Interphases in Ethylene–Vinyl Acetate Copolymer/Steel Sandwiches

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ABSTRACT: The properties of a polymer near an interface with a substrate can be different from the bulk properties. To characterize the interphasial zone, the influence of the thickness of a polymer inserted between two steel sheets is carried out. The chosen polymer is a semi-crystalline ethylene–vinyl acetate copolymer with different amounts of vinyl acetate. Dynamic mechanical spectroscopy measurements were performed directly on the assemblies using a three-point flexure test in order to characterize the mobility of the amorphous phase. The crystalline properties were analyzed by differential scanning calorimetry. The mechanical transition temperature, T_{mech}, corresponding to the temperature at which the loss factor goes through a maximum was examined. The results show that at high thicknesses T_{mech} remains constant. However, when the polymer thickness decreases, T_{mech} increases greatly, indicating a decrease of mobility of the chains. This effect is seen whatever the vinyl acetate content. The crystalline properties are also modified with a higher proportion of small crystals for thin layers. For interfacial energy-minimization reasons, the vinyl acetate groups of the copolymer chains are oriented toward the polar steel surface. These orientation phenomena probably induce some reorganization of the phases, leading to more crystals that constitute physical ties, reducing the mobility of the amorphous phase. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 347–353, 1997

INTRODUCTION

The properties of a polymer in contact with a substrate can be different from those of the bulk of the polymer. The region where the properties differ, localized near the interface with the substrate, is called the interphase. Modifications of the properties of the polymer in the vicinity of a substrate have been described several times. Influence on curing has been shown, e.g., for epoxy-based adhesives[1,2] and polyurethane.[3] Transcrystalline effects have been observed for thermoplastics in contact with metals or oxides[4,5] and graphite.[6] Also, simply, adsorption phenomena can produce modifications of the properties over distances greater than 1000 nm as determined by different experimental techniques.[7]

The study of polymer metal laminates used for their damping properties led us to consider the influence of the substrates on the polymer properties in steel/ethylene–vinyl acetate (EVA) copolymer sandwiches. The results obtained suggest the presence of an interphase. However, no direct study is possible due to the small thickness of the transition zones compared to the overall thickness of the polymer layer. Therefore, an indirect way to study the influence of the thickness of the polymer layer on the sandwich properties was considered. Indeed, when the polymer thickness decreases, the relative proportion of the interphasial zone increases and its contribution to the sandwich properties becomes greater. The study that we are presenting here concerns mainly EVA copolymers

which are semicrystalline polymers. We have therefore examined, on the one hand, the crystalline part of the polymer in the sandwich by DSC and, on the other hand, the amorphous phase by dynamic mechanical measurements performed on the steel/polymer/steel assemblies.

EXPERIMENTAL

Steel/polymer/steel sandwiches are studied as a function of the composition of the copolymer inserted. The substrate provided by SOLLAC (USINOR-SACILOR France) is a mild steel with a thickness equal to 0.35 mm. The surface is degreased in an ultrasonic bath containing trichloroethane. The material is then dried for 30 min at 120°C. Three copolymers of ethylene–vinyl acetate (EVA) with different amounts of vinyl acetate (VA)—14, 28, and 40 wt %—are considered. Adhesion of these EVA copolymers to metal is not very high as shown by spontaneous delamination in the cleavage test but the functionalization of the polymer with molecules such as maleic anhydride improves this behavior significantly.[8–11] Therefore, a fourth sample containing 28 wt % VA is studied for which about 1% maleic anhydride is grafted to the polymer chains (this polymer will be called grafted EVA). The sandwiches are obtained under press at 160°C for the nongrafted polymers and 180°C for the grafted one. The pressure of 1.5 MPa is applied during 5 min. Circulating water in the press platens ensures the cooling of the assemblies to room temperature in 6 min. Different polymer thicknesses ranging from 20 to 400 μm are obtained by inserting spacers between the two steel sheets.

Since the studied polymers are semicrystalline, we studied both the amorphous and crystalline phases using two different techniques. The amorphous phase can be analyzed by dynamic mechanical measurements performed on steel/polymer/steel sandwiches using a DMTA instrument from Polymer Laboratories. The global response of the sandwich submitted to a three-point flexure test is recorded. A sample 10 mm wide and 45 mm long is clamped in its extremities and submitted in the middle to sinusoidal vibrations. The apparatus measures the force to be applied to keep a constant deformation in flexion of 45 μm. Measurements are made at 1 Hz from -80 to $+80$°C with a scanning temperature of 2°C/min. The variation of the loss factor tan δ is studied as a function of temperature and is related to the
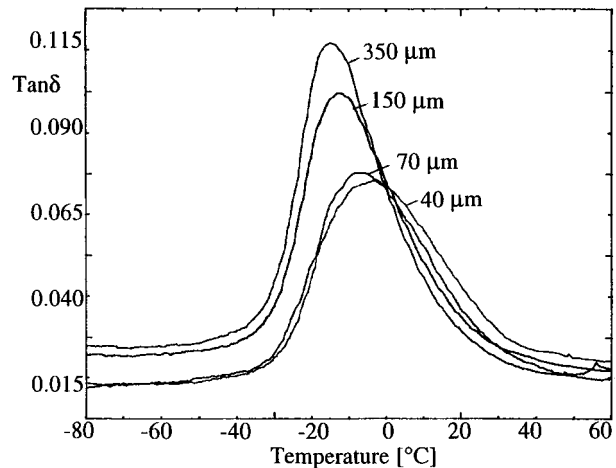

Figure 1 Loss factor tan δ peak as a function of temperature for different thicknesses of grafted EVA (28% wt).

damping properties of the assembly. The temperature corresponding to the maximum value of tan δ is called T_{mech}; it is related to the glass transition temperature of the polymer.

The crystalline properties of the polymer were studied by analyzing the melting endotherm obtained by differential scanning calorimetry (DSC from Mettler) between -80 and $+160$°C at a scanning rate equal to 10°C/min. As mentioned previously, the nongrafted EVAs only weakly adhere to the steel substrate. They are therefore removed from the assemblies by simple peeling. However, the grafted copolymer (28 wt % VA) bonds very firmly to the metal. Therefore, the crystalline polymer properties have to be studied directly inside the sandwich by using steel foils of 10 μm thickness. These sandwiches can then easily be cut and put directly into the DSC cell.

RESULTS

In Figure 1 is given the variation of tan δ as a function of the temperature for grafted EVA/steel sandwiches and polymer layers of thicknesses ranging between 40 and 350 μm. The amplitude of the damping peak in dynamic mechanical analysis decreases as expected due to the fact that the relative amount of viscoelastic material is smaller when the polymer thickness decreases. But, more interesting, the mechanical transition temperature, T_{mech}, is shifted toward lower temperatures when the thickness of the polymer layer increases. This is a general observation whatever
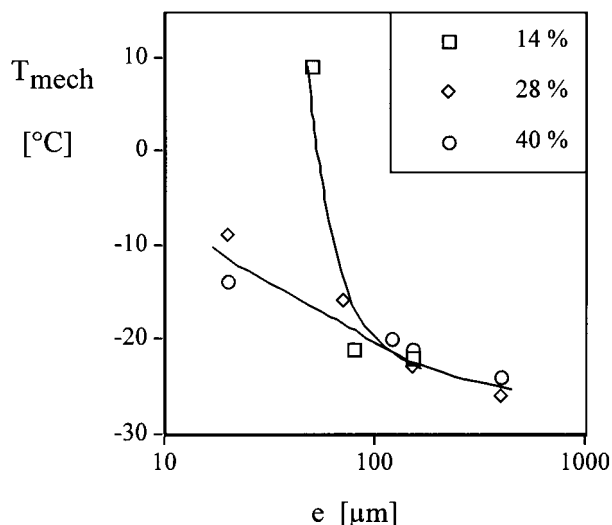
Figure 2 Influence of the polymer thickness on the mechanical transition temperature for EVAs containing 14, 28, and 40% wt of VA.

the VA content of the polymer as seen in Figures 2 and 3, where T_{mech} is plotted as a function of the EVA thickness for nongrafted EVAs (Fig. 2) and 28 wt % VA grafted and nongrafted EVA (Fig. 3). For nongrafted EVA, T_{mech} reaches a constant temperature, $-25°C$, for a thickness greater than $150-200$ μm. This value is independent of the amount of vinyl acetate in the copolymer. However, the value reached by the grafted EVA is significantly higher, $-15°C$.

To be sure that the observed variation cannot
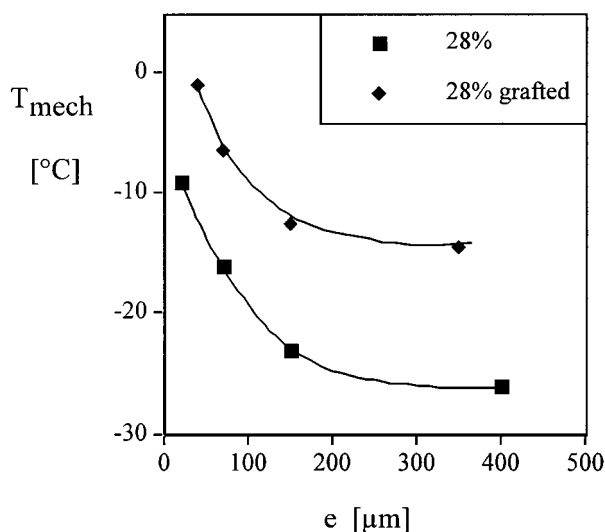
Figure 3 Comparison of the variation with the polymer thickness of the mechanical transition temperature for 28 wt % of grafted and nongrafted EVA.
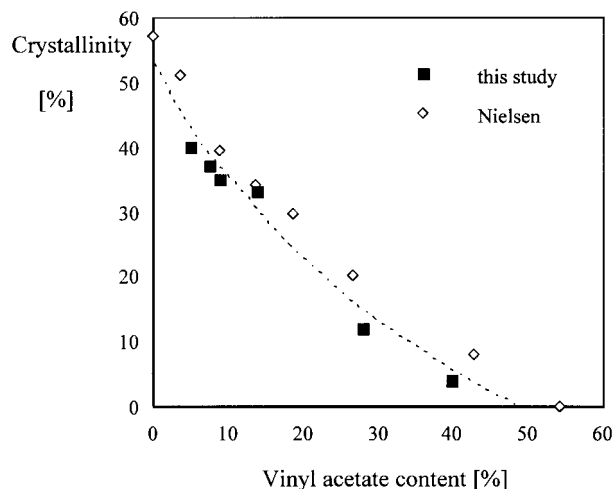

Figure 4 Variation of the degree of crystallinity as a function of VA content in EVA. Comparison with Nielsen's results.[13]

be attributed to mechanical coupling, other experimental work has been performed either when using weakly adhering polymers such as styrene–butadiene rubber or poly(vinyl acetate) or when using a strongly adhering polymer such as polyamide 11. Although this last polymer is semicrystalline, it differs from EVA by the fact that it is an homopolymer and not a copolymer. It has been shown that no evolution of T_{mech} occurs as a function of polymer thickness for these other studied systems at least in the range of thicknesses studied. Therefore, we are quite confident that the observed variations are a consequence of modifications in the polymer organization in a region close to the interface.

The degree of crystallinity of the copolymers has been calculated from DSC measurements using the melting enthalpy of polyethylene ($\Delta H_f = 280$ J/g),[12] the crystallizing comonomer. In Figure 4 is given the variation of the degree of crystallinity as a function of the concentration of VA groups in the copolymer. On the same plot are reported the results published by Nielsen.[13] As expected, the degree of crystallinity decreases when the amount of vinyl acetate increases, due to the presence of molecular side chains and to the lower degree of ordering of the polyethylene chains.[7] The sample containing 40% VA shows a very low degree of crystallinity of the order of 4%.
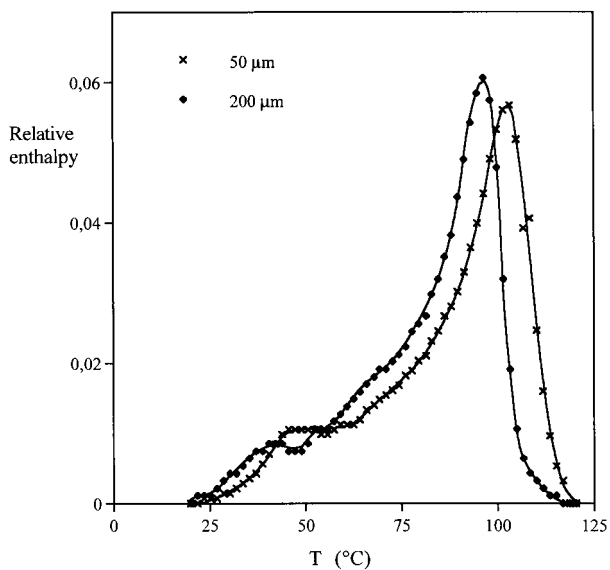
The melting peaks are rather complex and widespread, starting around room temperature (or slightly above) up to about 120°C. Two major components can be distinguished: one at low temperature around 45–50°C and a second one at
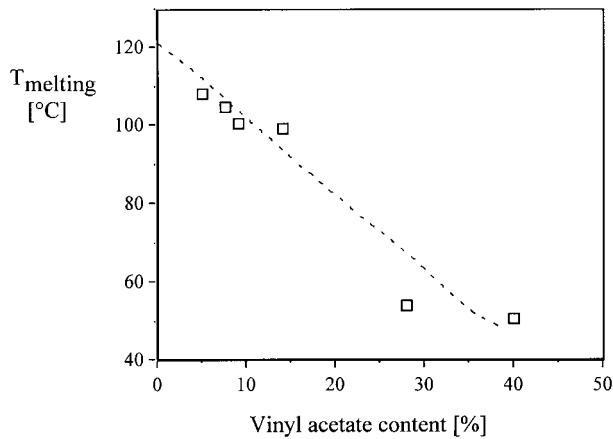
Figure 5 Melting temperature as a function of VA content in the copolymer.

Figure 7 DSC analysis of EVA (28% VA) for two polymer thicknesses (20 and 50 μm) in the sandwich.

higher temperature. The temperature corresponding to the maximum melting peak is plotted as a function of VA content in Figure 5. The extrapolated value for the melting temperature of pure PE is equal to 120°C.

Let us now consider the effect of the polymer thickness. For all the EVA studied, the degree of crystallinity remains constant when the thickness of the polymer in the sandwiches is changed. The results of the DSC analysis for EVA (14% VA) and polymer thickness of 50 and 200 μm are given in Figure 6, whereas the results for EVA (28% VA) and polymer thickness of 20 and 50 μm are

given in Figure 7. Position and shape of the melting peak are affected by the polymer thickness, which indicates that the perfection and the distribution of the crystals is altered. The contribution of the low-temperature peak is much more pronounced. For EVA containing 40% wt of VA which has very low crystallinity, the melting endotherm is located around 45–50°C and no high-temperature peak is present. These results show that the relative amplitude of the two peaks is influenced by the polymer thickness.

In Figure 8 are given the DSC results for the grafted sample (28% wt VA) analyzed in the sandwich with 10 μm-thick steel sheets. The contribution of the high-temperature peak is the most

Figure 6 DSC analysis of EVA (14% VA) for two polymer thicknesses (50 and 200 μm) in the sandwich.
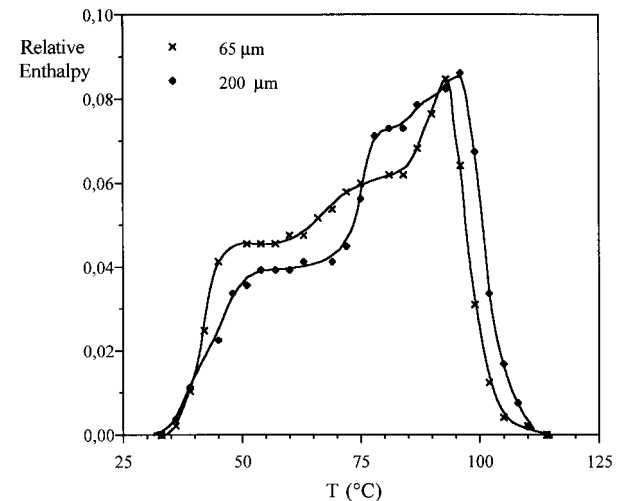
Figure 8 DSC analysis of grafted EVA (28% VA) for two polymer thicknesses (65 and 200 μm) in the sandwich.

important. As for the nongrafted samples, the proportion of crystals melting at the lowest temperature is slightly higher for the thinner film compared to thicker films, whereas the width of the peak at high temperature is smaller.

The influence of the substrate into contact with the polymer during the molding step is very important as shown by the behavior of EVA molded in contact with a low surface energy polymer such as polytetrafluoroethylene. It is observed that no significant variation in distribution of the different crystals with thickness contrary to what is observed with the steel substrate.

DISCUSSION

Considering first the results obtained by dynamic mechanical measurements, different conclusions can be reached for the mobility of the amorphous phase of the studied EVA copolymers. For polymer thicknesses above 150–200 μm, a constant value of T_{mech} ($-25°C$) is measured whatever the VA content. An identical value was given by Nielsen[13] and Reding et al.[14] This value is independent of the amount of VA in the copolymer. However, Nielsen's explanation is based upon the composition of the amorphous phase which remains constant as long as the amount of the comonomer (here VA) stays low enough so that the copolymer remains semicrystalline. According to Nielsen, this amount should be below 50–55% VA. Nevertheless, because the transition temperature is invariant even when 45–65% of VA is present in the copolymer and the material is essentially amorphous, Reding et al.[14] suggested that the observed transition is related to the motion of isolated $-CH_2-CHR-CH_2-$ groups, where R represents the acetate group. When the comonomer content increases, then the transition rises due to restriction in motion of the carbon atoms because of the interactions between the adjacent side groups. Finally, the value is in good agreement with the glass transition temperature obtained by DSC measurements. Now if we consider the grafted sample, the same trend is observed. However, a slightly higher T_{mech} value ($-16°C$) is found in agreement with a higher glass transition temperature as measured by DSC ($-19°C$).

The increase of the temperature of the dynamic mechanical transition T_{mech} with decreasing polymer thickness in the sandwich can be explained by the reduced mobility of the polymer chains in the vicinity of the interface with the steel surface.
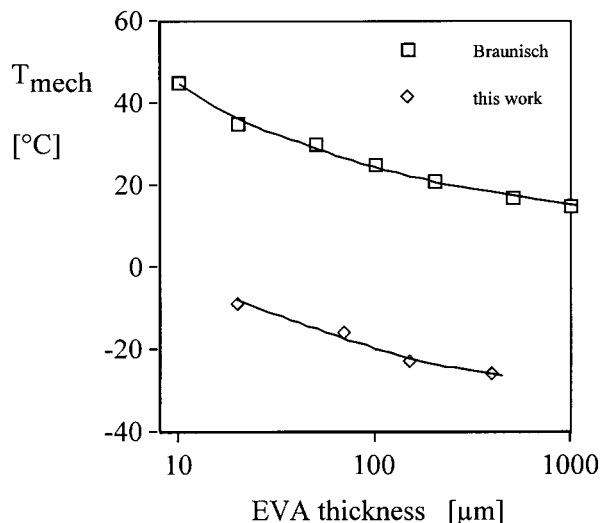
Figure 9 Comparison of the variation of T_{mech} published by Braunisch[15] and this work (28 wt % VA).

The increase of T_{mech} has already been reported in the literature for similar assemblies. The evolution of T_{mech} as a function of the thickness is very similar to that reported by Braunisch[15] for a VA copolymer introduced in a steel/polymer/steel sandwich as shown in Figure 9. Other studies of joints with epoxy resins have also shown a decrease of T_{mech} when the polymer thickness increases,[16] which has been attributed to the presence of an interphase of overcrosslinked polymer in contact with the substrate. Also, interfacial layers with specific structure and properties have been evidenced for poly(methyl methacrylate) films of different thicknesses.[17]

The study of the crystalline phase by DSC is complementary. Indeed, polyethylene (PE) is the only crystallizable comonomer in EVA copolymers. Melting of PE occurs at temperatures ranging from -10 to $120°C$ when the number of carbon atoms in the backbone chain ranges from 15 to 10^6. The stability of the crystals obtained with longer sequences of monomer units is higher than that constituted by shorter sequences and the melting is observed at higher temperatures. The value extrapolated in Figure 5 for the melting temperature of pure PE ($120°C$) is in good agreement with values reported in the literature.[18] It corresponds therefore to the PE chains, the best organized in the copolymers.

However, the DSC curves for EVA are more complex with a wide endotherm spread over several 10s of degrees. Multiple endotherms have been reported by different authors and several

explanations have been proposed. Bell and Dumbleton[19] attributed the double melting peak in nylon 66 and polystyrene to folded-chain crystals, on the one hand, and to less perfect bundle crystals, on the other hand. A crystal perfection difference has also been proposed by Mandelkern et al.[20] The PE sequences are quite strongly hindered in their crystallization by the VA groups either by their effect on the length of the PE sequences or by their association due to their polarity when present as pendant chains. By ^{13}C-NMR analysis, Bugada and Rudin[18] treated the VA units essentially as isolated, single units. However, Raffield[21] considered that there is an increased tendency for sequences of VA to be present in the crystalline phase when the concentration of the comonomer increases.

The observed phenomena for EVA copolymers may be attributed to the formation of an interphasial layer in which the amorphous chains are constrained differently than in the bulk. For interfacial energy-minimization reasons, the VA groups of the copolymer chains are oriented toward the steel substrate. These migration and orientation phenomena can be evidenced by contact angle measurements. An increase of the polar component of the surface energy when EVA copolymers are molded against a polar substrate was observed. Restructuration of the polar groups, dependent on the VA content and the mold surface, was also reported by Chihani et al.[22] A higher surface polarity is obtained for EVA molded against poly(ethylene terephthalate) compared to the perfluorinated ethylene–propylene copolymer. Physical interactions are sufficient for these orientation effects, as shown when comparing our results obtained for the nongrafted EVAs with those obtained for the grafted sample. Strong interfacial bonds such as chemical bonds present at the grafted EVA/steel interface are not needed to induce a reduction of the mobility of the polymer chains near the interface with the steel surface. The orientation phenomena of the acetate groups induce crystalline modifications which perturb the mobility of the amorphous phase. The melting endotherms given by DSC analysis show that more perturbed crystals of PE melting at low temperature are present for thinner polymer layers. These crystals constitute physical ties, reducing the mobility of the amorphous chains which link them and could explain the increase of T_{mech} with the polymer thickness.

The important increase of T_{mech} for EVA 14% VA compared to EVA 28% VA and EVA 40% VA could be explained by the fact that EVA 14% VA is the most crystalline copolymer (about 34% of crystallinity) and, consequently, the less amorphous. For this EVA, a small change in the crystalline organization will induce more restriction of the mobility of the amorphous chains. Indeed, because of the higher degree of crystallinity, the amorphous phase is linked to more numerous crystals compared to EVA 28% VA (13% of crystallinity) and EVA 40% VA (4% of crystallinity).

The decrease of the chains mobility in the interphasial zone is not the consequence of a direct effect of the presence of interfacial bonds between EVA and steel, but it is probably the consequence of a gradual change of the polymer properties near the interface, induced by a migration and an orientation of the polar acetate groups toward the steel surface. These phenomena induce modifications of the crystalline structure of EVA in the vicinity of the interface, which has a direct consequence on the polymer chains mobility.

However, the effect due to the confinement of the polymer should not be neglected in the possible orientation as shown by Schultz[23] for polypropylene and poly(ethylene oxide) for which the mobility of the amorphous phase is dependent on the crystalline phase. For partially crystalline PE, a simple two-phase model is inadequate to explain the structure obtained in a Raman spectroscopy study done by Mutter et al.[24] Two intermediate zones, one amorphous and the other one crystalline, between the crystals and the meltlike phase are evidenced; the second transition region contributes to the heat of fusion as measured by DSC.

CONCLUSION

By studying the influence of the thickness in polymer-laminated steel sheet sandwiches, it is clearly seen that the modifications of the polymer properties (of the crystalline as well as the amorphous phase) near the interface with the steel substrate indicate the formation of an interphasial layer of reduced mobility. For polymer layers less than 50–60 μm thick for which the relative proportion of the interphase is greatly increased compared to the bulk, the mobility of the amorphous phase is reduced significantly as shown by the important increase of the mechanical transition temperature, T_{mech}. The adhesion level between steel and EVA appears to have no detectable influence on the restriction of mobility of the chains in the interphasial zone. Changes in the

crystalline organization have been observed when the polymer thickness decreases; more numerous small crystals are present for thin layers of EVA. These crystals act as physical ties reducing mobility of the amorphous chains which link them. A possible explanation is based on the migration and orientation of polar acetate groups toward the steel surface, essentially during the heating step under press. This orientation is able to induce chain organization in the vicinity of the interface which reduces mobility of the amorphous phase, leading to an increase of T_{mech}.

In this study, it appears that a copolymer such as the ethylene–vinyl acetate copolymer shows a very complex structure easily affected by interfacial interactions. This influence is not detected (although it exists) for thick polymer films in the sandwiches for which the mechanical transition temperature is of the same order of magnitude as the glass transition temperature given by DSC measurements.

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