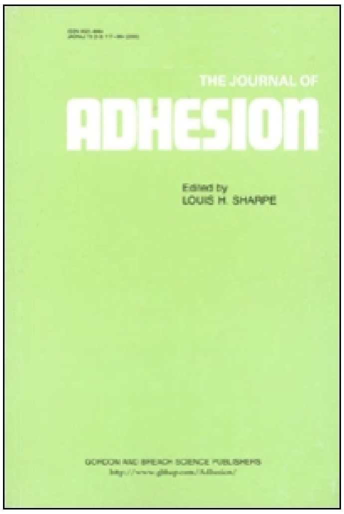

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Characterization of eva-based adhesives containing different amounts of rosin ester or polyterpene tackifier

María Luisa Barrueso-Martínez[a]; Teresa del Pilar Ferrándiz-Gómez[a]; María Dolores Romero-Sánchez[a]; José Miguel Martín-Martínez[a]
[a] Adhesion and Adhesives Laboratory, Department of Inorganic Chemistry, University of Alicante, Alicante, Spain

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CHARACTERIZATION OF EVA-BASED ADHESIVES CONTAINING DIFFERENT AMOUNTS OF ROSIN ESTER OR POLYTERPENE TACKIFIER

María Luisa Barrueso-Martínez
Teresa del Pilar Ferrándiz-Gómez
María Dolores Romero-Sánchez
José Miguel Martín-Martínez
Adhesion and Adhesives Laboratory, Department of Inorganic Chemistry, University of Alicante, Alicante, Spain

Different amounts (50–170 php—parts per hundred parts of EVA, 33–63 wt%) of two tackifiers (hydrogenated rosin ester, polyterpene resin) were added to an ethylene vinyl acetate (EVA) copolymer containing 28 wt% vinyl acetate. The EVA and the tackifier were characterized using infrared (IR) spectroscopy, DSC measurements, and stress-controlled plate-plate rheology. The properties and compatibility of the EVA-tackifier mixtures were studied using DSC, DMTA, and stress-controlled plate-plate rheology. Immediate adhesion was measured as a quantification of tack, and the T-peel strength of roughened styrene-butadiene rubber/EVA-tackifier adhesive joints was also obtained. The increase in the amount of tackifier noticeably changed the crystallinity of polyethylene blocks in the EVA, and the temperature at the cross-over between the curves of the storage and loss moduli as a function of the temperature was displaced to a lower value. Whereas the hydrogenated rosin ester was compatible with the amorphous ethylene vinyl acetate copolymer regions of the EVA (Tg value increased) reducing its crystallinity, the polyterpene resin was compatible with the polyethylene blocks of the EVA (T_g value was not modified), increasing its crystallinity. Immediate adhesion of the EVA-tackifier mixtures was improved by adding both hydrogenated rosin ester and polyterpene tackifiers. On the other hand, there was an optimum tackifier content at which the maximum T-peel strength value was obtained.

Keywords: EVA; Tackifier; Compatibility; DSC; DMTA; Hydrogenated rosin ester; Polyterpene resin

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Address correspondence to José Miguel Martín-Martínez, Adhesion and Adhesives Laboratory, Department of Inorganic Chemistry, University of Alicante, 03080 Alicante, Spain. E-mail: jm.martin@ua.es

INTRODUCTION

Hot melt adhesives are widely used in the packaging, furniture, bookbinding, and footwear industries. Most of the hot melt formulations are based on thermoplastic polymers such as ethylene vinyl acetate copolymer (EVA), polyolefin, polyamide, or polyester, with EVA copolymers being the most commonly employed. Tackifiers are commonly added to impart tack to hot melt and pressure-sensitive adhesive formulations based on EVA and block rubber copolymers (styrene-butadiene-styrene, SBS; styrene-isoprene-styrene, SIS) [1, 2]. Tackifiers have higher glass transition temperature (T_g) and lower molecular weight compared with EVA and, therefore, their addition modifies its viscosity, rheology, and adhesion among other properties [3, 4]. If EVA and tackifier are miscible, an increase in T_g is obtained and the viscoelastic properties of EVA are modified. However, if EVA and tackifier are immiscible, two T_g values are obtained and the properties of the mixture correspond to those of their individual components.

EVA-tackifier compatibility has been already described [3–10]. Takemoto *et al.* [5] have studied the miscibility of EVA copolymers and different tackifiers by means of phase diagrams and applying the Flory-Huggins theory. The viscoelastic properties of EVA hot melt adhesives have been studied by different researchers [6–10], and several models have been proposed. The effect of the nature, molecular weight, and content of tackifier in styrene-butadiene-styrene rubber adhesives has been analyzed by Class and Chu [11–13], and they established the preferential interaction of different tackifiers with each block of the copolymer (styrene or butadiene). On the other hand, Komornicki *et al.* [14] studied the viscoelastic and mechanical behaviour of hot-melt formulations based on mixtures of EVA, a terpene phenolic resin, and increasing amounts of a synthetic Fisher-Tropsch wax. They concluded that a too-high tackifier-EVA ratio provided decreased mechanical properties and that the tackifier inhibited the EVA crystallization when the EVA-tackifier mixture was cooled down. Furthermore, Shin and Hamed [15] showed that wax does not affect the glass transition temperature of a homogeneous EVA/rosin blend. However, wax addition increases the EVA-rich phase, resulting a higher rubbery response. The T-peel fracture energies of EVA/tackifier/wax blends bonded to polypropylene film are controlled by two factors: (1) a weak boundary layer of wax, which has a deleterious effect on bonding, and (2) on the other hand, an increased rubbery response in the stick-slip region, which tends to strengthen joints.

In a previous study [4], the effects produced by adding two tackifiers of different natures to three EVA copolymers with different VA contents (28–40 wt%) was studied. The addition of a rosin ester to EVA produced a compatible mixture, whereas for the polyterpene resin a less compatible mixture was obtained. The increase in the VA content decreased the crystallinity of EVA and both the storage and loss moduli also decreased, but the peel strength and the immediate adhesion increased. The immediate adhesion of EVA-tackifier mixtures was also affected by both the compatibility and the rheological properties. In fact, a relationship between the storage modulus (E′)—obtained from dynamic mechanical thermal analysis (DMTA) experiments—of the EVA-tackifier mixtures and the immediate adhesion to thin rubber substrates was obtained. The mixtures containing the polyterpene tackifier showed higher moduli than those containing the rosin ester and, therefore, higher peel strength values were obtained. An increase in the VA content increased the flexibility of the EVA-tackifier blends and a decrease in peel strength was obtained. In this study, the tackifier content in the EVA-tackifier mixtures was not varied and, therefore, to complete the study, the effect of adding different amounts of two different tackifiers to an EVA copolymer containing 28 wt% vinyl acetate have been studied in this paper. The compatibility (miscibility) and viscoelastic properties of EVA-tackifier mixtures were assessed from rheological and thermal experiments, and their adhesion to styrene-butadiene rubber was also studied.

EXPERIMENTAL

Materials

The two tackifiers used in this study were a hydrogenated rosin ester provided by Arizona Chemical AB (Sandarne, Switzerland) and a synthetic polyterpene tackifier provided by Hercules BV (Rijswick, The Netherlands). Some properties of these tackifiers are

TABLE 1 Properties of the Tackifiers Used in this Study [16, 17]

Tackifier	Chemical nature	Colour[a]	Softening Point (°C) (Ring & Ball)	Average molecular weight [a] M_n	Average molecular weight [a] M_w
H	Hydrogenated rosin ester	< 1 [b]	75	307	323
T	Polyterpene resin	6 [c]	112–118	563	989

[a] Data provided by Hercules B. V. and Arizona Chemical.

[b] Gardner scale 63, 1:1 in toluene.

[c] Gardner scale ASTM D1544–86.

given in Table 1 [16, 17]. Those tackifiers were selected because of their different degrees of polarity, different softening points, and average molecular weight. As was already established [3–5, 9, 11–13], these parameters determine the compatibility between the tackifier and the EVA.

The EVA copolymer used in this study was provided by ELF Atochem España S.A. (Madrid, Spain). Its vinyl acetate content is 28 wt%, and it has a melt flow index of 135–175 g/10 min and a softening point of 90°C [18]. The hardness of EVA is 70 Shore A and its density is 0.95 g/cm^3.

Experimental Techniques

Preparation of the EVA-Tackifier Blends

The adhesives contain 50, 100, and 170 php tackifier with respect to EVA (equivalent to 33, 50, and 63 wt%, respectively); to avoid early deterioration of the adhesives, 2 wt% antioxidant (Irganox 1010 provided by Ciba Geigy, Barcelona, Spain) was also added. The adhesives were prepared as follows: The tackifier and the antioxidant were simultaneously added at 120–130°C in a Pyrex glass beaker (diameter = 11.5 cm) placed on the hot plate of a magnetic stirrer. The mixture was stirred using a Heidolph RZR 2000 (Heidolph-Electro, Kelheim, Germany) stirrer provided with a hemispherical spindle of 9 cm diameter and 3 cm height. The mixture was allowed to melt completely before EVA was added. Then, the temperature was gradually raised up to 170–180°C and the mixture was stirred at 60 rpm for 50 min. Finally, the EVA/tackifier mixture was poured on a silicone pad and allowed to solidify under ambient conditions. The nomenclature of the adhesives used in this study contains the capital letter B followed by the capital letter H or T (H = hydrogenated rosin ester; T = polyterpene tackifier), and the amount of tackifier in php (50, 100, or 170).

Fourier Transform Infrared (FTIR) Spectroscopy

Transmission-IR spectra of the tackifiers were obtained. A small amount of toluene solutions of the tackifiers (4 wt%) was placed on a KBr window. The solvent was then removed by evaporation at room temperature for 2 h. The measurements were carried out in transmission mode using a Nicolet FTIR 205 spectrometer (ThermoNicolet, Madison, WI, USA). Two hundred scans per measurement were carried out and the resolution of the system was 4 cm^{-1}.

Differential Scanning Calorimetry (DSC)

DSC measurements were carried out in a Rheometrics Scientific DSC PLUS V vs. 5.41 system (Rheometric Scientific, Surrey, UK). Two heating runs were performed for the tackifiers. The tackifiers were initially heated from −50 to 180°C (heating rate = 10°C/min), then suddenly cooled down to −50°C, and after that a second heating run (under the same experimental conditions) was carried out. The glass transition temperature (T_g) values were determined from the DSC curves obtained in the second heating run. Although different procedures were tested, that given above was used in this study to remove the thermal history of the tackifiers. The thermal properties of EVA were obtained by heating from −100 to 180°C (heating rate = 10°C/min), and those for the EVA-tackifier mixtures were obtained by heating from −50 to 180°C (heating rate = 10°C/min).

Plate-Plate Stress-Controlled Rheology

The viscoelastic properties of the tackifiers, the EVA, and the EVA-tackifier mixtures were obtained in a shear stress controlled Bohlin CS50 viscoelastometer (Bohlin Instruments UK, Gloustershire, UK). A plate-plate geometry was used. The diameter of the upper plate was 20 mm and the gap was 0.35 mm. Oscillatory experiments were carried out to determine the viscoelastic properties (mainly the elastic or storage modulus, G', and the viscous or loss modulus, G'') of the tackifiers, EVA, and EVA-tackifier mixtures. Discs of samples of 20 mm diameter and about 0.5 mm thick were used. Experiments were performed by melting the sample at 110°C and then the temperature was gradually decreased to 25°C (cooling rate = 5°C/min). The target strain (which is related to the amplitude of the sinusoidal movement of the plate) was 10^{-3} for the EVA-tackifier mixtures and EVA, and 10^{-4} for the tackifiers.

Dynamical Mechanical Thermal Analysis (DMTA)

Dynamic viscoelastic measurements were performed in a Rheometrics Scientific DMTA Mk III apparatus (Rheometrics Scientific, Surrey, UK), using the 3-point bending mode; the storage modulus, E', and the tan δ values were obtained. The EVA and the EVA-tackifier mixtures were heated from −80°C to 100°C using a heating rate of 5°C/min, a frequency of 0.3 Hz, and a peak-peak amplitude of 64 μm. The dimensions of the samples were 0.6 × 10 × 20 mm.

Brookfield Viscosity

Brookfield viscosity measurements of the EVA-tackifier mixtures were carried out using a Brookfield RD DV-I viscosimeter (Brookfield

Engineering Labs., Stoughton, MA, USA) provided with a thermocell device, which allows the measurements under controlled high temperature. Viscosity measurements were obtained at 180°C, using the CS4-21 spindle at a rotational speed of 10 rpm.

Immediate Adhesion

The tack of the EVA-tackifier blends is not easy to measure. Immediate adhesion between two 0.2 mm thick smooth vulcanized SBR rubber strips was used in this study as an indirect way to estimate the tack. The immediate adhesion was estimated as the force necessary to separate the two SBR rubber strips joined using an adhesive film without application of pressure. A T-peel test was carried out 30 s after joints were produced, following the procedure described below.

T-Peel Strength Measurements

Adhesion was estimated from T-peel strength measurements of vulcanized styrene-butadiene rubber strips (150 mm × 30 mm × 4 mm)/EVA-tackifier mixture joints. The surfaces of the rubber pieces were heated at 100°C using an infrared lamp, and afterwards the molten adhesive at 170°C was spread over one of the two rubber test pieces. Immediately afterwards, the two rubber strips were placed in contact under a pressure of 0.8 MPa for 10 s to achieve a suitable joint. The adhesive joints were kept at 25°C and 50 wt% relative humidity before undergoing the T-peel test. The T-peel tests were carried out 30 min after joint formation. The T-peel strength was measured in an Adamel L'Homargy DY-32 test instrument (peel rate = 0.1 m/min) (Adamel L'Homargy, Ivry sur Seine, France). The values obtained were the average of three replicates; the standard deviation in the measurements was lower than 0.7 kN/m.

RESULTS AND DISCUSSION

Characterization of the Raw Materials

The IR spectrum of EVA is given in Figure 1. The IR spectrum shows the bands due to ester groups in the vinyl acetate regions (C=O stretching at 1739 cm^{-1}, symmetric and asymmetric C–O–C stretching at 1238, 1025, and 608 cm^{-1}). The other bands in the IR spectrum correspond to methyl and methylene groups.

The two tackifiers used in this study were a hydrogenated rosin ester (H) and a polyterpene tackifier (T). The IR spectra of the tackifiers (Figure 1) show C=O bands due to stretching of aromatic rings (1695 cm^{-1}) and C–O bands due to stretching of ester groups in the

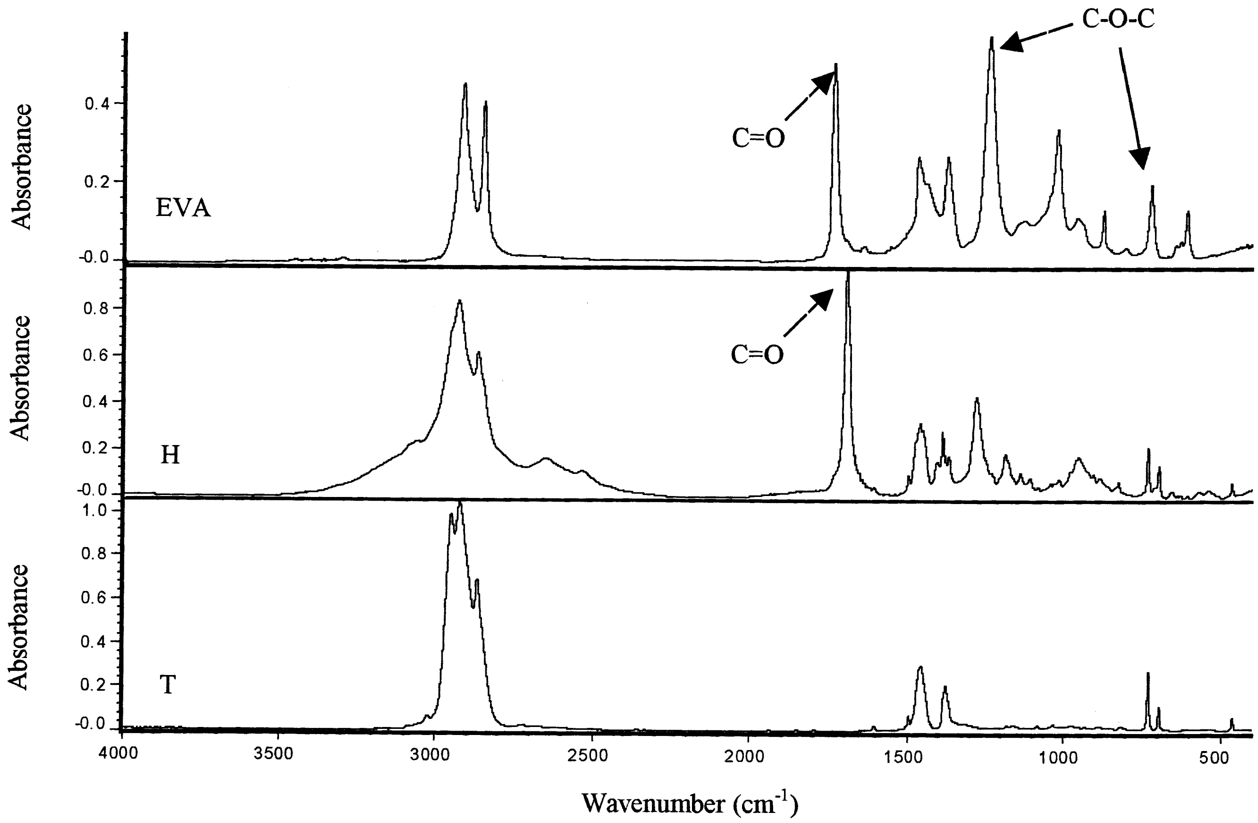

FIGURE 1 IR spectra of the EVA and the tackifiers.

H tackifier (1240, 1171, 1124 cm^{-1}), whereas the IR spectrum of the T tackifier shows only C–H bands due to aliphatic and cycloaliphatic groups (2869, 2954, 1381 cm^{-1}), and C–H and C–C bands due to aromatic rings (3041, 2000–1600 cm^{-1}, and 1605, 1495, 1454 cm^{-1}, respectively). Therefore, the two tackifiers used in this study differ in polarity; the rosin ester is more polar than the polyterpene tackifier.

The rheological properties of the tackifiers were measured in a plate-plate rheometer. Figure 2 shows the variation of the storage (G′) and loss (G″) moduli as a function of the temperature for the two tackifiers. Both tackifiers show similar features. At low temperature, the storage modulus is higher than the loss modulus and an abrupt decrease in G′ is produced by increasing the temperature, due to a sudden collapse of the tackifier structure. This corresponds to the typical rheological behaviour of a solid-like material. The storage and loss moduli are higher for the T tackifier, and the structure collapses at higher temperature. Therefore, the solid-like character of the T tackifier is greater than for the G tackifier. On the other hand, a cross-over between the storage and loss moduli is produced for both tackifiers,

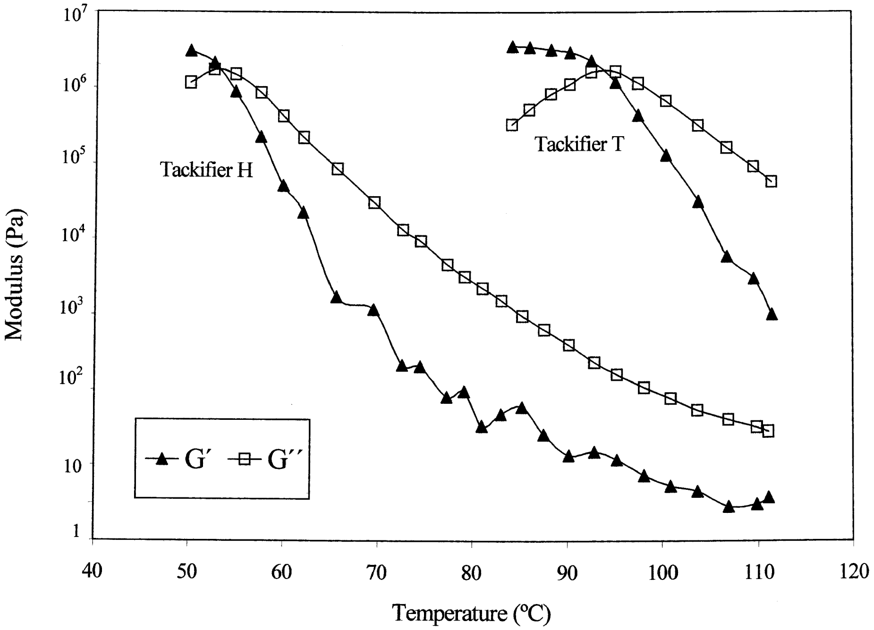

FIGURE 2 Variation of the storage (G′) and loss (G″) moduli as a function of the temperature for the tackifiers.

which corresponds to the transition from solid-like to liquid-like regime. The T tackifier shows the cross-over at higher temperature than the G tackifier (Table 2), because of the higher softening point and average molecular weight of the T tackifier (Table 1). On the other hand, the values of temperature and moduli in the cross-over of the storage and loss moduli are similar to those in the maximum of the loss modulus (G″) curves and, thus, the collapse of the tackifier structure seems to be associated with the change in rheological behaviour from solid-like to liquid-like material, rather than to differences in the glass transition temperature.

The thermal properties of the tackifiers were determined using DSC. The thermograms obtained from the second DSC run of the tackifiers (Figure 3) show the glass transition temperature (T_g) values located at 36 and 64°C for the H and T tackifiers, respectively.

Characterization of EVA-Tackifier Mixtures

The viscoelastic and rheological properties of the EVA-tackifier mixtures were obtained using Brookfield viscosity measurements, plate-plate rheometry, and DMTA. Figure 4 shows the variation of the Brookfield viscosity at 180°C of the EVA-tackifier mixtures as a function of their tackifier content. The viscosity always decreases by increasing the amount of tackifier; the BH (EVA-rosin ester mixtures) and BT (EVA-polyterpene resin mixtures) series show similar values and trend. The marked decrease in Brookfield viscosity of the

TABLE 2 Moduli and Temperatures at Cross-Over Between the Curves of the Elastic and Viscous Moduli as a Function of the Temperature for the EVA, Tackifiers, and Adhesives

Sample	Modulus at cross-over (Pa)	Temperature at cross-over (°C)
EVA	$4.0\ 10^4$	54.4
H	$1.6\ 10^6$	53.5
T	$1.6\ 10^6$	93.7
BH50	$3.0\ 10^4$	44.8
BH100	$2.4\ 10^4$	38.6
BH170	$3.1\ 10^4$	35.5
BT50	$2.5\ 10^4$	44.3
BT100	$6.5\ 10^4$	34.0
BT170	$7.0\ 10^5$	24.7

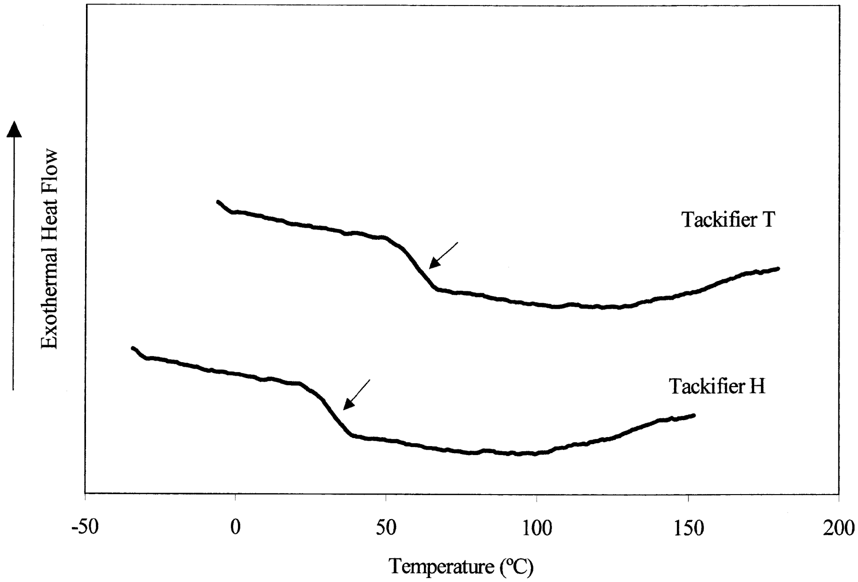

FIGURE 3 DSC thermograms of the tackifiers. Second DSC run experiments.

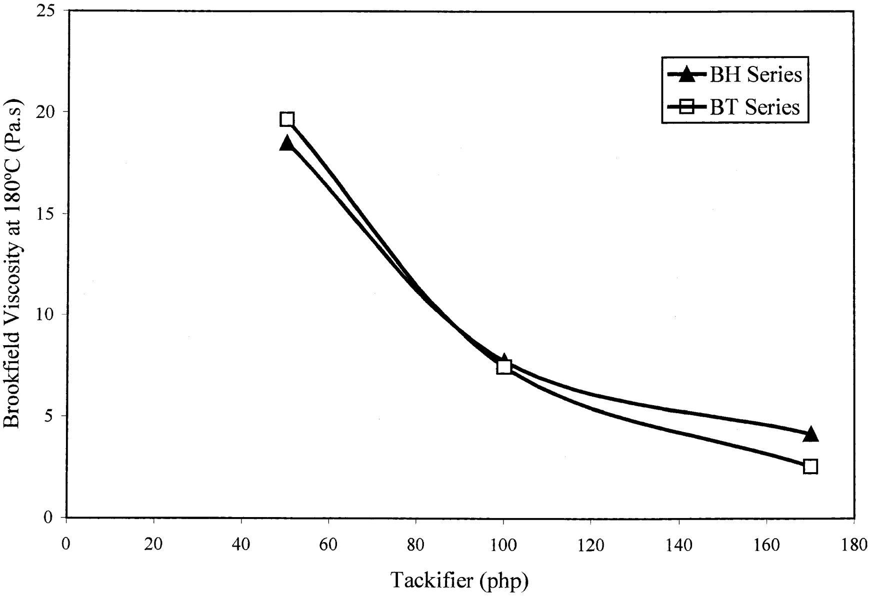

FIGURE 4 Variation of the Brookfield viscosity of the EVA-tackifier mixtures as a function of their tackifier content.

adhesives can be ascribed to the low molecular weight of the tackifiers as compared with that of the EVA. In these blends, the tackifier acts as a solvent for the EVA.

Figures 5a and 5b show the variation of the storage modulus (G′) as a function of the temperature for the EVA and the mixtures containing different amounts of the H (Figure 5a) or T tackifier (Figure 5b). The storage modulus is always decreased by increasing temperature and, in general, a more marked decrease (noticed as a knee) is produced at low temperature, due to the softening of the EVA. Addition of tackifier decreases the storage modulus of EVA to a greater extent in the mixtures containing higher amounts of tackifier; similar behaviour is obtained for the mixtures containing H or T tackifier. This trend is in agreement with the variations in Brookfield viscosity of the EVA-tackifier mixtures. On the other hand, the addition of tackifier allows the softening of the EVA to be produced at lower temperature (for several EVA-tackifier blends the knee cannot be obtained under the experimental conditions used in this study), indicating that the tackifier decreases the crystallinity of EVA, to a greater extent as the amount of tackifier increases, due to the amorphous structure of the tackifiers. Furthermore, the slope of the knee in the curves of Figures 5a and 5b becomes steeper as the tackifier content in the EVA-tackifier mixtures increases, confirming the change in the crystallinity of EVA by addition of the tackifier.

All EVA-tackifier mixtures show a cross-over between the curves of the storage and loss moduli as a function of the temperature, and Figure 6 shows, as a typical example, the cross-over for the BH50 mixture. The cross-over corresponds to the state of the material at which the solid-like and liquid-like behaviour is similar, *i.e.*, the relaxation temperature of the mixture. Therefore, for a temperature below the cross-over the solid-like behaviour is dominant over the liquid-like behaviour, and for a temperature higher than that of the cross-over, the liquid-like behaviour of the EVA-tackifier mixture is dominant. The moduli and temperature at cross-over are given in Table 2. The temperature at the cross-over is similar for EVA and H tackifier, whereas for the T tackifier the cross-over is located at high temperature. On the other hand, the two tackifiers show higher moduli at cross-over than EVA. EVA-tackifier mixtures show lower moduli at cross-over than the tackifiers and closer to that of EVA, and always the temperature at cross-over is lower than for both the EVA and the tackifiers (Table 2), indicating that the rheological behaviour of these blends is different than for their components. The temperature at which the cross-over is produced decreases by increasing the tackifier content (Table 2) and, whereas the moduli at cross-over are relatively similar for all

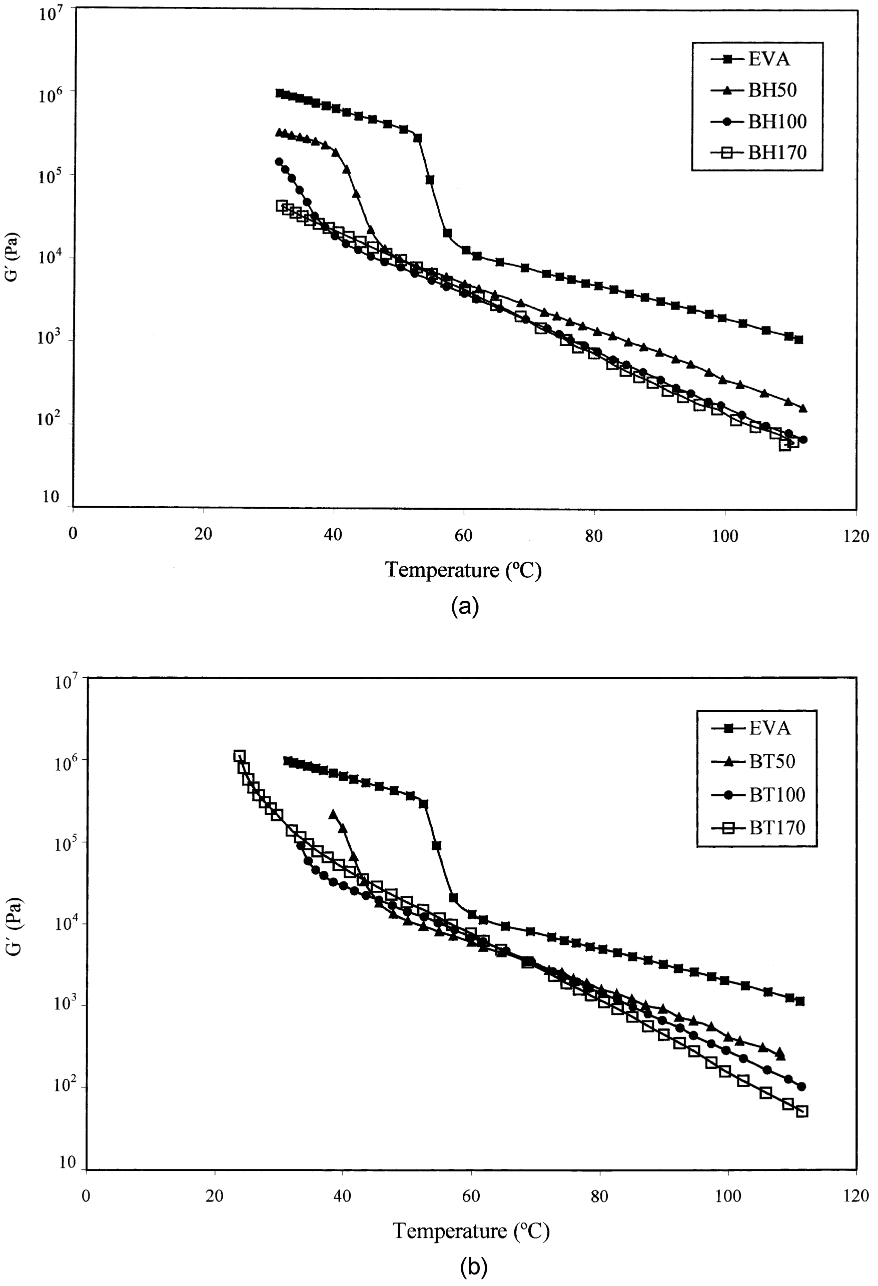

FIGURE 5 Variation of the storage modulus (G′) as a function of the temperature for the EVA copolymer and the mixtures containing different amounts of (a) H tackifier, and (b) T tackifier.

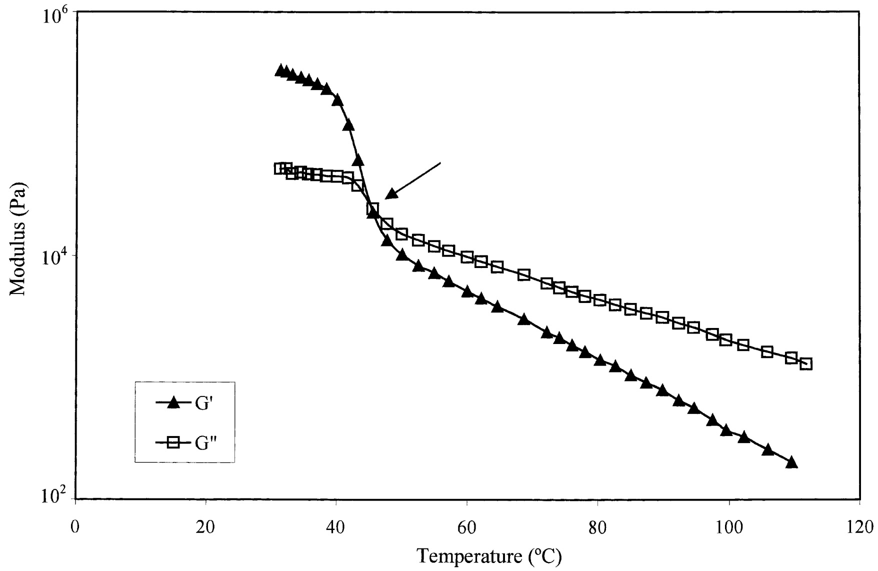

FIGURE 6 Variation of the storage (G′) and loss (G″) moduli as a function of the temperature for the BH50 mixture.

mixtures containing the tackifier H, an increase is observed for the mixtures containing the T tackifier. Furthermore, the temperature at cross-over is higher in the EVA-T tackifier series and the difference with respect to the EVA-H tackifier series became more important as the tackifier content increased.

All of those features indicate that the addition of the tackifier affects the crystallinity of the EVA, decreasing its softening point to lower temperature, and to a greater extent by increasing the tackifier content in the mixture. The polar tackifier (rosin ester) is less compatible with the polyethylene blocks of the EVA and, therefore, the moduli at the cross-over are of the same order as for EVA (polyethylene is the hard segment block and contributes more to the modulus). However, the polyterpene resin is mainly nonpolar and should be more compatible with the polyethylene segments in the EVA, contributing to increases in the moduli (polyethylene blocks are dominant in the EVA used in this study).

DMTA was also used to study the viscoelastic behaviour of the adhesives at low temperature (where the glass transition of EVA is obtained) and under bending stresses. Figures 7a and 7b show the variation of tan δ as a function of the temperature for the EVA and the BH and BT series, respectively. The curve corresponding to the EVA shows a glass transition temperature at −18°C. The addition of the tackifiers produces different effects in the BH and BT series. For the BH series (EVA-hydrogenated rosin ester mixtures) an increase in the tackifier amount produces a displacement of the glass transition temperature of EVA (located at the maximum in tan δ curves) to higher temperatures and higher tan δ values (*i.e.*, higher loss modulus or lower storage modulus—tan $\delta = G''/G'$). This means that the rosin ester is compatibilized with EVA leading to an increase in T_g value and a reduced degree of crystallinity in EVA; the higher the tackifier amount in the mixture, the higher the T_g value and the tan δ value at the maximum. On the other hand, the BT adhesive series (EVA-polyterpene tackifier mixtures) shows a different behaviour. All mixtures containing the tackifier T show a slightly higher Tg (around 8°C) than EVA, but there is no significant change in this value by increasing the tackifier content. Furthermore, the tan δ value at the maximum is drastically decreased by adding the T tackifier and by increasing the tackifier amount in the adhesive. Therefore, for the BT series there is the creation of an entanglement between the polyterpene resin and the polyethylene blocks of EVA, leading to a decrease in tan δ value, and to a slight increase in T_g value. These effects are more marked by increasing the tackifier content in the mixture.

DSC measurements also provide information about the changes in compatibility and crystallinity of EVA by the addition of the tackifiers. Figure 8 shows, as a typical example, the DSC thermograms for BT100 and BH100 mixtures. The glass transition temperatures of EVA, tackifiers, and EVA-tackifier mixtures are given in Table 3. The compatibility of the two tackifiers with EVA obtained using DSC is in agreement with those obtained using DMTA and plate-plate rheology. The BH series show T_g values located between the T_g of the EVA and that of the H tackifier. The BH series show only one T_g at higher temperatures than for the EVA (−25°C) and the increase in tackifier content produces a more marked increase of T_g. These results confirm the compatibility between the rosin ester and the EVA. Furthermore, the crystallinity of EVA is reduced because the melting enthalpy ΔH_m (Table 3) of the BH mixtures also decreases, and this effect is more marked by increased tackifier content.

However, for the BT series the T_g values are relatively similar to that for EVA (Table 3), indicating poor compatibility between the EVA and the T tackifier. The melting enthalpy, however, is increased by adding tackifier to the EVA and by increasing the tackifier content in the adhesive, likely indicating the increased crystallinity of the

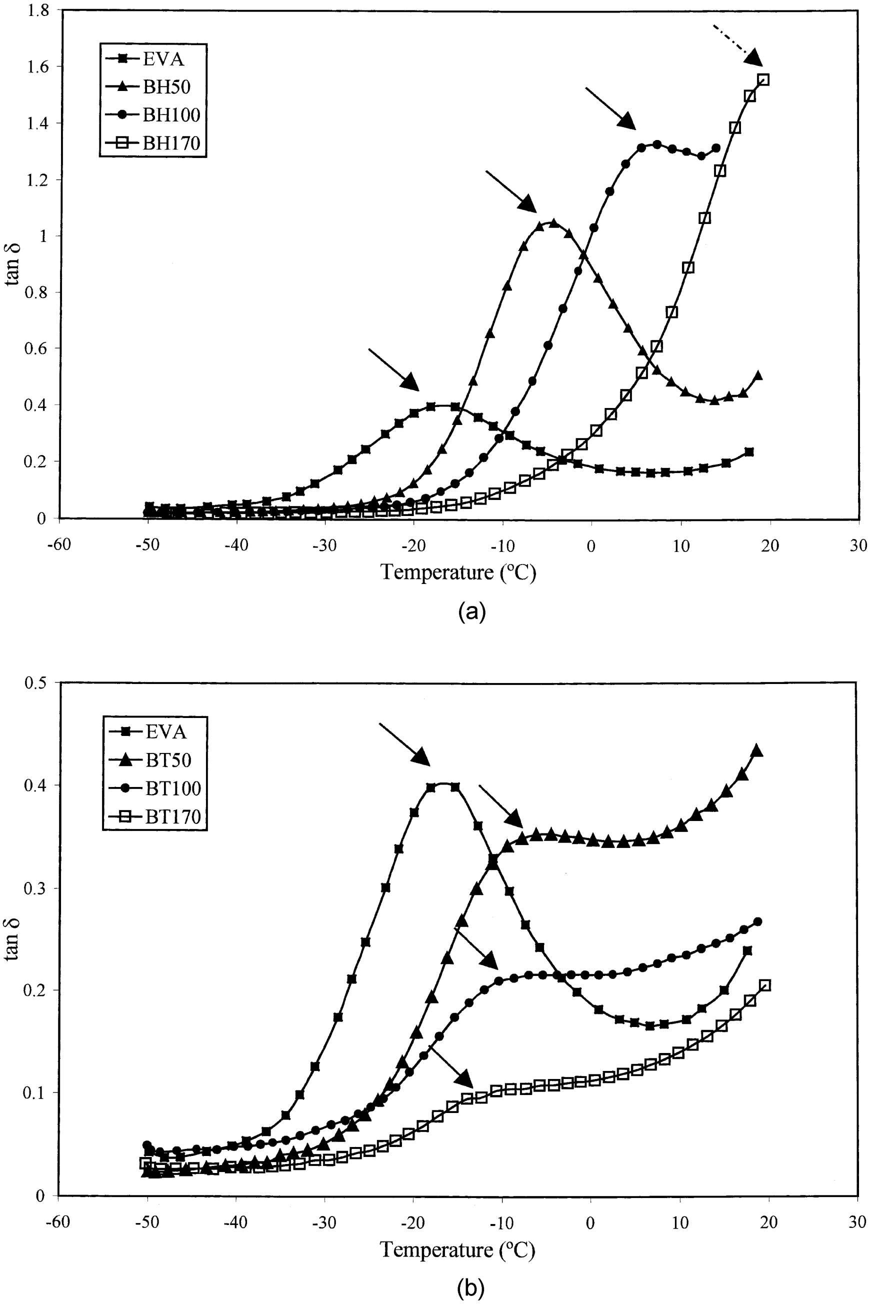

FIGURE 7 Variation of tan δ as a function of the temperature for the mixtures containing (a) H tackifier and (b) T tackifier.

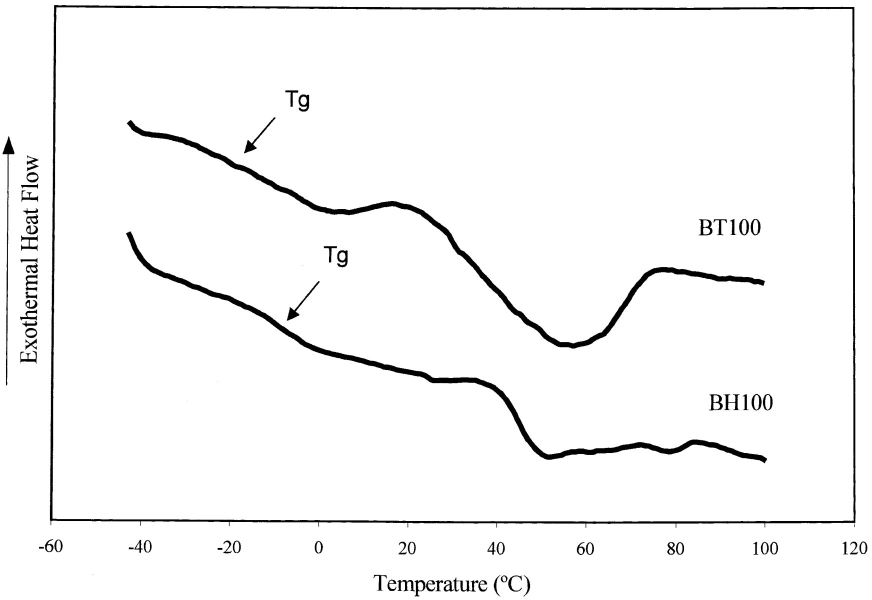

FIGURE 8 DSC thermograms of BT100 and BH100 mixtures.

EVA by incorporation of the polyterpene resin. This hypothesis needs to be clarified in the near future.

The different degree of compatibility between the H or T tackifiers and the EVA should affect the tack and the immediate adhesion of the adhesives. Tack was not measured in this study. The immediate adhesion was determined from T-peel test experiments as described in the above section "Brookfield Viscosity". The immediate adhesion

TABLE 3 Glass Transition Temperature (Tg) and Melting Enthalpy (ΔH_m) Values of EVA, Tackifiers, and EVA-Tackifier Mixtures in DSC Experiments

Sample	Tg (°C)	ΔH_m(cal/g)
EVA	−25	9.60
H	36	—
T	64	—
BH50	−16	3.54
BH100	−8	2.16
BH170	2	1.02
BT50	−18	3.42
BT100	−18	4.72
BT170	−21	2.76

values of the thin SBR rubber/EVA-tackifier mixture joints are shown in Figure 9. In general, there is an increase of the immediate adhesion as the tackifier content in the EVA-tackifier mixture increases, and an adhesion failure was always obtained. This indicates that the failure can be ascribed to the surface properties and to the composition of the mixtures in the vicinity of the interface between the rubber and the EVA-tackifier mixture. The increase in the immediate adhesion is more pronounced in the mixtures containing the H tackifier, and the differences in the immediate adhesion obtained in the joints produced with the mixtures containing the H and T tackifiers become more marked as the tackifier content increases. The immediate adhesion is always higher in the joints produced with the BH series adhesives, because the higher EVA-H tackifier compatibility and reduced crystallinity favours a greater immediate adhesion. Furthermore, the increase in the crystallinity of EVA-T tackifier mixtures allows poor immediate adhesion because the adhesive film is stiffer and under peel stresses its resistance to breakdown is poor.

The increase in the tackifier content produces a decrease in the elasticity and hardness of the EVA-tackifier mixtures and, therefore, the mechanical stresses induced during the peel experiment must be

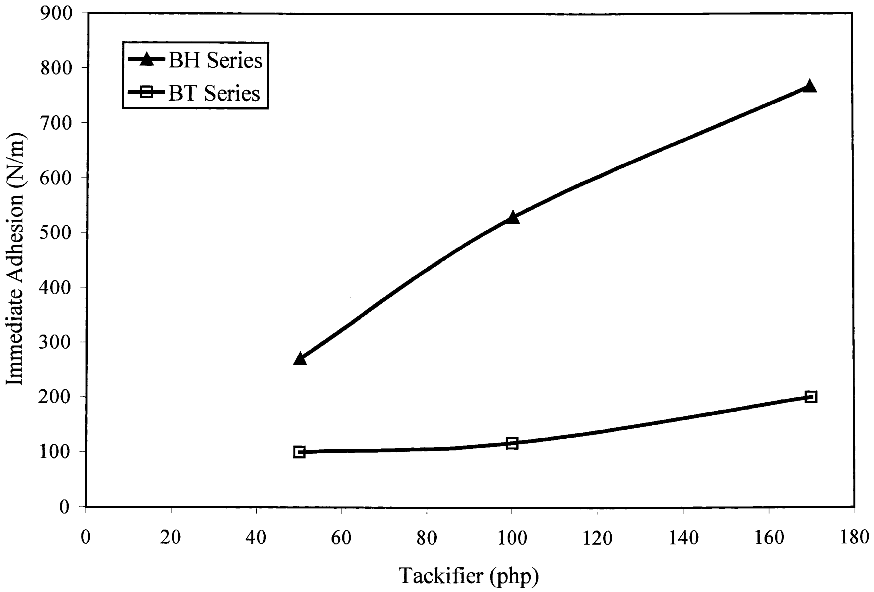

FIGURE 9 Variation of the immediate adhesion in thin SBR rubber/EVA-tackifier mixture joints as a function of the tackifier content.

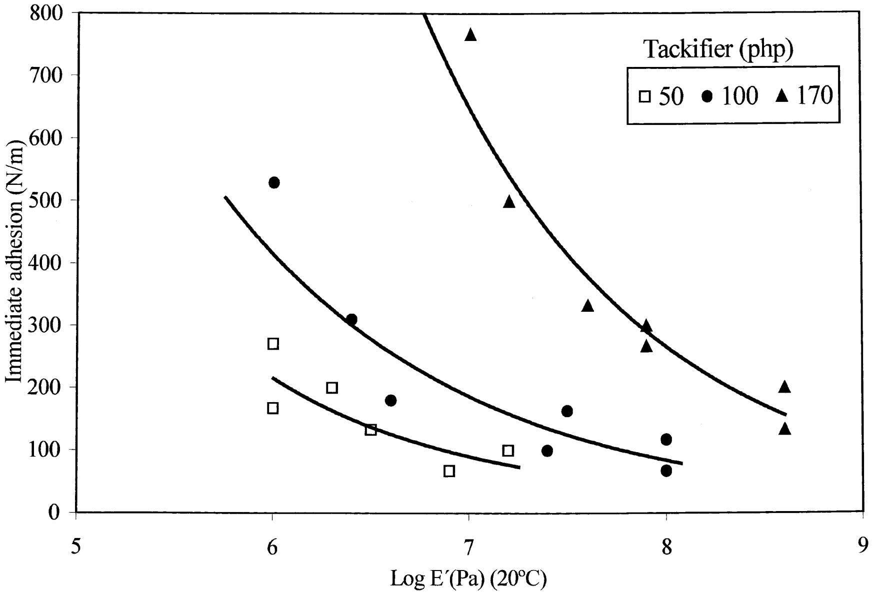

FIGURE 10 Variation of the immediate adhesion of thin SBR rubber//EVA-tackifier mixture EVA-tackifier mixture joints as a function of the storage modulus at 20°C of the EVA-tackifier mixtures.

more important in the adhesives containing a lower amount of tackifier. Figure 10 shows the variation of the immediate adhesion as a function of log E′ for the mixtures containing 50, 100, and 170 phr of the two tackifiers. Additional experimental values have been included in Figure 10 to show the trend more accurately. According to Figure 10, a higher value of storage modulus (E′) in the EVA-tackifier mixtures (*i.e.*, improved elastic behaviour) generates a lower immediate adhesion. For a given amount of tackifier, the EVA-tackifier mixtures showing the lowest E′ values correspond to those containing the rosin ester for which the highest immediate strength is obtained. Similarly, the EVA-tackifier mixtures containing the polyterpene tackifier show the highest E′ values and the lowest immediate adhesion.

The adhesion of EVA-tackifier mixtures was estimated from T-peel strength tests of SBR rubber/EVA-tackifier mixture joints (Figure 11). The peel strength of SBR rubber/EVA joint was 4 kN/m and an adhesion failure was obtained. However, for the joints produced with EVA-tackifier mixtures, a cohesive failure in the adhesive was always obtained and, therefore, the peel strength values will mostly depend on the mechanical and cohesion properties of the EVA-tackifier

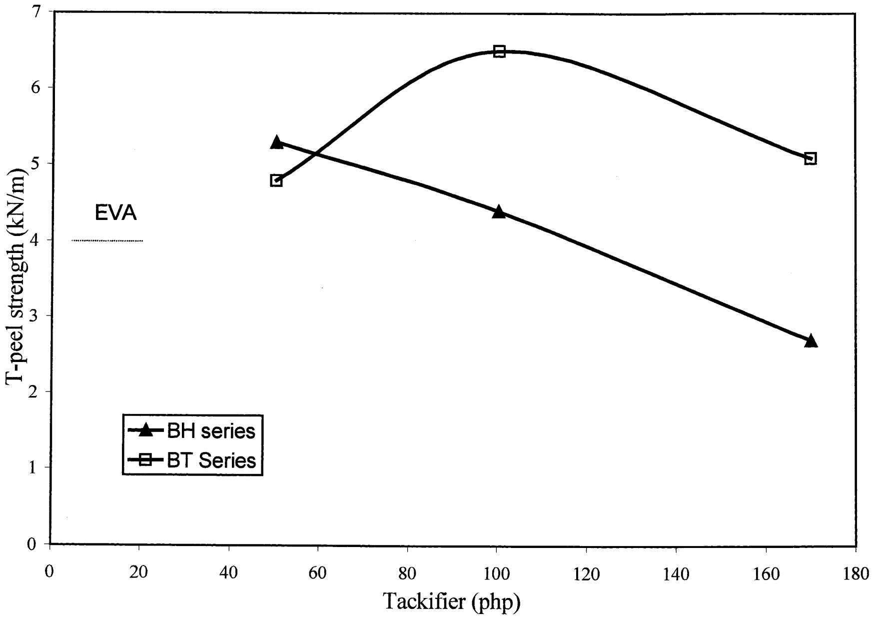

FIGURE 11 Variation of the T-peel strength of SBR rubber/EVA-tackifier mixture joints as a function of the tackifier content.

mixtures. Thus, because the mixtures of the BT series are more crystalline than those of the BH series, higher peel strength values are obtained in the SBR rubber/BT mixture joints. Furthermore, the peel strength values decrease with increasing H tackifier content in the mixtures because of the improved compatibility with the EVA (Figure 7a) and their lower crystallinity.

CONCLUSIONS

Addition of different amounts of two tackifiers to EVA produced marked variations in Brookfield viscosity; the higher the tackifier content, the lower the viscosity. The nature of the tackifier and its content determined the degree of compatibility and the crystallinity of EVA, obtained from plate-plate rheology, DMTA, and DSC experiments. The hydrogenated rosin ester was less compatible with the polyethylene blocks of EVA and, therefore, its addition reduced the crystallinity and increased the compatibility (*i.e.*, an increase in T_g was obtained) with EVA. As a result, the immediate adhesion to thin SBR rubber increased (this can be related to the improved EVA-H tackifier compatibility) but the peel strength was reduced because a cohesive failure in the adhesive was obtained (this can be related to the lower crystallinity). Conversely, the polyterpene tackifier was more compatible with the polyethylene blocks of EVA, and its addition increased is stiffness and crystallinity. Therefore, the joints produced between the SBR rubber and the BT series showed low immediate adhesion but high peel strength.

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