with a polymer, a blend

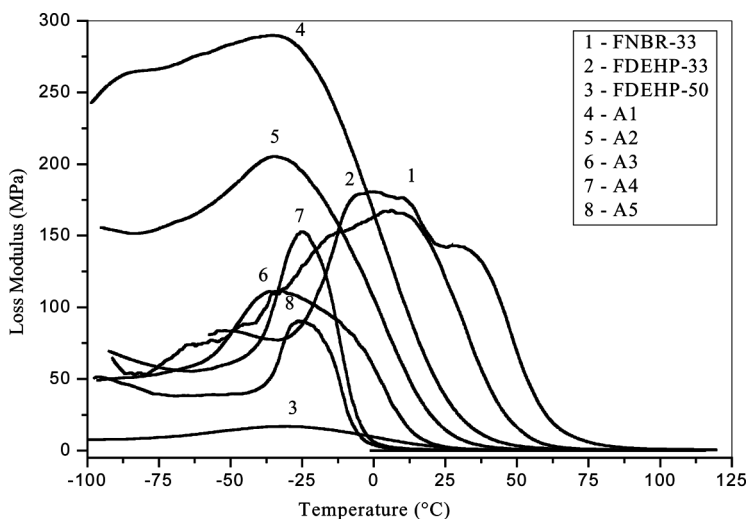


Figure 6: Loss modulus of (PVC/NBR/DEHP) blends.

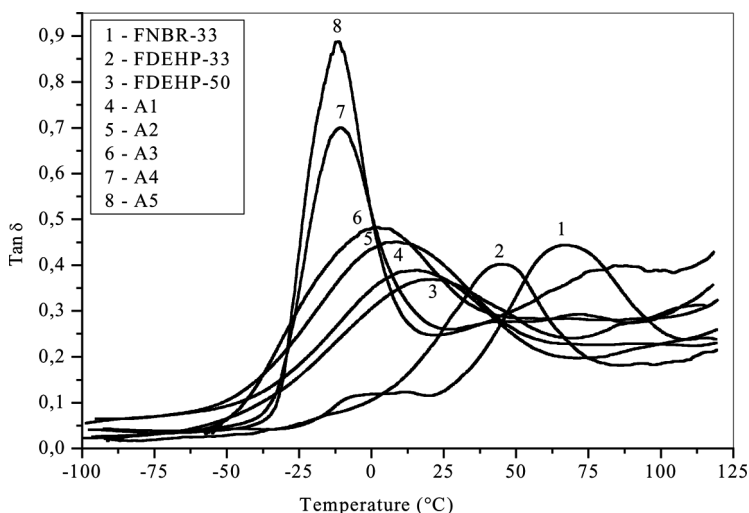


Figure 7: Tan δ of (PVC/NBR/DEHP) blends.

of the two should show single T_g [13] and that sharp transitions suggest good compatibility, while broad transitions are typical of less compatible blends. In order to quantify this trend, the full width at half maximum (FWHM) of the tan δ curve was measured for each sample (see Figure 7). The damping curves were used because these have good definition in the temperature range over which the glass transition takes place. Glass transition temperature is often used as an indicator of the general plasticizing effect [14]. The presence of a single loss peak for each blend composition is a clear symptom of the miscibility of PVC/NBR/(DEHP-ESO) blends (shown in Figure 8). Figure 8 shows

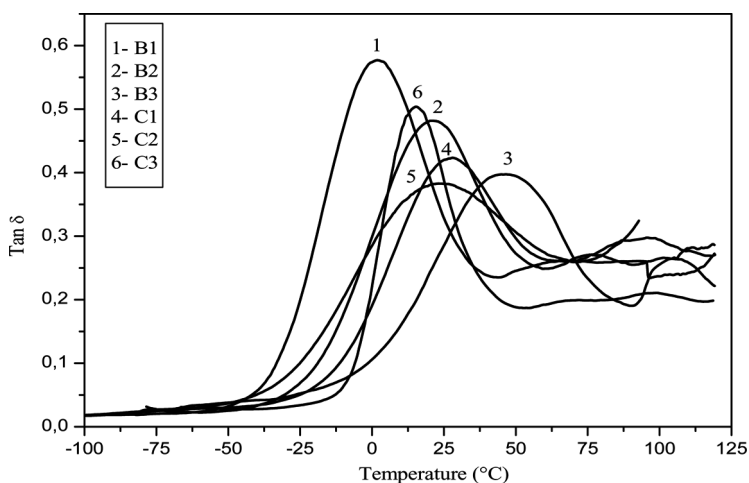


Figure 8: Tan δ of (PVC/NBR/(DEHP-ESO)) blends.

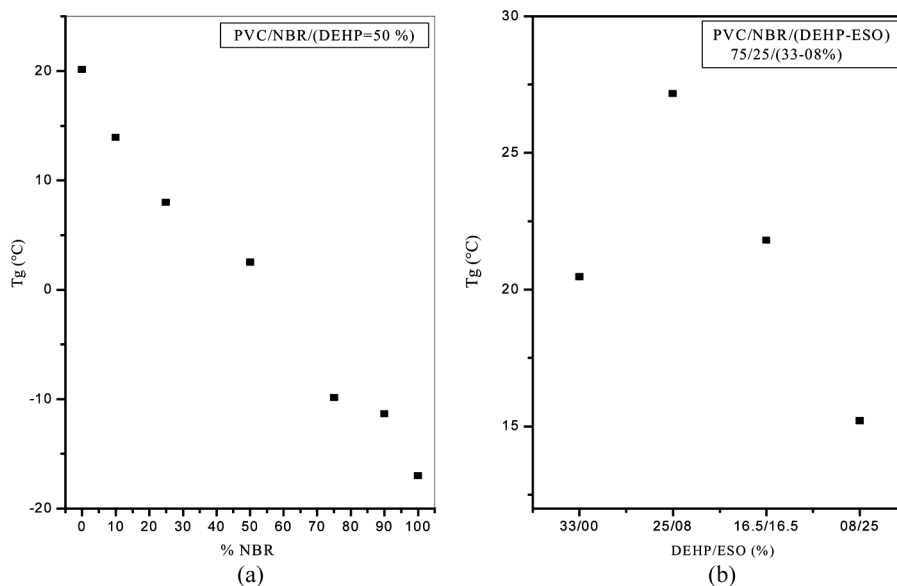


Figure 9: Variation of T_g of (PVC/NBR/DEHP) blends (a), and (PVC/NBR/(DEHP-ESO) blends (b).

that when ESO in combination to DEHP is added in the blend (sample C1, C2, and C3) T_g decreases. Figures 9(a) and (b), are plots of the glass transition temperatures of the various formulations. These results confirm that the addition of both DEHP and NBR causes a reduction in T_g of the PVC blends but that DEHP has a more efficient plasticizing action than that of NBR. Mixtures of ESO and DEHP have a plasticizing action intermediate between the two. It is accepted that the higher the $\tan \delta$ ($\tan \delta$ max) the greater the mechanical losses. These losses are related to energy input required for the motion of the molecular chain of the polymer as the transition is being approached [15]. The peak of FNBR-33 is higher and broader than of the FDEHP-33; this shows that the compatibility of PVC with DEHP is better than with NBR. Also with respect to the plasticization; NBR appears to be less effective than DEHP [16].

Table 2 summarizes the transition temperature T_g , and the FWHM of all the PVC blends prepared. From the results shown in Table 2, it is quite evident that blends with different composition have one T_g . This indicates that the blend PVC/NBR/DEHP-ESO is miscible. By comparing the FWHM, it broadens from 20 to 49°C. $\tan \delta$ peak shows that FWHM of DEHP-50 is higher than that of FDEHP-33. This is due to the presence of inhomogeneous distribution of plasticizer and the presence of unplasticized micro domains of PVC. From these results which confirm that the addition of both DEHP and NBR causes a reduction in T_g of the PVC compound, but DEHP has more efficient plasticizing action than NBR, so the mixture of DEHP and ESO have a better

Table 2: T_g of loss modulus or of $\tan \delta$ and FWHM of $\tan \delta$ from DMA curves.

Sample	T_g ($^{\circ}\text{C}$)		
	Loss Modulus ^a ($^{\circ}\text{C}$)	Tan δ ($^{\circ}\text{C}$)	FWMH ^b ($^{\circ}\text{C}$)
FNBR-33	0.90	67.90	35
FDEHP-33	9.90	45.00	32
FDEHP-50	-32.40	20.10	45
A1	-31.60	13.90	46
A2	-34.40	8.00	51
A3	-35.20	2.50	49
A4	-24.80	-9.90	27
A5	-25.60	-11.30	24
B1	-22.50	1.90	33
B2	-8.40	20.50	30
B3	9.10	45.40	40
C1	13.90	27.20	26
C2	-1.80	21.80	23
C3	-17.50	15.40	20

^aTransition temperature is based on the $\tan \delta$ peak, or on the loss modulus transition peak at 1 Hz in DMA.

^bFWHM (full width at half maximum) here is defined as the breadth (duration of temperature) of the transition peak at half of its maximum peak value.

plasticizing action than the two. Referring to the ESO effect on T_g and FWHM, as shown in Table 2, there is a decrease when the amount of ESO increases in blends, due to the polar nature of ESO plasticizer.

CONCLUSIONS

The miscibility increases with the addition of NBR in the presence of a combination of ESO with DEHP. It is concluded from this study that ESO in combination with DEHP has a plasticizing effect. ESO favors the miscibility between PVC molecules. Epoxidized sunflower oil was found to be a possible alternative for DEHP at up to 50%, displaying statistically similar physical properties in the areas of tensile strength at break, Young's modulus and hardness. In terms of glass transition temperature, ESO showed significantly higher performance than DEHP.

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