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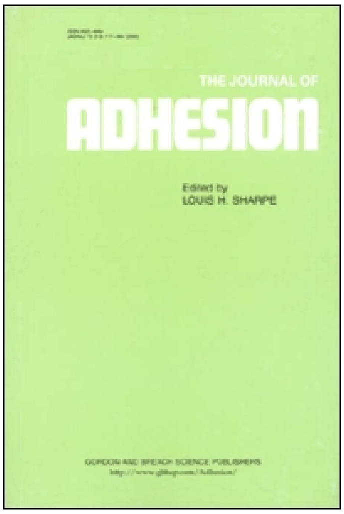

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Poly(Ethylene-co-Vinylacetate) Based Hot Melt Adhesives: I. Relating Adhesive Rheology to Peel Adhesion

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Poly(Ethylene-co-Vinylacetate) Based Hot Melt Adhesives: I. Relating Adhesive Rheology to Peel Adhesion

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The successful selection of bonding conditions for hot melt adhesives depends on melt morphology and rheological properties. Rheological properties were determined for model poly(ethylene-co-vinylacetate) hot melt adhesives. T-Peel fracture energies of joints consisting of two polypropylene films bonded with these adhesives were determined. Rheological data suggest that the EVA and its blends form homogeneous melts. Tackifiers and wax lower melt viscosity and elasticity but increase the activation energy for melt flow. Adhesives with higher melt activation energy, as well as lower elasticity and viscosity, show little dependence of peel strength on bonding temperature and require little time to reach the equilibrium bond strength. The equilibrium T-Peel strengths of adhesives containing wax are almost independent of bonding temperature. This may result from the existence of a weak boundary layer of wax or to their high flowability.

Keywords: Poly(ethylene-co-vinylacetate) (EVA); hot melt adhesives; formulation; T-Peel strength; rheology; weak boundary layer

INTRODUCTION

A typical ethylene vinyl acetate (EVA)-based hot melt adhesive (HMA) is composed of four main components; polymer, tackifier, wax,

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and antioxidant. The polymer contributes strength and toughness, while tackifier enhances wetting and tack. The wax lowers the melt viscosity and reduces cost. The antioxidant reduces thermal degradation during processing. HMAs are widely used in packaging, paper laminating, non-woven textiles, and in book bindings [1].

Holt melt adhesives are spread onto substrates in the melt state followed by solidification upon cooling. Knowledge of the flow behavior of an adhesive melt is essential for coating process design; in addition, the morphology of a molten polymer blend sometimes may be inferred from melt flow behavior [2–5]. When melt viscosities at different temperatures, normalized by the zero shear viscosity, superimpose to form a mastercurve, it has been suggested that the melt forms a compatible blend or that it possesses a temperature-independent morphology. Plots of log G' *vs.* log G'' also have been used to deduce whether blends are heterogeneous or homogeneous [6–10]. Compatible melts have been found to have log G' *vs* log G'' plots which are temperature and composition independent.

The rheology of EVA-based hot melt adhesives containing various contents of a compatible terpene-phenolic tackifier have been studied by Marin and coworker [11]. They proposed a model allowing one to predict the plateau modulus, viscosity, and glass transition temperature.

Polypropylene (PP) and high density polyethylene (HDPE) have been bonded to butyl rubber at different temperatures by Yamakawa [12]. When the bond was formed below the melting point of the thermoplastic, weak bonding, with apparent interfacial failure, was observed. Joint strengths about 2 to 3 times higher and cohesive failure were found when bonds were formed at temperatures higher than the melting point. Formation of diffuse interface between the rubber and polyolefin, confirmed by ATR and interference microscopy, was the proposed reason.

The peel strength of a rubber/gold joint increases with increasing bonding time, then reaches a plateau. The relationship between peel strength and bonding time obeyed first order kinetics [13], and the activation energy for the joint was similar to the activation energy for the viscosity.

At present, little is known concerning the melt behavior and morphology of EVA-based hot melt adhesives. Furthermore, few systematic studies of these adhesives bonded to simple substrates have been published. This situation provided the impetus for the studies carried out in this work.

EXPERIMENTAL

Materials and Speciments Preparation

Two tackifiers were used; one is an aliphatic-aromatic hydrocarbon resin (C5–C9, Escorez 2393, Exxon Company) and the other is a hydrogenated rosin ester (rosin, Foral 105, Hercules Company). Raw materials, including poly(ethylene-co-vinylacetate) (EVA, Escorene 7750, Exxon Company), the two tackifiers, and wax, were combined to give a total batch weight of 45 g. Compositions were melt blended at 120°C for 6 minutes in a Haake mixer. To reduce thermal degradation, 0.25 parts by weight of antioxidant (Irganox 165, Ciba Geigy Company) was added. Mixtures were compression molded at 120°C for 10 minutes under 20 tons (88×10^3 kg) force to form sheets 1.5 mm thick. Four different formulations were prepared (Tab. I).

A Rheometrics Mechanical Spectrometer was used to measure G', G'', η^*, and tan δ at various temperatures and rates. A sample 25 mm in diameter and 1.5 mm thick was placed between two parallel plates and kept at temperature for 5 minutes. G', G'', η^*, and tan δ were measured in nitrogen at 5% strain from 0.1 to 100 rad/sec.

An adhesive layer 0.23 mm thick and a 0.16 mm brass spacer were placed between two sheets of polypropylene (0.13 × 200 × 50 mm).

TABLE I Formulations (parts by weight)

	Components				
Sample	*EVA*	*rosin*	*C5–C9*	*Wax*	*Antioxidant*
EVA	100				
ER	50	50			0.25
ERW	45	45		10	0.25
E5	50		50		0.25
E5W	45		45	10	0.25

The sandwich was placed between two chrome plates, and pressed at temperature and 3400 kg/m^2 load for times from 5 to 400 sec using a hot sealer (Sencorp System Inc.). After bonding, the tapes were cooled in air to room temperature. The total thickness of specimens was 0.42 ± 0.02 mm (with an adhesive thickness of 0.16 ± 0.02 mm). Strips, 25 mm wide and 175 mm long (including 150 mm of bonded PP/HMA/PP and 25 mm of free PP film on one side), were cut for testing. The bond strengths of the laminates were determined at 21° C and 50 mm/min in a T-Peel geometry using an Instron. Peeling energy was determined from the peeling force by the following equation

$$G = 2F/b, \qquad (1)$$

where G = peeling energy (N/m); F = average force required to peel a specimen apart (N); b = width of the test specimen (m).

RESULTS AND DISCUSSION

Melt Rheology

Melt Viscosity Plots of the complex viscosity of formulations EVA, ER, E5, ERW, and ESW (Tab. I) *vs.* frequency at different temperatures are shown in Figure 1. As expected, the complex viscosity decreases as temperature increases. Tackifiers and wax reduce the complex viscosity of EVA. Addition of C5–C9 to the EVA reduces viscosity slightly more than rosin addition. Similarly, ERW has higher viscosity than E5W.

The addition of tackifiers and wax to EVA reduces the entanglement density and, hence, lowers viscosity. Wax addition further reduces viscosity by acting as a lubricant which reduces the internal friction between chains[14].

Rosin is expected to have better compatibility with EVA than does C5–C9 due to polar interactions between the rosin ester groups and the acetate groups of the EVA. The hydrocarbon C5–C9 has no polar functionality. This could account for the rosin-tackified EVA having somewhat higher viscosity than the C5–C9-tackified EVA [15].

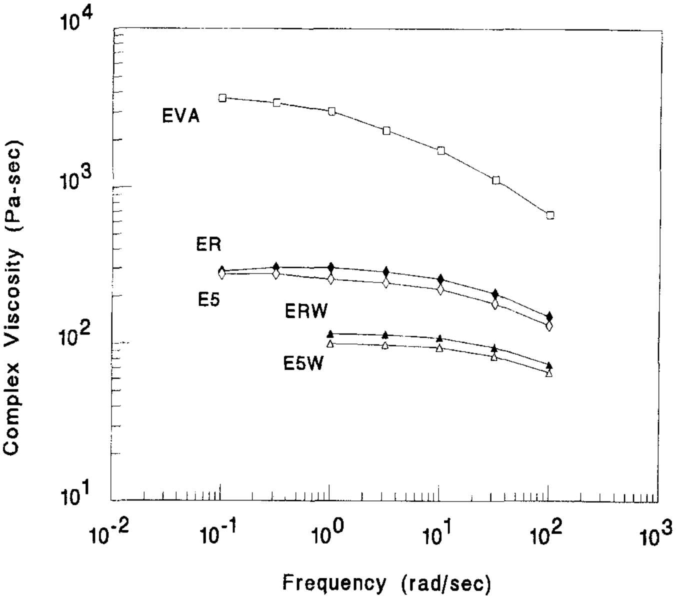

FIGURE 1 Effect of rosin or C5–C9 and wax addition on the complex melt viscosity of EVA measured at 122°C and different frequencies.

Melt Elasticity It is seen in Figure 2 that almost all values of tan δ at 122° C are greater than 2 except those of EVA at frequencies above 5 rad/sec. This indicates that melt elasticity is low. Values of tan δ rank in the following order: EVA < ER < E5 < ERW < E5W, which is the reverse of that for the viscosities. EVA has the highest melt elasticity and the highest complex viscosity. Addition of wax and tackifier to EVA decreases melt viscosity, as well as melt elasticity.

Activation Energy of Melt Viscosity The activation energy (Ea) for complex viscosity in the Newtonian region was calculated from the slopes of the of the $\ln(\eta^*)$ *vs.* 1/T plots, shown in Figure 3. Results are listed in Table II. Wax and tackifier addition increase the activation energy of melt flow.

Complex Melt Viscosity Mastercurve By plotting (η^*/η^*_0) against $(\eta^*_0\ \omega)$, a master curve for EVA, ER, E5, ERW, and E5W could be

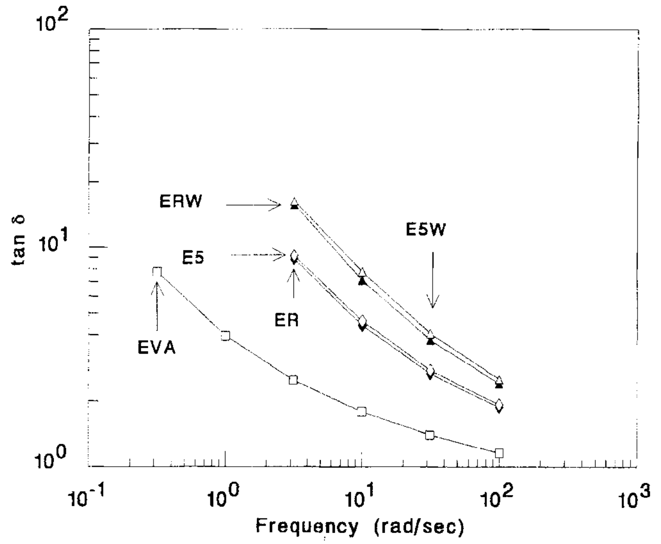

FIGURE 2 Effect of rosin or C5–C9 and wax addition on the complex melt loss tangent of EVA measured at 122°C and different frequencies.

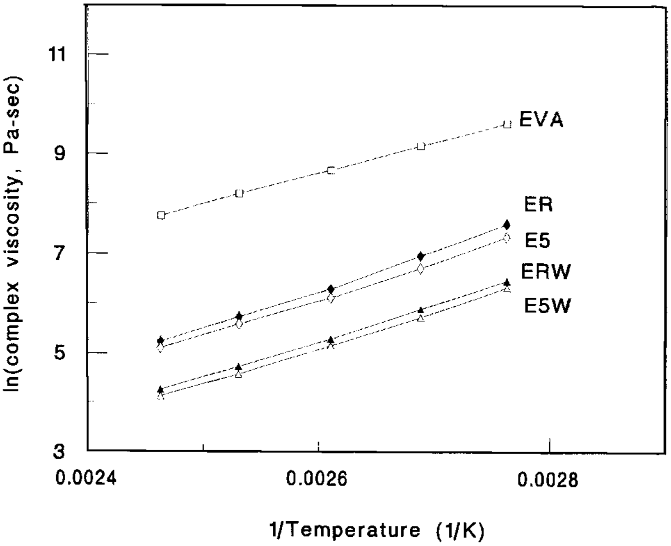

FIGURE 3 Zero shear rate complex viscosity plotted against reciprocal temperature for various compositions.

generated (Fig. 4). The success of the simple reduction scheme indicates that these five adhesives form homogeneous melts [2–5].

Log G′ vs. Log G″ Plot An attempt was made to substantiate further whether the EVA blends are homogeneous by constructing log G' *vs.* log G'' plots. All the data form a mastercurve as shown in

TABLE II Activation energy of melt viscosity for EVA, ER, E5, ERW, and E5W

	Activation energy (Kcal/mole)
EVA	9.88
ER	15.74
E5	14.73
ERW	14.19
E5W	14.13

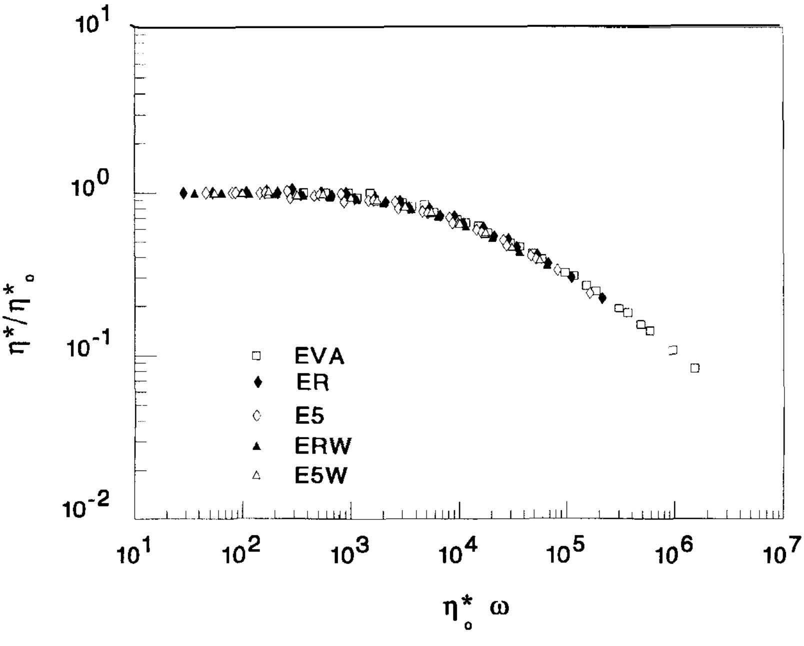

FIGURE 4 Complex melt viscosity master curve for EVA, ER, E5, ERW, and E5W measured at different temperatures and frequencies.

Figure 5. Log G' *vs.* log G'' of rosin- and C5–C9-tackified EVA, with or without wax, are independent of temperature and composition for G'' above about 100 Pa. This further suggests that these blends are homogeneous at temperatures above 89°C [6–10]. Deviations are found at G'' less than about 100 Pa, probably due to measurement limitations.

Effect of Bonding Conditions on T-Peel Strength

The T-Peel fracture energies of the pure EVA bonded at four different temperatures and for various times, and tested at 21°C and 50 mm/min, are plotted in Figure 6. Peel strength reaches a plateau when bonding time is about 65 sec for all four bonding temperatures. Relatively steady, interfacial failure, with random fluctuations, is observed

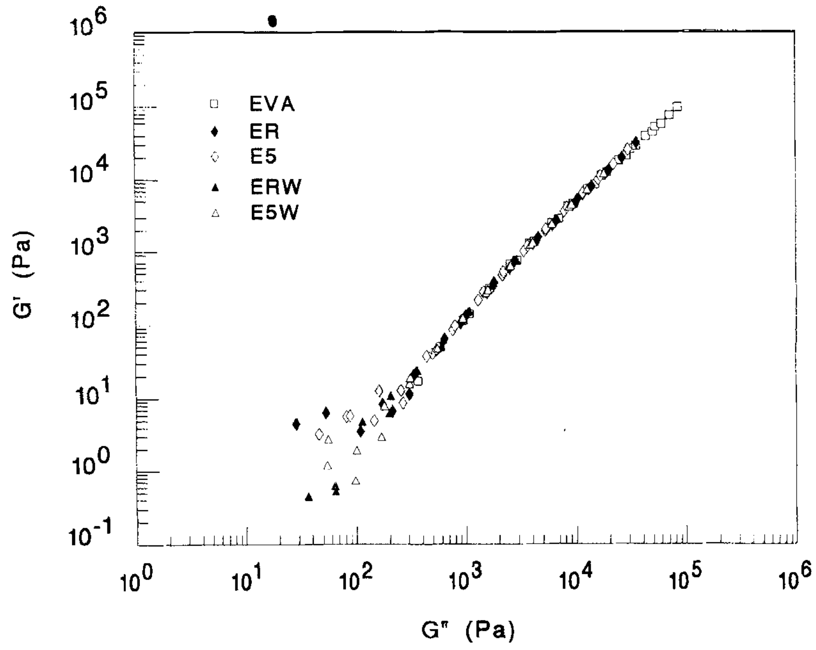

FIGURE 5 Log G' Vs. log G'' plot for EVA, ER, E5, ERW, and E5W measured at different temperatures and frequencies.

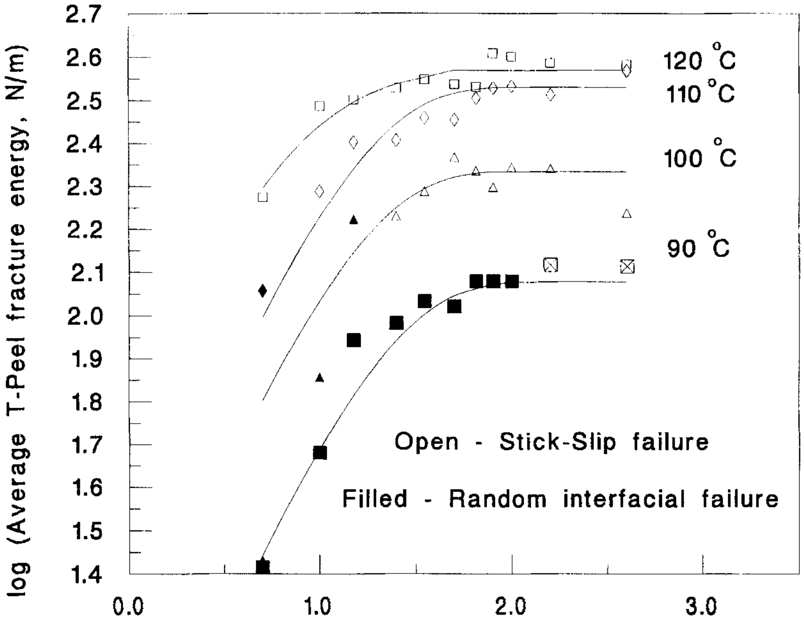

FIGURE 6 Average T-Peel fracture energy of EVA at different bonding temperatures and times.

for bonds prepared at 90, 100, and 110° C, when the bonding time is less than 100, 15, and 5 sec, respectively. Interfacial stick-slip failure is observed for other bonding times and temperatures. Cohesive failure of the EVA is absent.

T-Peel fracture energies of ER, E5, ERW, and E5W bonded between PP films at different temperatures and times are plotted in Figures 7–10, respectively. Interfacial stick-slip failure is observed for all bonding conditions. Fracture energies of ER and E5 reach a plateau when bonding time is about 35 sec at each temperature. The fracture energy of ERW levels off at bonding times greater than 30 sec for all four temperatures. However, the fracture energy of E5W reaches a plateau for a bonding time of less than 5 sec at 90, 100, 110, and 120° C.

The bond strength of the pure EVA is strongly dependent on bonding temperature, while rosin and C5–C9 tackified EVA show less de-

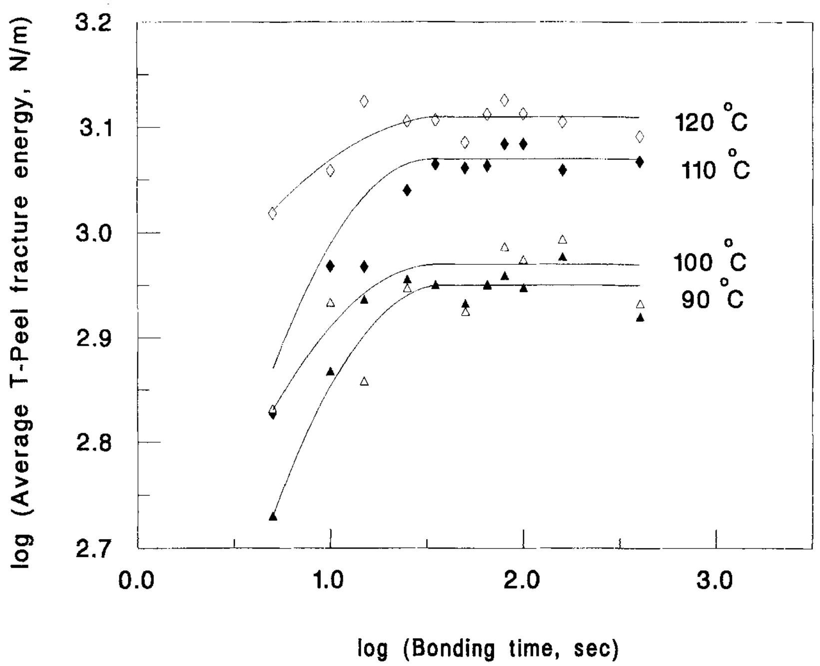

FIGURE 7 Average T-Peel fracture energy of ER at different bonding temperatures and times.

pendence on bonding temperature (Fig. 11). The fracture energies of the rosin and C5–C9 tackified EVA containing wax exhibit little change in bond strength as bonding temperature increases. Stick-slip failure is observed for all five adhesives bonded at each of the four temperatures.

Correlation between T-Peel Strength and Rheological Properties

The five adhesives form homogeneous melts, indicating that the components are uniformly distributed. When the adhesive melt is spread onto the PP, it flows and fills surface microcavities. As bonding temperature increases, viscosity decreases (Fig. 1), and the melt will flow more easily. Also, surface tension decreases as temperature increases [13], which results in more intimate contact. Thus, fracture energy increases with bonding temperature, until

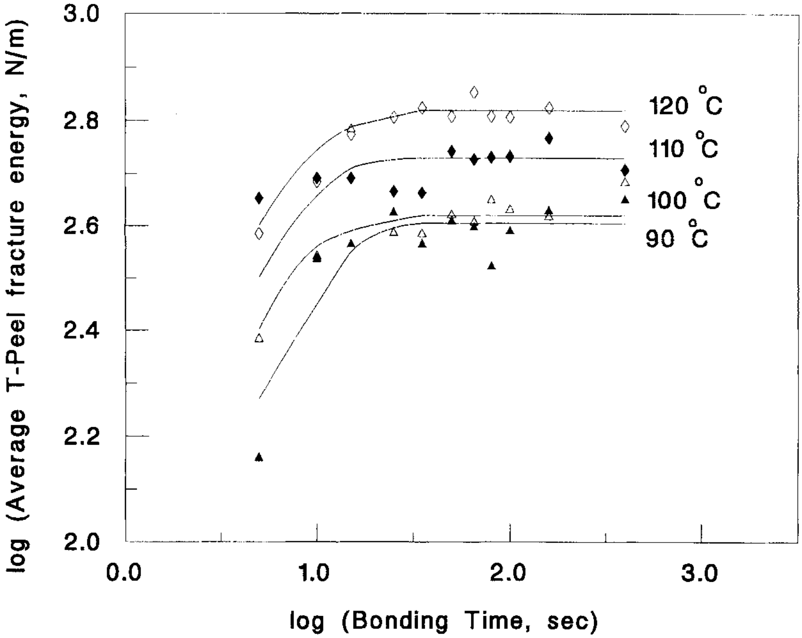

FIGURE 8 Average T-Peel fracture energy of E5 at different bonding temperatures and times.

equilibrium wetting is obtained. This explains why the time required to reach equilibrium is reduced as tackifiers and wax are added.

Furthermore, when a viscoelastic material is subject to a constant load, an instantaneous elastic deformation takes place, followed by a viscous deformation to an equilibrium deformation. After the load is released, only the elastic deformation is recovered. The less elastic the material, the less the recovery. Elasticity can be gleaned by examining the loss tangent and complex melt viscosity. If tan δ is greater than 2, the elastic contribution to the complex melt viscosity is less than 10%. Tan δ values of ER and E5 are greater than 2, and those of ERW and E5W are much greater than 2 (Fig. 2). Therefore, the elastic contribution in the tackified EVA melts, with or without wax, can be neglected. This is why the fracture energies of the tackified EVAs, with or without wax, show little

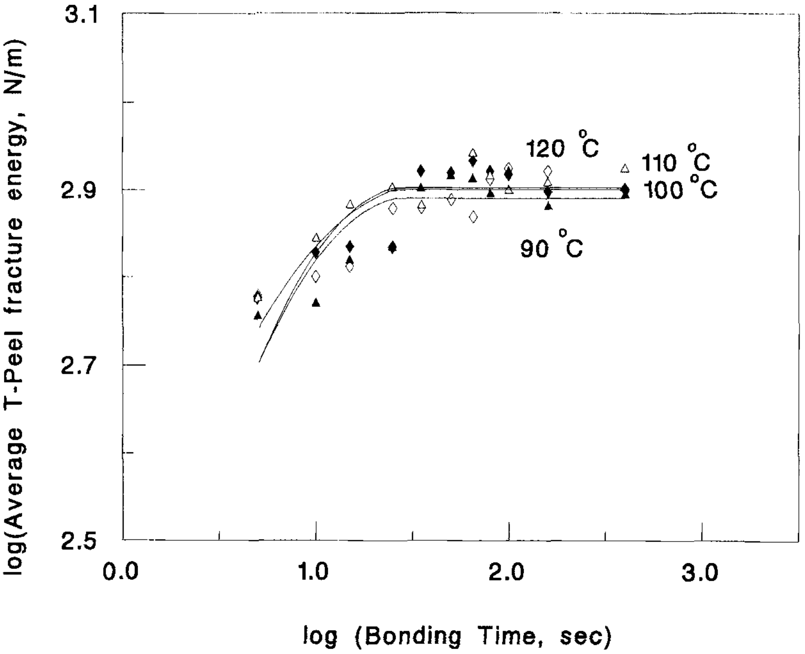

FIGURE 9 Average T-Peel fracture energy of ERW at different bonding temperatures and times.

bonding temperature dependence. However, melt elasticity is significant in the complex melt viscosity of EVA, due to its low tan δ. The elasticity of the EVA results in recovery after deformation of the EVA melt. Thus, EVA may lose some of its intimate contact with the PP film upon recovery. As bonding temperature increases, tan δ increases and intimate contact increases. This is perhaps why, in part, the fracture energy of EVA is dependent on bonding temperature.

The adhesives containing tackifiers with wax or without wax have the same viscosity activation energy. Based on this, it was expected that adhesives with wax may have the same bonding temperature dependence as with those without wax [13]. However, the adhesives containing tackifiers and wax have bond strengths which are almost independent of the bonding temperature. This may be due to a weak boundary layer of wax between the PP and adhesive. Such a layer

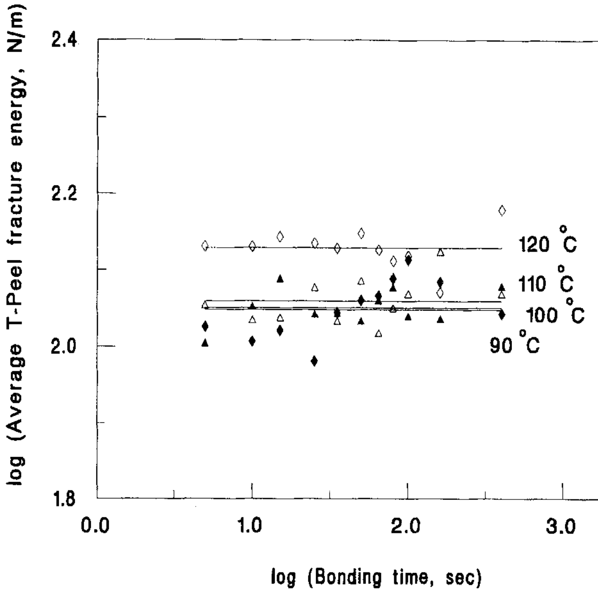

FIGURE 10 Average T-Peel fracture energy of E5W at different bonding temperatures and times.

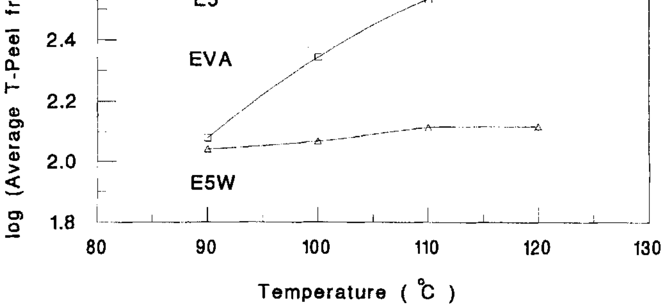

FIGURE 11 Average T-Peel fracture energy of five model adhesives at different bonding temperatures.

could provide a joint strength independent of bonding temperature. Another possibility recognizes that the adhesives with wax have very low melt viscosity. Thus, they can flow very easily so that the temperature dependence is negligible.

CONCLUSIONS

Rosin, C5–C9, and wax addition to EVA lower melt viscosity and melt elasticity, while increasing the activation energy for melt viscosity. Complex melt viscosity and log G' *vs.* log G'' mastercurves of EVA and its blends can be constructed. This suggests that EVA with 45 wt% rosin and 10 wt% wax, and a corresponding composition with hydrocarbon resin, form homogeneous melts. Rosin-containing adhesives have higher melt viscosity than those with C5–C9. Melts of lower viscosity require shorter time to reach equilibrium T-Peel strengths due to better wettability. The adhesives containing wax have similar activation energy for viscous flow as those without wax. The equilibrium T-Peel strengths of tackified EVA (with no wax) depends on the temperature, but that of tackified EVA with wax is independent of the temperature. This is may be due to a weak boundary layer of wax or to their high flowability.

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