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www.elsevier.com/locate/ijadhadh

PII: S0143-7496(18)30254-9
DOI: https://doi.org/10.1016/j.ijadhadh.2018.11.001
Reference: JAAD2289

To appear in: *International Journal of Adhesion and Adhesives*
Accepted date: 1 November 2018

Cite this article as: María Alejandra Moyano, Rodrigo París and José Miguel Martín-Martínez, Viscoelastic and adhesion properties of hot-melts made with blends of ethylene-co-n-butyl acrylate (EBA) and ethylene-co-vinyl acetate (EVA) copolymers, *International Journal of Adhesion and Adhesives,* https://doi.org/10.1016/j.ijadhadh.2018.11.001

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Viscoelastic and adhesion properties of hot-melts made with blends of ethylene-co-n-butyl acrylate (EBA) and ethylene-co-vinyl acetate (EVA) copolymers

María Alejandra Moyano[1], Rodrigo París[2], José Miguel Martín-Martínez[1*]

[1]Adhesion and Adhesives Laboratory, University of Alicante, 03080 Alicante, Spain.

[2]Advanced Materials, DC Technology and New Ventures of Repsol, Repsol, Madrid, Spain.

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***Corresponding author**: José Miguel Martín-Martínez.

e-mail: jm.martin@ua.es

Phone no. (+34)965903977; Fax no. (+34)965909416.

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Abstract

Several hot-melts (HMAs) were prepared by using blends of ethylene-co-n-butyl acrylate (EBA) and ethylene-co-vinyl acetate (EVA) copolymers - EBA/EVA. HMAs were prepared with mixtures of EVA copolymers with 18 (EVA18) and 27 (EVA27) wt% vinyl acetate contents and EBA copolymer with 27 wt% n-butyl acrylate, polyterpene resin and mixture of microcrystalline and Fischer-Tropsch waxes. HMAs made with EBA/EVA blends showed lower viscosities and reduced shear thinning than the ones made with EBA or EVA due to differences in compatibility, but both the set time and the open time were not affected as they depended mainly on the wax nature and amount. The increase of the vinyl acetate (VA) content in EVA copolymer reduced the crystallinity of the EBA/EVA blends. Even EBA copolymer was more compatible with EVA27 than with EVA18 (the α- and β-transitions shown in DMTA plots were closer) and the compatibility did not vary with the EBA content in the blends. The addition of polyterpene resin and the mixture of waxes decreased the compatibility of the EBA/EVA blends, the higher compatibility was observed for the HMAs made with only one copolymer. The tack of the HMAs depended on their EBA/EVA contents, EBA/EVA27 HMAs showed broader temperature interval with high tack as well as higher tack, while the tack of EBA/EVA18 HMAs blend decreased and the temperature interval with tack was shortened and shifted to lower temperatures. Adhesion to polypropylene film was improved in HMAs made with 75 wt% EBA/25 wt% EVA18 and 50-75 wt% EBA/50-25 wt% EVA27. The adhesion to aluminum film of EBA or EVA hot melts was improved only in the joints made with EBA/EVA 27 HMAs, more noticeably when they contained higher EBA content.

Keywords: A. Hot-melt; B. Polyolefins; D. Tack; D. Viscoelasticity.

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1. INTRODUCTION

Hot-melt adhesives (HMAs) are solvent-free solid materials at room temperature which becomes relatively low viscous at high temperatures (generally above 160ºC); when applied at high temperature they rapidly set upon cooling. In comparison with solvent and waterborne adhesives, HMAs form strong bonds quickly, they can join different substrates, they are easy to handle, and do not produce residues [1]. The main components of HMAs are typically polymer, tackifier, wax and antioxidant. The polymer imparts the mechanical strength and toughness to HMA, while the tackifier enhances wetting and tack, the wax lowers the melt viscosity, and the antioxidant inhibits/delays thermal degradation during processing [2].

Ethylene-co-vinyl acetate (EVA) copolymer-based HMAs are the most commonly used in packaging; EVA copolymers with vinyl acetate (VA) contents between 18 and 40 wt% and different melt flow indexes (MFIs) are used - Figure 1 [1,3]. EVA hot-melts made with copolymers of high ethylene content show improved adhesion to non-polar substrates (for example, polyethylene) and high mechanical strength, while the ones made of copolymers with higher amount of vinyl acetate show improved adhesion to polar substrates (for example, paper), high flexibility and high tack [4,5]. Although effective, EVA hot-melts show relatively long open time and fair performance at low temperature. On the other hand, the melt viscosity of HMA should be sufficiently low for allowing application without blocking the dispenser nozzle. EVA hot-melts exhibits outstanding viscosity retention upon ageing at elevated temperature but they slowly release acetic acid which can lead to corrosion of the application equipment [3]. However, ethylene-co-n-butyl acrylate copolymer (EBA)-based hot-melts are thermally stable at application temperature and they do not release chemicals.

Because of the glass transition temperature (T_g) of EBA copolymer is about -50ºC (T_g of EVA copolymer is around -30ºC), its performance at low temperature is better than for EVA copolymer, and therefore EBA hot-melts show higher flexibility at low temperature than EVA hot-melts. Furthermore, EBA copolymer has lower density, good elongation-at-break and tensile strength, and it is slightly less polar than EVA [6], these properties are due to the existence of longer hydrocarbon chain pendant group (C4 in EBA vs C2 in EVA) and an acrylate (Figure 1) instead of an acetate group; therefore, differences in the compatibility of EBA copolymer with tackifiers and waxes in HMAs with respect to that of EVA can be anticipated.

Figure 1. Chemical structure of the EVA and EBA copolymers.

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The compatibility, tack and viscoelastic properties of EBA HMAs made with pentaerythritol rosin ester and waxes of different nature (Fischer-Tropsch and microcrystalline) has been studied recently [7], and it has been shown that the increase in the compatibility of EBA copolymer with microcrystalline wax led to increased tack and open time, and reduced viscosity of the HMAs. In contrast, the addition of a mixture of microcrystalline and Fischer-Tropsch wax caused better balance in the rheological properties and higher thermal stability of the EBA HMAs. On the other hand, the influence of adding tackifiers of different nature to EBA copolymer has been addressed earlier [8], and it has been shown that the viscosity of EBA hot melts varied significantly by changing the tackifier nature, and that EBA copolymer showed broad tackifier compatibility, even though aliphatic and aromatic hydrocarbon resins were less compatible. Furthermore, the most compatible EBA HMAs were obtained with rosin ester, polyterpene and cycloaliphatic-aromatic hydrocarbon tackifiers, and these HMAs showed the highest tack and adhesion. On the other hand, EBA HMAs show enhanced bond strength and overall performance at elevated temperature, flexibility at low temperatures, oil resistance, high tack and broad compatibility with a variety of tackifiers and waxes than EVA HMAs [6,9]. However, EBA HMAs have limited mechanical properties as compared to EVA hot-melts.

In order to overcome the limitations of EVA and EBA HMAs, EVA+EBA blends can be used for preparing HMAs with better balanced properties. Hansen [9] has proposed HMA compositions based on mixing EVA (melt flow index : 500 g/10min; vinyl acetate content : 23-30 wt%), EBA (melt flow index : 400 g/10min; n-butyl acrylate content : 30-38 wt%) and tackifier which had adequate open time (at least 5 seconds) and good creep resistance at temperatures significantly lower than EVA HMAs. In another patent, Liedermooy et al. [10] described HMAs intended for packaging of frozen products made with EBA (melt flow index : 850 g/10min; n-butyl acrylate content : 33 wt%), EVA (vinyl acetate content : 10-40 wt%), rosin ester and paraffin or microcrystalline wax, which showed low viscosity at 135ºC and good adhesion to polyolefin substrate. Hanner et al. [11,12] have shown that HMAs made with EBA+EVA mixture, rosin ester or terpene-phenolic resin and paraffin, microcrystalline or Fischer-Tropsch wax had high heat resistance, fast setting time and good adhesion at low temperatures. In order to optimize those properties, high melt flow index copolymers (greater than 750 g/10min) and co-monomer contents of 30-40 wt% for EBA copolymer and 20-35 wt% for EVA copolymer were needed. Recently, Cimino et al. [13] have prepared different binary mixtures of ethylene copolymers (EVA, EBA and EBA+EVA mixture) and different tackifiers intended to enhance the reversible adhesion in art conservation products, and they found good miscibility of urea-aldehyde and hydrogenated

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hydrocarbon resins, ketone and rosin ester tackifier with the copolymers; furthermore, all tackifiers modified the copolymers properties. Although some binary mixtures of EVA+EBA and tackifiers have been studied, the addition of wax was not considered and the influence of the amounts of EBA and EVA copolymers in the mixtures on the properties of the binary blends was not considered. Therefore, the few existing literature has shown the potential of the use of EBA+EVA blends for preparing HMAs intended for applications at low temperature, but a detailed and systematic study on the structure, properties, compatibility and adhesion of HMAs made with EBA+EVA blends have not been addressed yet.

In this study the thermal, rheological, compatibility and adhesion properties of HMAs made with different EBA+EVA blends of different co-monomer content (18-27 wt%) have been analyzed. Ethylene copolymers with similar melt flow index (150 g/10min) have been selected, and the vinyl acetate content of EVA copolymer was changed between 18 and 27 wt%. In previous studies [9-13] higher melt flow indexes of EBA and EVA copolymers have been used, but in this work ethylene copolymers with lower MFI values have been selected considering that they are sufficiently fluid for processing but the mechanical properties and cohesion of the resulting HMAs should be higher.

2. EXPERIMENTAL

2.1. Materials

EBA copolymer containing 27 wt% n-butyl acrylate (Alcudia PA27150), and EVA copolymers containing 18 wt% (Alcudia PA410) and 27 wt% vinyl acetate (Alcudia PA442) were used; all copolymers were supplied by Repsol (Madrid, Spain). All copolymers have similar MFI (150 g/10min). Some characteristics of the copolymers taken from their technical data sheets are given in Table 1.

Table 1. Some properties of the ethylene copolymers.

Polyterpene resin (Piccolyte C115) supplied by Pinova Inc. (Georgia, USA), and Fischer Tropsch wax (Sasolwax-H1) and microcrystalline wax (Ibercer 3080), both supplied by Iberceras (Madrid, Spain), were used for preparing HMAs. For avoiding thermal deterioration of HMAs, 0.5 wt% Irganox 1010 antioxidant (BASF, Kaisten, Switzerland) was added.

Accepted manuscript

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2.2. Preparation of the hot melts

HMAs were prepared in Pyrex glass beaker internally coated with aluminum foil placed on a hot plate. The hot plate was pre-heated at 90-120°C and the wax mixture was added. Once the wax was melted, the temperature was increased to 130°C and then the tackifier and the antioxidant were added. Once a homogeneous mixture was obtained, EBA or EVA or EBA+EVA blend was added and then the temperature was raised to 180ºC allowing its melting. Afterwards, the Pyrex glass beaker was capped with three entrances glass lid which were connected to nitrogen stream (to prevent oxidation), a thermometer (for controlling the temperature), and a stirrer connected to Heidolph RZR-2000 stirring unit (Heidolph Instruments, Kelheim, Germany). The ternary blends were stirred at 80 rpm and heated at 180ºC for 1 hour; afterwards, the HMAs were allowed to cool down at room temperature and removed from the glass beaker.

EBA+EVA blends without tackifier and waxes were prepared in Pyrex glass beaker internally coated with aluminum foil placed on a hot plate. The hot plate was pre-heated at 130ºC and the corresponding amounts of EBA and EVA copolymers were added. Then, the temperature was raised to 180ºC allowing its melting, the antioxidant was added, and afterwards, the Pyrex glass beaker was capped with three entrances glass lid which were connected to nitrogen stream, a thermometer, and a stirrer. EBA+EVA blends were stirred at 80 rpm and heated at 180ºC for 1 hour; afterwards, they were allowed to cool down at room temperature and removed from the glass beaker.

The compositions of HMAs consist in 39.8 wt% of EBA or EVA or EBA+EVA blend (weight ratio of EBA to EVA : 75:25, 50:50, 25:75), 39.8 wt% of polyterpene resin, 12.1 wt% of Fischer Tropsch wax, and 7.8 wt% of microcrystalline wax. This composition was selected on the results obtained in our previous study [7]. For avoiding deterioration, 0.5 wt% Irganox 1010 antioxidant was added. The nomenclature used for HMAs consists in the words “EBA”, “EVA” or “EBA/EVA”, followed by the co-monomer content and “-“, and then the amounts in weight of EBA and EVA copolymer. For example, EBA/EVA27-25/75 corresponds to the HMA made with a blend of 25 wt% EBA and 75 wt% EVA with 27 wt% vinyl acetate, 39.8 wt% polyterpene resin, 12.1 wt% of Fischer Tropsch wax and 7.8 wt% of microcrystalline wax,

2.3. Experimental techniques

2.3.1. Brookfield viscosity. The viscosity of the HMAs was measured in a Brookfield RD DV-I viscometer provided with Thermosel (Brookfield Engineering Laboratories Inc., Stoughton, MA, USA) at 160ºC by using SC4-21 spindle. The viscosities of the HMAs were measured according to ASTM D3236-88 standard, 10 g of HMA was used and

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the measurements were carried out in shear rate interval between 0.5 and 50 s^{-1}. Two experiments per sample were carried out and they were similarly consistent, one of them was selected in this study.

2.3.2. Rheological properties. The rheological properties of the HMAs were measured in a Bohlin CS-50 plate-plate rheometer (Bohlin Instruments Ltd., Gloucestershire, UK), using an upper plate of 20 mm. The HMA was melted at 200ºC and the gap was adjusted to 0.4 mm, and the experiments were performed in temperature range between 200ºC and 30ºC by using a cooling rate of 5 ºC min^{-1}, an oscillation frequency of 1 Hz and 0.5 % strain. All experiments were carried out in the region of linear viscoelasticity. Two experiments per sample were carried out and they were similarly consistent, one of them was selected in this study.

The variation of the storage modulus as a function of the temperature of HMA is related to the solidification of the adhesive after application. Thus, just after applying a HMA at high temperature on a substrate, the adhesive starts to cool down and a sharp increase of the storage modulus is produced; the temperature at which the sharp increase in the storage modulus (G´) starts can be related to the open time, and the temperature at which G´ is stabilized is related to the set time and open time of the HMA [14]. Figure 2 shows a scheme of the viscoelastic changes followed by the HMA upon cooling down and the regions at which the open and set times can be distinguished. The time after applying HMA during which can flow and wet-out the substrate on which is applied (open time) determines the beginning of the solidification and loss of tackiness of the HMA. On the other hand, the set time can be estimated by the change in G´ and temperature values during the sharp increase of G´ (Figure 2) and can be interpreted microscopically as the recrystallization of the HMA [15] which depends mainly on the wax nature and its compatibility with the rest of the components (polymers and tackifiers) of the HMA formulation [7].

Figure 2. Assignment of the different viscoelastic changes produced during the cooling down of a HMA in the curve of variation of the storage modulus (G´) as a function of the temperature.

2.3.3. Softening point. The softening points of the HMAs were measured in a Mettler Toledo FP900 Thermosystem calorimeter (Schwerzenbach Mettler Toledo GmbH, Germany) by using FP83 dropping point cell. HMA samples were prepared according to ASTM D3104 standard and a cup holder with a bottom opening of 6.35 mm diameter completely filled with HMA was used. Three experiments per sample were carried out and the results obtained were averaged.

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2.3.4. Tack measurement. The tack of HMAs was measured in a Texture Analyzer TA.XT2i equipment (Stable Microsystems, Surrey, UK) by using the probe tack test. Tack was measured between 30ºC and 200ºC by using stainless steel flat end cylindrical probe. Samples were prepared by heating the adhesive (2g) at 180 ºC placed over a stainless steel plate of dimensions 7x7x0.01 cm, pressing at 290 kPa for 10 seconds, and letting it cool down to room temperature. Homogeneous films of 1mm thick were obtained. The probe was approached to the HMA surface at a speed of 0.1 mm s^{-1}, then a force of 5 N during 1 second was applied, and finally the probe was withdrawn at a pulling rate of 1 mm s^{-1} until complete de-bonding was produced. Two experiments per sample were carried out and they were similarly consistent, one of them was selected in this study.

2.3.5. Dynamic mechanical thermal analysis (DMTA). The viscoelastic properties and compatibility of the EVA+EBA blends and the HMAs were studied in a TA Q800 dynamic mechanical analyzer (TA Instruments, Lukens Drive, New Castle, USA) using two points bending geometry (single cantilever). EVA+EBA blends or HMA films of about 10 mm thick were used, and they were prepared by placing 2.5 g sample in rectangular aluminum mould of dimensions 3.5x1.3 cm; the HMA was heated at 130 ºC until complete filling of the mould. The amplitude of deformation was 64 microns, the frequency was 1 Hz, and the temperature was varied from -80ºC to 90°C by using a heating rate of 5 °C min^{-1}. The amplitude selected in DMA measurements is higher than usual (amplitudes of 20-30 µm for single cantilever geometry) for assuring higher deformation of the test sample to enhance the viscoelastic response, and it is in the region of linear viscoelasticity (it ends at 70 µm). Two experiments per sample were carried out and they were similarly consistent, one of them was selected in this study.

2.3.6. T-peel test. The adhesion of the HMAs was evaluated by T-peel tests of polypropylene film-HMA-polypropylene film and aluminum foil-HMA-aluminum foil joints. Before applying the HMA, the substrates were surface treated. Grease and contaminants of aluminum foil surface were removed by 2-propanol wiping, allowing the solvent to evaporate for 10 minutes. On the other hand, for increasing its surface energy, the polypropylene film (PP) was surface treated with air atmospheric pressure rotating plasma jet in a PlasmaTreat GmbH system (Steinhagen, Germany) provided with a rotating nozzle with an opening ring of 4 mm, angle shot of 14º and rotation speed of 1900 rpm. The experimental conditions for the surface treatment of the PP film were one torch pass, 10 m min^{-1} torch speed, 5 mm nozzle-PP surface distance, 20 kV discharge, and 17 kHz frequency.

For preparing the joints, the HMA was applied at 180 ºC on an area of 15x80 mm of one substrate, and immediately after the other substrate was placed on top by pressing

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manually. Then, the joint was pressed at 290 kPa for 10 seconds for obtaining homogeneous adhesive film of about 200 µm thick. One hour after joint formation, T-peel tests were carried out in a Instron 4411 universal testing machine (Instron Ldt., Buckinghamshire, UK) by using a peeling rate of 10 mm min^{-1}. Five replicates were tested and averaged for each adhesive joint.

3. RESULTS AND DISCUSSION

3.1. Rheological and viscoelastic properties of the HMAs

Figures 3a and 3b show the variation of the Brookfield viscosity at 160 ºC as a function of the temperature for HMAs made with EBA, EVA and EBA/EVA blends containing 18 and 27 wt% vinyl acetate blends, respectively. Although the three copolymers used in this study has the same melt flow index, the Brookfield viscosities of the HMAs made with only EVA (EVA18 or EVA27) are near 5000 mPa.s, while the one for the HMA made with EBA has higher Brookfield viscosity (about 7000 mPa.s). The higher Brookfield viscosity of EBA hot-melt with respect to EVA hot-melts can be attributed to the interactions between the polar acrylate groups of EBA copolymer and the polyterpene resin. Surprisingly, the Brookfield viscosities of the EBA/EVA hot-melts are lower than the ones of the EVA and EBA hot melts (EBA/EVA27-50/50 is an exception) indicating the creation of new interactions between the two copolymers and the rest of the components of the HMAs. Furthermore, the Brookfield viscosities are somewhat lower for the EBA/EVA18 hot-melts. On the other hand, the HMAs made with EBA or EVA copolymers show noticeably shear thinning that is substantially reduced in the EBA/EVA hot-melts, this is an indication of different structure in the HMAs made with EBA/EVA blends.

Figure 3a. Variation of the Brookfield viscosity at 160ºC of the EBA, EVA18, and EBA/EVA18 hot-melts as a function of the shear rate.

Figure 3b. Variation of the Brookfield viscosity at 160ºC of the EBA, EVA27, and EBA/EVA27 hot-melts as a function of the shear rate.

Figure 4 shows the variation of the Brookfield viscosity at 160ºC of the EBA/EVA18 and EBA/EVA27 hot-melts as a function of their EVA copolymer content. The lower viscosities correspond to the HMAs made with blends of 50-25 wt% EBA and 50-75 wt% EVA. Addition of 25 wt% EVA produces the same Brookfield viscosity, irrespective of its vinyl acetate content. However, depending on the vinyl acetate content of EVA, different viscosities are obtained in the rest of the HMAs.

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Figure 4. Variation of the Brookfield viscosity at 160ºC of the EBA/EVA hot-melts as a function of their EVA content. Brookfield viscosity was determined at a shear rate of 7 s^{-1}.

The Brookfield viscosity is a rheological parameter and the different trends obtained in Figures 3a and 3b can be ascribed to differences in the viscoelastic properties of the HMAs. The viscoelastic properties of the HMAs were studied by plate-plate rheology. Figures 5a and 5b show the variation of the storage modulus (G´) as a function of the temperature for the HMAs made with EBA+EVA containing 18 and 27 wt% vinyl acetate, respectively. The values of the storage moduli of the HMAs made with the EVA/EBA blends are higher than for the ones made with only EBA or EVA, more noticeably in the HMAs made with EBA/EVA27 blends. Therefore, the viscoelastic properties of the EBA/EVA HMAs are different than the ones made with one copolymer. Whereas the curves of variation of the storage modulus (G´) of the EBA/EVA27 hot-melts as a function of the temperature are somewhat similar below 100ºC, irrespective of the amounts of the EBA and EVA copolymers, the ones for the curves of G´ vs temperature of the EBA/EVA18 hot-melts vary differently depending on their EVA18 content. Thus, below 100ºC, the storage modulus is higher in the EBA/EVA18-50/50 hot-melt, the storage moduli of the other EBA/EVA18 hot-melts are intermediate between the ones of the EBA and the EVA18 hot-melts.

Figure 5a. Variation of the storage (G´) modulus as a function of the temperature for EBA, EVA18 and EBA/EVA18 hot-melts. Plate-plate rheology experiments.

Figure 5b. Variation of the storage (G´) modulus as a function of the temperature for EBA, EVA27 and EBA/EVA27 hot-melts. Plate-plate rheology experiments.

According to Figure 2, the open and set times can be estimated from the plots of variation of G´ as a function of the temperature. According to Figures 5a and 5b, the set and open times are somewhat similar in the EBA/EVA18, EBA/EVA27, EBA and EVA hot-melts. In fact, the open time is related to the softening point of the HMAs that depends strongly on the nature and amount of wax [15]. Table 2 shows that the softening points of the HMAs vary between 103ºC and 107ºC, irrespective of the composition of the HMA. Therefore, similar open and set times are obtained in all HMAs. Similarly, the values of the temperature at which the sharp increase in G´ is produced (T_s) – Table 3 – are very similar in all HMAs (98-106ºC), and the values of T_s and softening point are related each other. On the other hand, the range of temperature between the beginning and the ending of the sharp increase of G´ (ΔT_c)

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given in Table 3 is related to the solidification rate of the HMA [16], and, therefore, to the set time. Similar values of ΔT_c are found in all HMAs, indicating similar set times.

Table 2. Softening points of the EBA/EVA hot-melts.

Table 3. Some results obtained from the plate-plate rheology experiments of the EBA/EVA hot-melts.

Figure 6 shows as typical examples the variation of the storage (G´) and loss (G´´) moduli as a function of the temperature for EBA/EVA18-25/75 and EBA/EVA27-25/75 hot-melts. All HMAs show a cross-over between the storage and loss moduli. Above the temperature at the cross-over (T_c), the HMA is dominantly viscous and at temperature below T_c, the elastic rheological behavior is dominant. In general, the values of T_c of the EBA/EVA hot-melts are higher than for the ones of the EBA or EVA HMAs (Table 3), and they increase by increasing the EVA content in the EBA+EVA blend; on the other hand, the values of T_c are higher in the EBA/EVA27 than in the EBA/EVA18 hot-melts. Furthermore, the values of the modulus at the cross-over (G_c) of the EBA/EVA hot-melts are lower than for the ones of the EBA or EVA HMAs, and they decrease by increasing the EVA18 content in the EBA/EVA blend, they are lower and similar in all EBA/EVA27 hot-melts. Therefore, the cross-over modulus and temperature are clearly affected by the vinyl acetate content of the EVA in the EBA/EVA hot-melts. It can be expected that the increase of the vinyl acetate content decreases the crystallinity of EVA copolymer which will result in lower values of the storage modulus of the EBA/EVA27 hot melts; furthermore, the temperature at the cross-over should increase by decreasing the crystallinity of the HMA because of the higher viscous component, the higher is the EVA copolymer content in EBA/EVA HMA, the higher is the value of T_c.

Figure 6. Variation of the storage (G´) and loss (G´´) moduli as a function of the temperature for the EBA/EVA18-25/75 and EBA/EVA27-25/75 hot melts.

3.2. Compatibility of the HMAs

The rheological properties of the HMAs are determined by the compatibility between their components, and in this study the compatibility was assessed by dynamic mechanical-thermal analysis (DMTA). The cloud point measurement is widely used to examine the compatibility of the polymer blends. The cloud point is the temperature at which the clear and molten polymer blend cools to give the first indication of a cloud or haze [17,18]; the lower is the cloud point, the more compatible is the polymer blend. However, the cloud point method is not sufficiently accurate because of it is difficult to

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measure when some amount of solid is present [19]. On the other hand, DMTA gives detailed information about the chemical and physical structures of the polymers and, in many cases, this is the most sensitive technique for determining the glass transitions and other structurally related transitions in polymers, being particularly useful for studying the miscibility of the polymer blends though the variation of their structural relaxations. These relaxations are evidenced through peaks in the tan delta vs temperature curves [20]. For ethylene-based copolymers three structural relaxations named as α, β and γ have been observed between -140ºC and 60ºC [20-22]. The α structural relaxation transition appears at high temperature and is associated to movements of large sections of the main chains themselves once the crystallites begin to melt. The β structural relaxation occurs at intermediate temperature and is attributed to segmental motions of disordered chains, occurring within the interfacial regions associated to the lamellar crystallites. The γ structural relaxation appears at low temperature (near -130 ºC for EVA copolymer) and corresponds to the glass transition of the polyethylene. In these study, only the α and β structural relaxations are evidenced. The closer are these structural relaxations, the higher is the compatibility of a polymer blend [7].

For better understanding of the compatibility between the different components in the EBA/EVA hot-melts, the compatibility between the blends of copolymers only, i.e., without tackifier and waxes, was analyzed. The EBA copolymer shows two structural relaxations at -22ºC and 32ºC (Figure 7a) whereas the EVA18 copolymer shows the two structural relaxations at higher temperatures (2ºC and 37ºC). On the one hand, the addition of EVA18 increases the temperature and decreases the maximum tan delta value of the β structural relaxation of the EBA copolymer, and the temperature of the α structural relaxation decreases, more markedly by increasing the EVA18 content in the blend (Figure 7a). Therefore, the compatibility of the EBA+EVA18 blends increases by increasing their EVA18 content, because of the β structural relaxation is displaced to higher temperature, indicating easier movements of large sections of the main polymer chains once the crystallites begin to melt and higher segmental motions of disordered chains within the interfacial regions associated to the lamellar crystallites.

Figure 7a. Variation of tan delta as a function of the temperature for EBA copolymer, EVA18 copolymer and EBA+EVA18 blends.

According to Figure 7b, the EBA copolymer shows two structural relaxations at -22ºC and 30ºC whereas the β structural relaxation appears at -5ºC and the one of the α structural relaxation appears a 30ºC in the EVA27 copolymer. The temperatures and

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maxima of tan delta of the α structural relaxation do not vary in the EBA/EVA27 blends, irrespective of their EVA27 content. However, the addition of EVA27 decreases the temperature of the β structural relaxation of the EBA copolymer, the decrease is less important in 75 wt% EBA+25 wt% EVA27 blend, more important in 50 wt% EBA+50 wt% EVA27 blend, and it is similar in 25 wt% EBA+75 wt% EVA27 blend. Therefore, the EBA copolymer is compatible with EVA27 and the compatibility does not vary when EVA27 content is 50 wt% or higher. On the other hand, the EBA copolymer is more compatible with EVA27 than with EVA18 due to the proximity of the α and β structural relaxations. Besides, the addition of 50 wt% or higher amount of EVA27 increases the values of the maxima of tan delta and narrows the tan delta peak because of the decrease of the crystallinity in the EBA/EVA27 blends (due to lower polyethylene content) [23].

Figure 7b. Variation of tan delta as a function of the temperature for EBA copolymer, EVA27 copolymer and EBA+EVA27 blends.

The addition of the polyterpene resin and the mixture of microcrystalline and Fischer-Tropsch waxes changes the compatibility of the EBA+EVA blends. According to Figures 8a and 8b, the addition of the tackifier and the wax mixture shifts both the α and β structural relaxations to higher temperature in the EBA/EVA18 and EBA/EVA27 hot-melts, with respect to EBA, EVA18 and EVA27 HMAs. This trend can be attributed to lower compatibility of the copolymers with the microcrystalline and Fischer-Tropsch waxes, in agreement with previous study [7]. The higher compatibility corresponds to the HMAs made with one copolymer only, as the temperature interval between the α and β structural relaxations increases more than 10ºC in the EBA/EVA hot-melts with respect to EBA or EVA HMAs. The lower compatibility corresponds to EBA/EVA18-50/50 and EBA/EVA27 containing 50 wt% or more EVA27. On the other hand, in general, the maxima of tan delta are higher in the EBA/EVA hot-melts than in the EBA or EVA HMAs indicating lower crystallinity.

Figure 8a. Variation of tan delta as a function of the temperature for EBA, EVA18 and EBA/EVA18 hot-melts.

Figure 8b. Variation of tan delta as a function of the temperature for EBA, EVA27 and EBA/EVA27 hot-melts.

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3.3. Adhesion properties of the HMAs

The differences in the compatibility and the viscoelastic properties of the EBA/EVA HMAs have strong influence on their tack. The tack of the HMAs is mainly imparted by the tackifier and depends strongly on the miscibility with the other components in the formulation, specially, the components that contribute to the amorphous phase in the blend [3], i.e. the co-monomers (vinyl acetate, n-butyl acrylate). According to Figures 9a and 9b, the tack of the HMAs increases by increasing the temperature up to 54-79ºC and decreases by increasing more the temperature. The maximum tack values of the EBA/EVA27 hot-melts are always higher than the one of EVA27 HMA and decrease by increasing their EVA27 content (Table 4); furthermore, the increase of the content of EVA27 displaced the maximum tack of the EBA/EVA27 hot-melts to higher temperature and the range of temperature with tack becomes narrower (Table 4, Figure 9b). On the other hand, the maximum tack values of the EBA/EVA18 hot-melts are lower than the ones of the EBA and EVA18 HMAs (particularly in EBA/EVA18-50/50) and the range of temperature with tack becomes narrower; furthermore, the temperature at which the maximum tack is obtained is somewhat similar in all EBA/EVA18 HMAs (Table 4, Figure 9a). The trends in the maximum tack values of the HMAs can be related to the trends in the compatibility and the lower tack values correspond to the EBA/EVA18 hot-melts.

Figure 9a. Variation of the tack as a function of the temperature for EBA, EVA18 and EBA/EVA18 hot-melts.

Figure 9b. Variation of the tack as a function of the temperature for EBA, EVA27 and EBA/EVA27 hot-melts.

Table 4. Values of the maximum tack and the temperature of maximum tack for EBA/EVA hot-melts.

The adhesion properties of the EBA/EVA hot-melts were assessed by T-peel tests of joints made with non-polar (PP film) and polar (aluminum foil) substrates. In general, the T-peel strength of PP film-EBA/EVA HMA-PP film joints decreases by increasing their EVA content, but unexpected higher T-peel strength values are found in the joints made with EBA/EVA18-25/75, EBA/EVA27-25/75 and EBA/EVA27-50/50 HMAs (Figure 10a). On the other hand, the T-peel strength value of the joint made with EBA HMA is higher than the ones of the joints made with EVA18 and EVA27 HMAs. Whereas an adhesion failure is obtained in all joints with low T-peel strength value, the loci of failure in the joints made with EBA/EVA18-25/75, EBA/EVA27-25/75 and EBA/EVA27-50/50 HMAs is stick-slip (SS). The stick-slip failure occurs when the peel

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force alternates between an initiation (peak) and an arrest value, the failure is produced at the interface between the adhesive and the substrate. This kind of locus of failure has been attributed to alternating rubbery and glassy response of the adhesive during adhesion test [23]. Therefore, at the onset of the stick rheological behavior, the crack growths slowly and the force increases rapidly, the elastic energy is stored. Peeling remains stable if the stored elastic energy does not exceed a critical value but one is exceeded, rapid peeling ensues and continues until the excess energy is released, the force falls below a critical value, and the energy is insufficient to sustain such a high peeling rate so the crack reverts to the original slow rate completing a cycle of stick-slip oscillation [23].

Figure 10a. Variation of the T-peel strength of PP film-EBA/EVA18 hot melt-PP film joints as a function of their EVA18 content. Locus of failure : A : Adhesion failure; SS : Stick-slip.

Figure 10b. Variation of the T-peel strength of PP film-EBA/EVA27 hot melt-PP film joints as a function of their EVA27 content. Locus of failure : A : Adhesion failure; SS : Stick-slip.

According to Figures 11a and 11b, similarly to the PP film-EBA/EVA HMA-PP film joints, the T-peel strength of the Al foil-EBA/EVA HMA-Al foil joint made with EBA HMA is higher than for the joints made with EVA18 or EVA27 HMAs. Whereas the T-peel strength values of Al foil-EBA/EVA HMA-Al foil joints made with the EBA/EVA18 HMAs are low and they decrease by increasing their EBA content, the ones made with the EBA/EVA27 HMAs are high, even greater than the one made with EVA27 HMA. Although some joints show mixed failure, the most ones show an adhesion failure. The highest T-peel strength values correspond to the joints made with EBA/EVA27-25/75 and EBA/EVA27-50/50 HMAs, these HMAs also show higher T-peel strength values in the PP film-EBA/EVA HMA-PP film joints.

The variations in the T-peel strength values of the joints made with EBA/EVA hot-melts can be related to their structure. Polyethylene (PE) domains in the copolymers contribute to their crystalline fraction while the n-butyl acrylate or vinyl acetate domains form the amorphous fraction. A higher decrease of the PE content in the blend by adding EVA27 copolymer, together with the higher compatibility of these blends, promotes better adhesion to both polar and non-polar substrates, since the peel adhesion can be mainly ascribed to the amorphous fractions of the copolymer.

Figure 11a. Variation of the T-peel strength of Al foil-EBA/EVA18 hot melt-Al foil joints as a function of their EVA18 content. Locus of failure : A : Adhesion failure; AC : Mixed (adhesion+cohesive failure of the adhesive).

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Figure 11b. Variation of the T-peel strength of Al foil- EBA/EVA27 hot melt-Al foil joints as a function of their EVA27 content. Locus of failure : A : Adhesion failure; AC : Mixed (adhesion+cohesive failure of the adhesive).

4. CONCLUSIONS

The use of EBA/EVA blends produced balanced properties in HMAs. EBA/EVA HMAs showed lower viscosity and shear thinning than EBA or EVA HMAs due to the differences in their compatibility. The set and open times of the EBA/EVA HMAs were not affected by their EVA content or by their vinyl acetate content as they depended on the wax nature and amount mainly. However, the increase of the vinyl acetate content in the EVA copolymer decreased the crystallinity of the EBA/EVA blend resulting in lower storage modulus for EBA/EVA27 blends. Even the EBA copolymer is more compatible with EVA27 than with EVA 18 (the temperatures of the α and β structural relations were closer) and the compatibility did not vary with the EBA content, the addition of the polyterpene resin and the mixture of waxes reduced the compatibility of the blends of EBA and EVA copolymers. The tack of the EBA/EVA HMAs depended on the vinyl acetate content, the EBA/EVA27 HMAs showed high tack in broader temperature interval while the EBA/EVA18 HMAs showed lower tack than EBA HMA, the temperature interval with tack was shortened and shifted to lower temperature. On the other hand, the adhesion of the EBA/EVA HMAs to polypropylene film substrate was improved in the joints made with EBA/EVA18-75/25, EBA/EVA27-75/25 and EBA/EVA27-50/50 HMAs which showed stick-slip failure. Finally, the adhesion of the EBA/EVA HMAs to aluminum substrate was improved only in the joints made with EBA/EVA27-75/25 and EBA/EVA27-50/50 HMAs due to the higher proportion of amorphous fraction and higher compatibility of the polymer-resin-wax blends.

Acknowledgments. Financial support by Technology and New Ventures Department of Repsol S.A. (Madrid, Spain) (grant no. REPSOL5-12I) is acknowledged.

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TABLES

Table 1. Some properties of the ethylene copolymers. Values taken from their technical data sheets.

Property	**EBA**	**EVA18**	**EVA27**
Melt flow index (190ºC, 2.16 kg) (g/10 min)	150	150	150
Co-monomer content (wt%)	27	18	27
Co-monomer content (mol%)	7.5	7.5	10.7
Density (23ºC) (kg/m^3)	925	937	950
Melting point (ºC)	76	81	67
T_g (DSC) (ºC)	-50	-30	-30
Softening point (Ring & ball) (ºC)	100	100	89
Tensile strength (MPa)	3	8	5
Elongation-at-break (%)	550	648	700
Shore A hardness	76	83	74

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Table 2. Softening points of the EBA/EVA hot-melts.

Hot-melt	Softening point (ºC)
EBA	104
EVA18	104
EVA27	107
EBA/EVA18-75/25	104
EBA/EVA18-50/50	106
EBA/EVA18-25/75	103
EBA/EVA27-75/25	105
EBA/EVA27-50/50	106
EBA/EVA27-25/75	106

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Table 3. Some results obtained from the plate-plate rheology experiments of the EBA/EVA hot-melts.

Hot-melt	T_s (ºC)	ΔT_c (ºC)	T_c (ºC)	G_c (kPa)
EBA	100	41	82	73
EVA18	98	39	80	26
EVA27	104	41	83	50
EBA/EVA18-75/25	103	44	84	22
EBA/EVA18-50/50	104	42	93	18
EBA/EVA18-25/75	101	41	86	14
EBA/EVA27-75/25	106	41	91	7
EBA/EVA27-50/50	102	41	93	6
EBA/EVA27-25/75	104	44	95	7

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Table 4. Values of the maximum tack and the temperature of maximum tack for EBA/EVA hot-melts.

Hot-melt	Maximum tack (kPa)	Temperature of maximum tack (ºC)
EBA	1234	63
EVA18	1355	69
EVA27	762	66
EBA/EVA18-75/25	1153	67
EBA/EVA18-50/50	548	79
EBA/EVA18-25/75	1067	69
EBA/EVA27-75/25	1279	54
EBA/EVA27-50/50	1105	63
EBA/EVA27-25/75	1036	62

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FIGURES

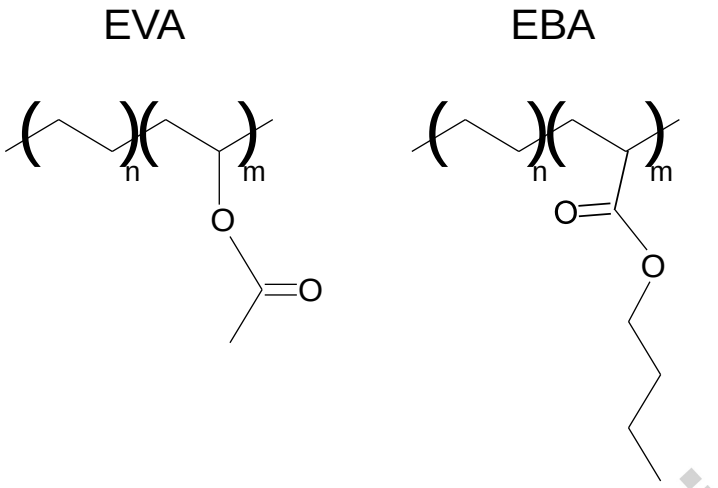

Figure 1. Chemical structure of the EVA and EBA copolymers.

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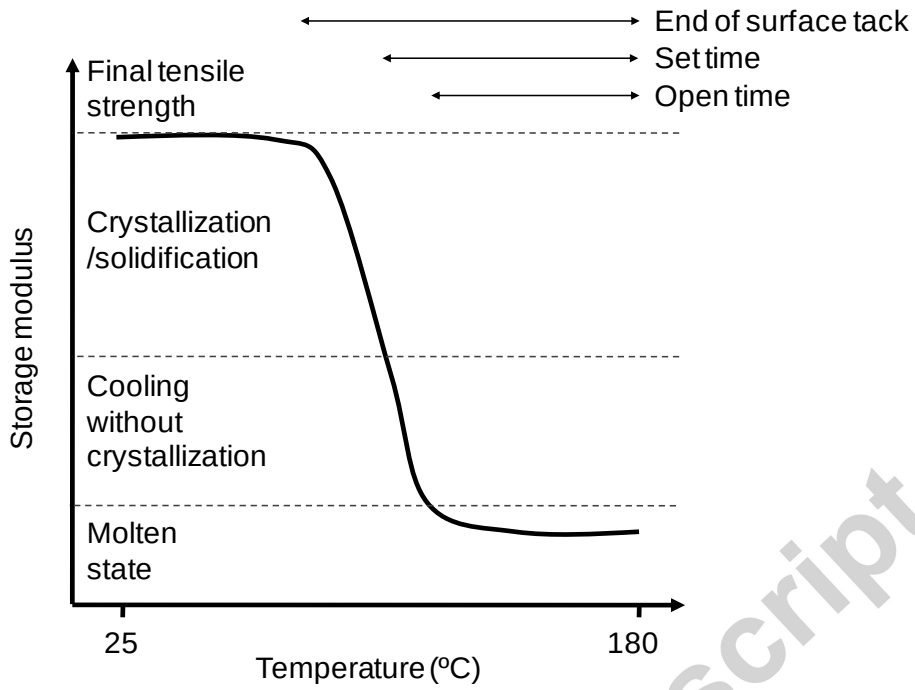

Figure 2. Assignment of the different viscoelastic changes produced during the cooling down of a HMA in the curve of variation of the storage modulus (G´) as a function of the temperature.

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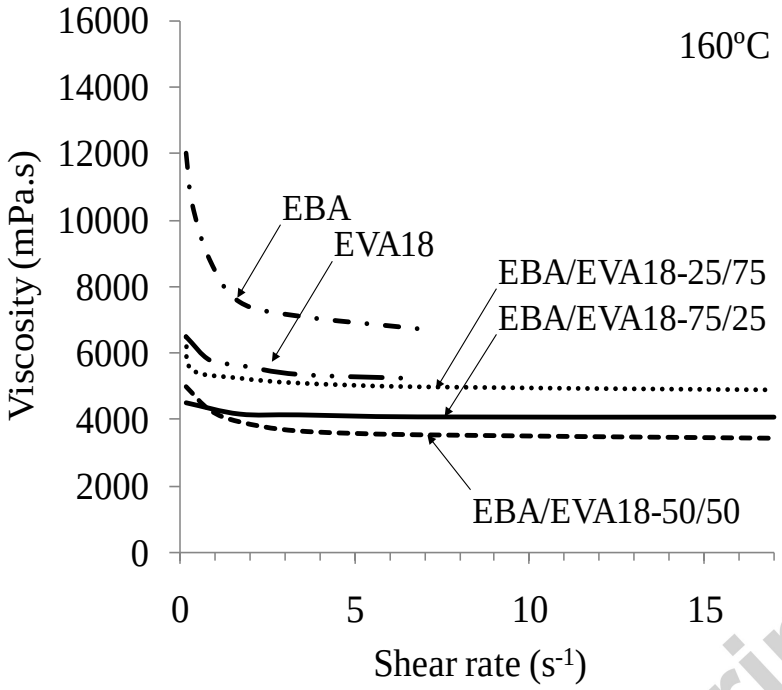

Figure 3a. Variation of the Brookfield viscosity at 160ºC of the EBA, EVA18, and EBA/EVA18 hot-melts as a function of the shear rate.

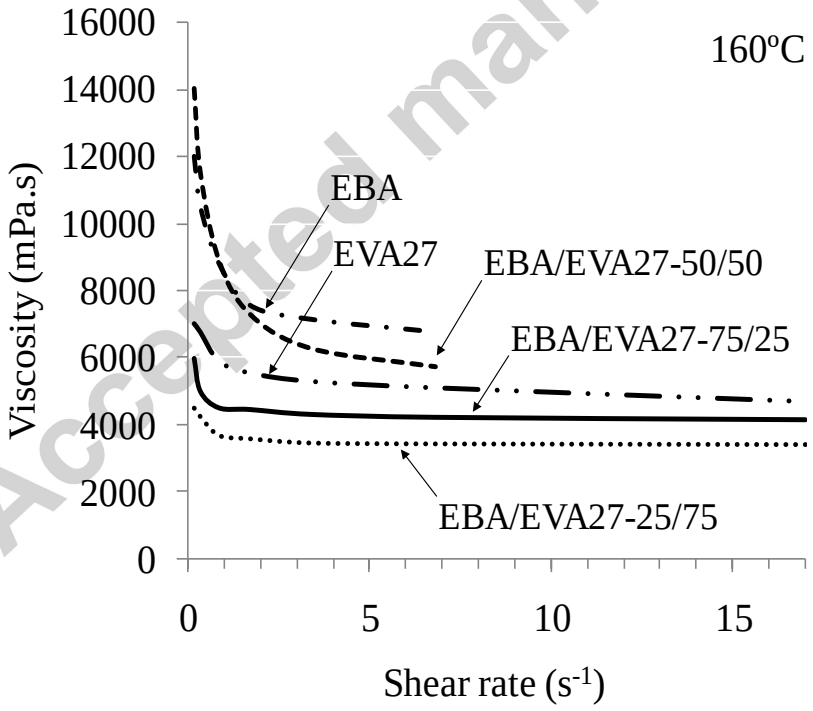

Figure 3b. Variation of the Brookfield viscosity at 160ºC of the EBA, EVA27, and EBA/EVA27 hot-melts as a function of the shear rate.

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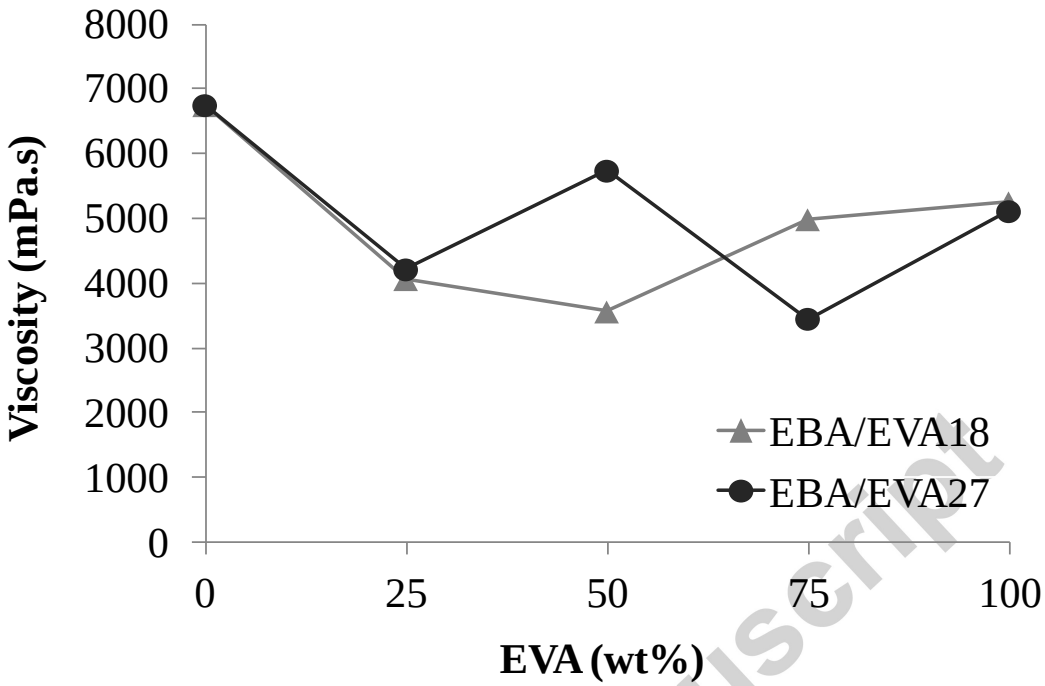

Figure 4. Variation of the Brookfield viscosity at 160ºC of the EBA/EVA hot-melts as a function of their EVA content. Brookfield viscosity was determined at a shear rate of 7 s^{-1}.

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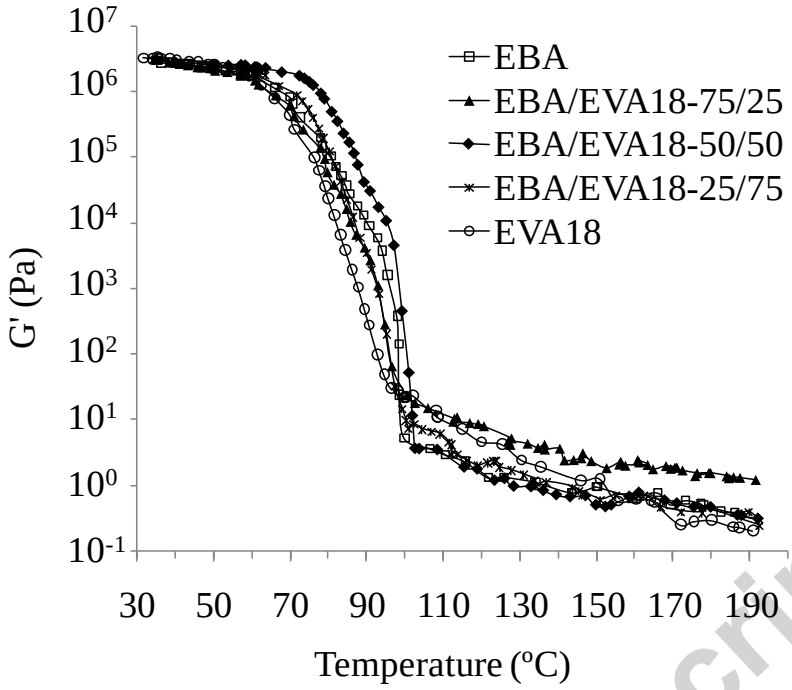

Figure 5a. Variation of the storage (G´) modulus as a function of the temperature for EBA, EVA18 and EBA/EVA18 hot-melts. Plate-plate rheology experiments.

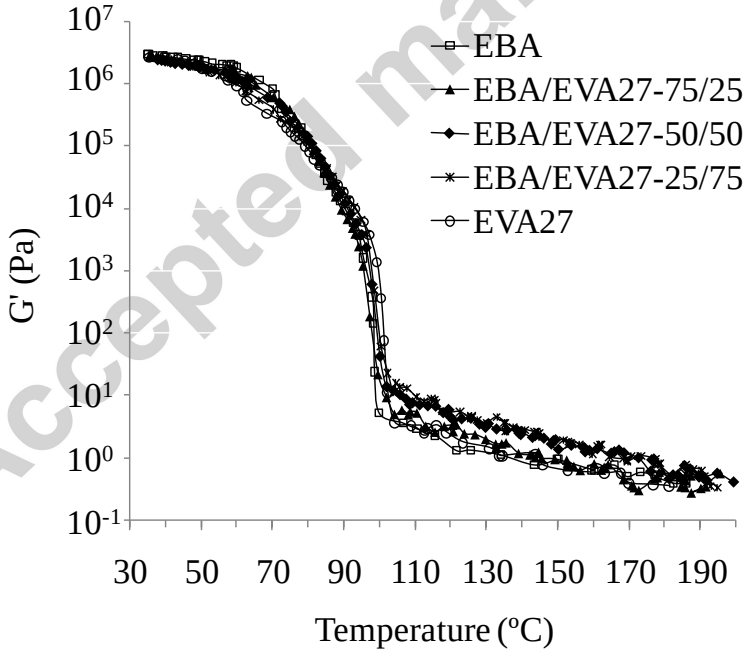

Figure 5b. Variation of the storage (G´) modulus as a function of the temperature for EBA, EVA27 and EBA/EVA27 hot-melts. Plate-plate rheology experiments.

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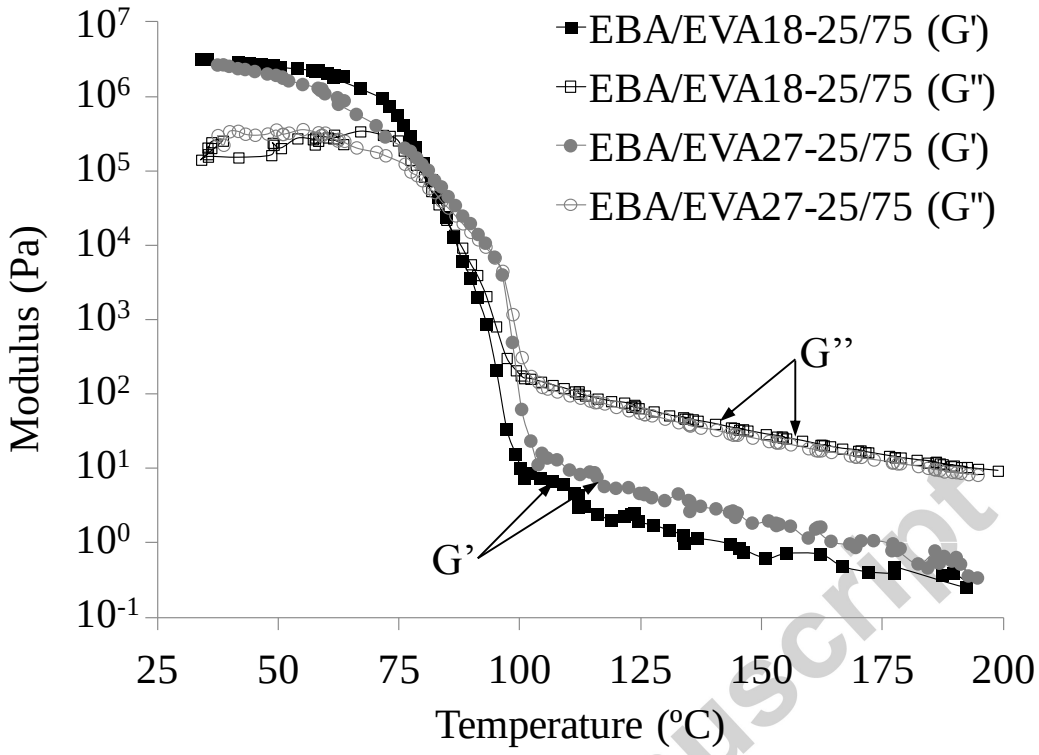

Figure 6. Variation of the storage (G´) and loss (G´´) moduli as a function of the temperature for EBA/EVA18-25/75 and EBA/EVA27-25/75 hot-melts.

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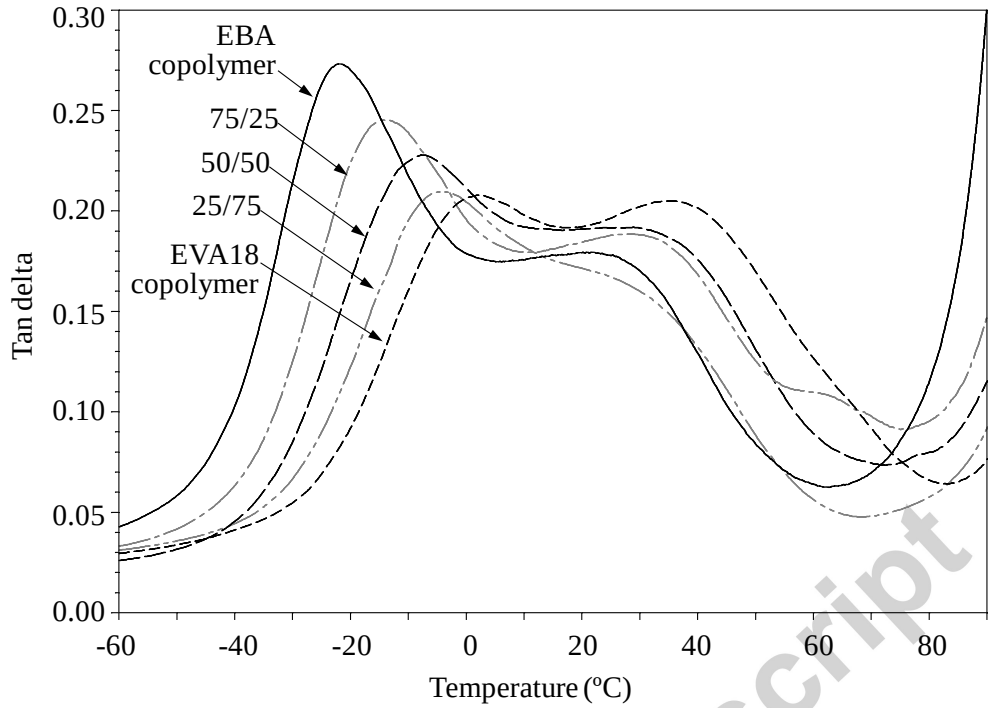

Figure 7a. Variation of tan delta as a function of the temperature for EBA copolymer, EVA18 copolymer and EBA+EVA18 blends.

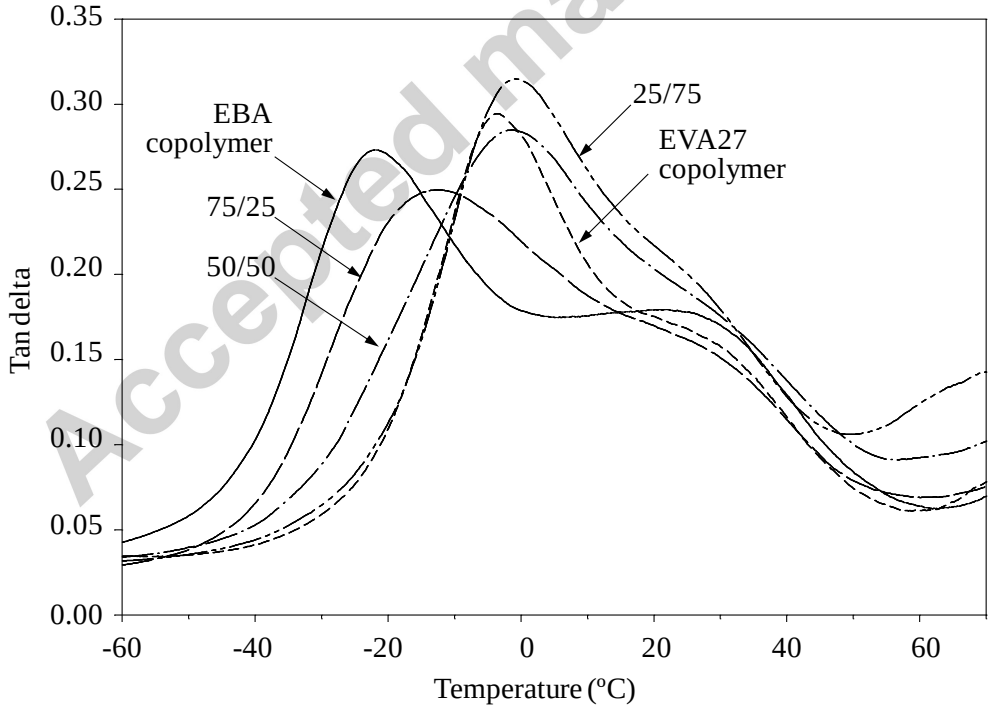

Figure 7b. Variation of tan delta as a function of the temperature for EBA copolymer, EVA27 copolymer and EBA+EVA27 blends.

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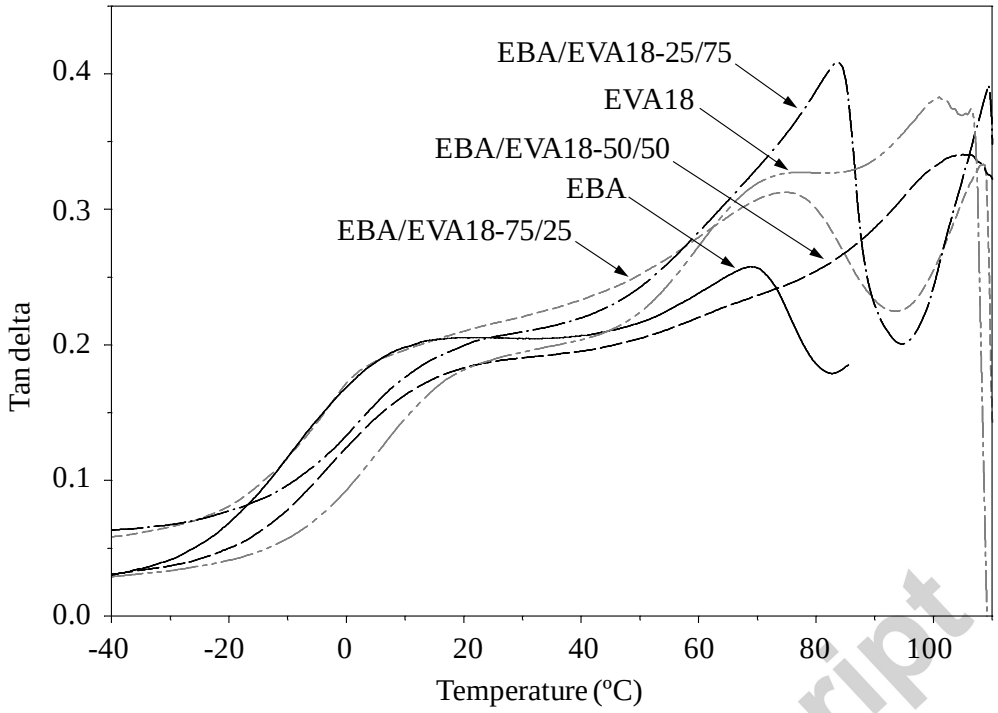

Figure 8a. Variation of tan delta as a function of the temperature for EBA, EVA18 and EBA/EVA18 hot-melts.

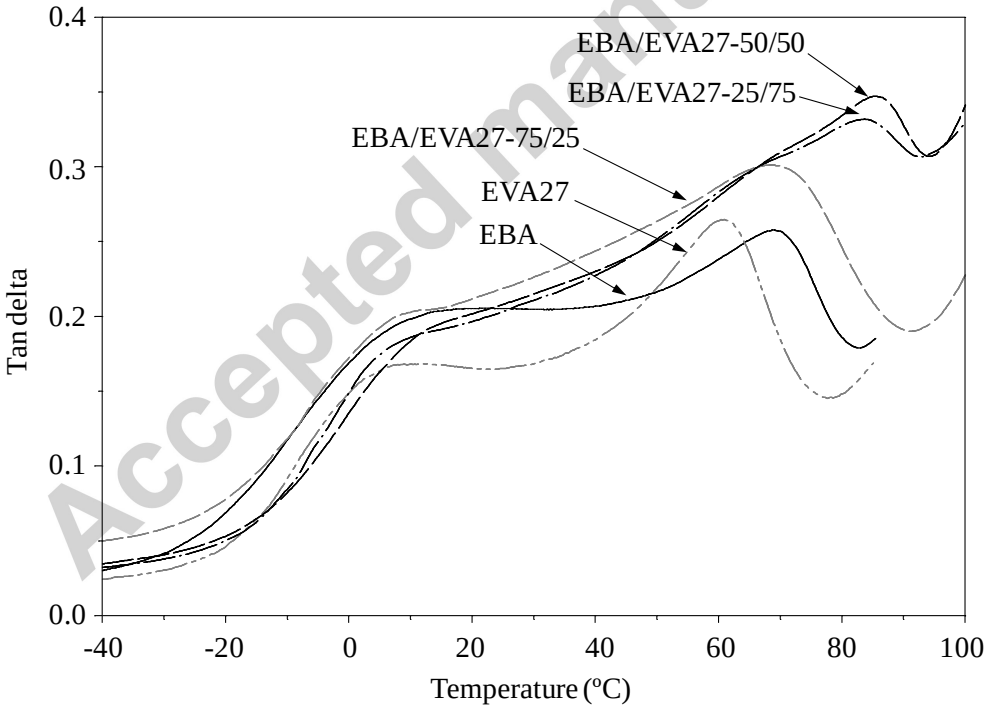

Figure 8b. Variation of tan delta as a function of the temperature for EBA, EVA27 and EBA/EVA27 hot-melts.

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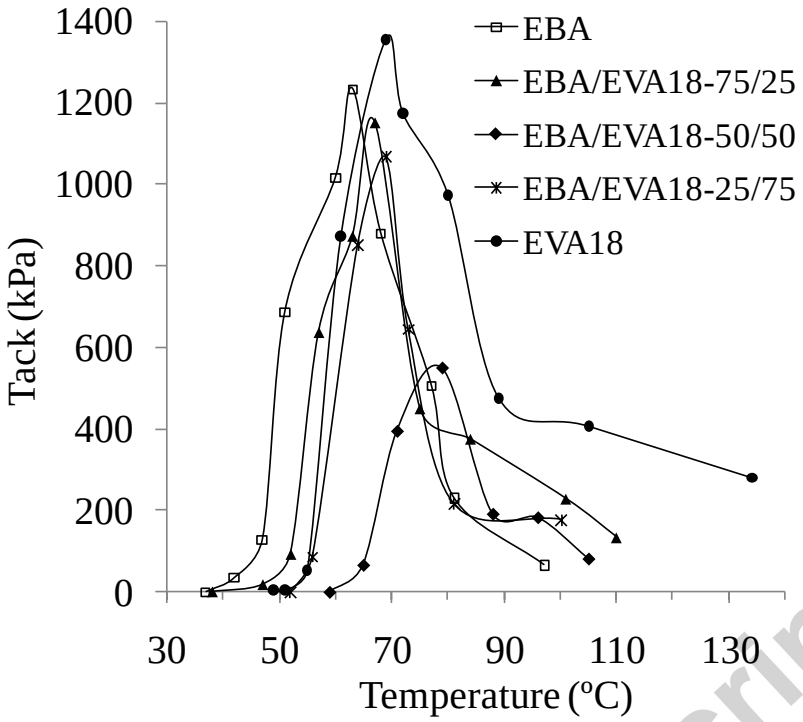

Figure 9a. Variation of the tack as a function of the temperature for EBA, EVA18 and EBA/EVA18 hot-melts.

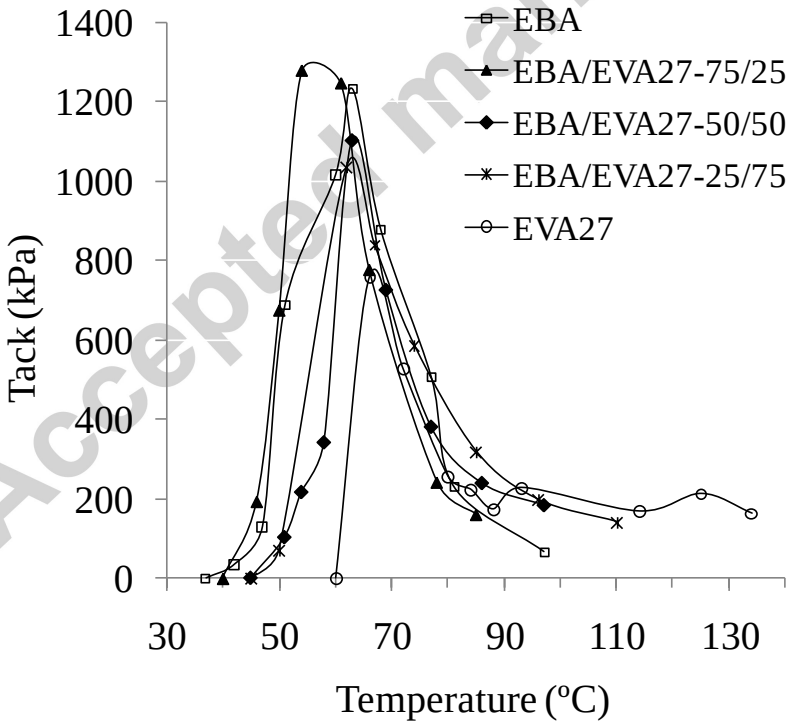

Figure 9b. Variation of the tack as a function of the temperature for EBA, EVA27 and EBA/EVA27 hot-melts.

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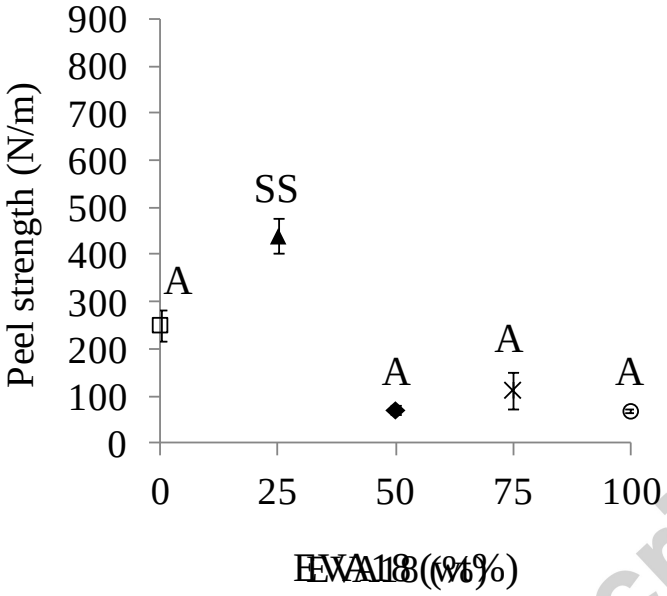

Figure 10a. Variation of the T-peel strength of PP film-EBA/EVA18 hot-melt-PP film joints as a function of their EVA18 content. Locus of failure : A : Adhesion failure; SS : Stick-slip.

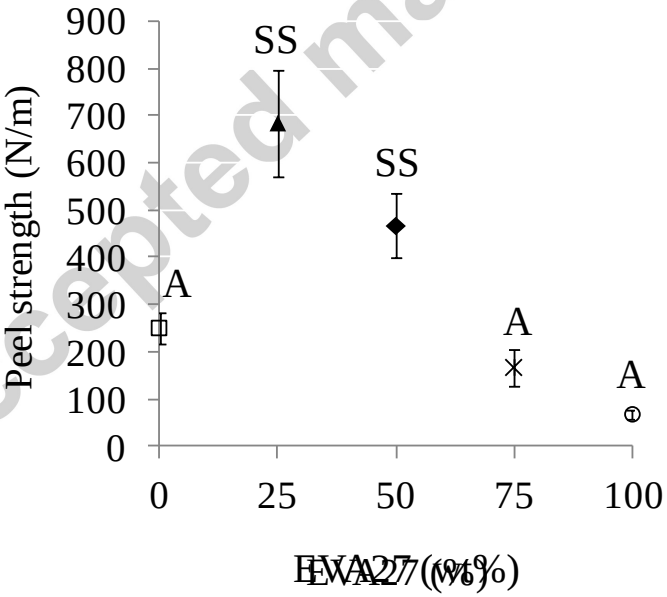

Figure 10b. Variation of the T-peel strength of PP film-EBA/EVA27 hot-melt-PP film joints as a function of their EVA27 content. Locus of failure : A : Adhesion failure; SS : Stick-slip.

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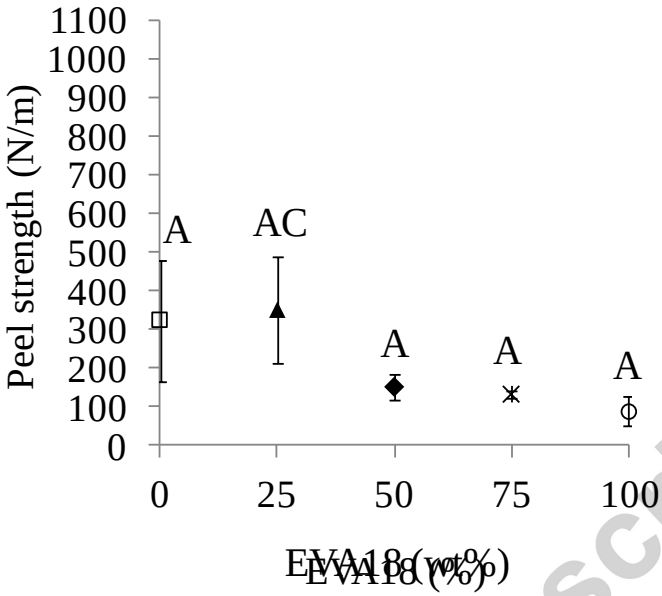

Figure 11a. Variation of the T-peel strength of Al foil-EBA/EVA18 hot-melt-Al foil joints as a function of their EVA18 content. Locus of failure : A : Adhesion failure; AC : Mixed (adhesion+cohesive failure of the adhesive).

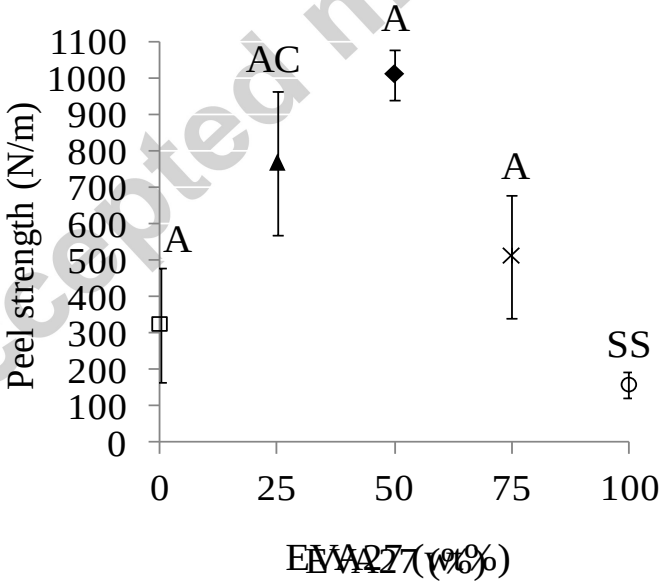

Figure 11b. Variation of the T-peel strength of Al foil- EBA/EVA27 hot-melt-Al foil joints as a function of their EVA27 content. Locus of failure : A : Adhesion failure; AC : Mixed (adhesion+cohesive failure of the adhesive).

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