Rheological behavior and adhesion properties of EVA-based hot-melt adhesives: use of computation tools

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ABSTRACT *A general relationship is established between the physical parameters of a hot-melt adhesive formulation and its composition. These physical parameters include the glass transition temperature, the melt viscosity, and viscoelastic properties. The computational tools presented may help in choosing the right proportions of polymer and components to fulfill the processing and mechanical requirements for any particular application. These tools have been used in regard to hot-melt adhesives based on vinyl acetate and alkyl acrylate ethylene copolymers. The effects of polymer molecular weight, wax content, and resin content on the processing and mechanical properties are examined using these concepts.*

KEYWORDS
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Hot-melt adhesives (HMA) may be considered as specialties formulations, tuned to meet some specific process requirements in various industries. Formulators rely on numerous polymers, resins, and waxes, and they will adjust the blend composition to fulfill the customer's requirements. Among the key properties are the melt viscosity (depending on the dispensing device), the open time, the setting time, and the temperature range.

Extensive laboratory tests are carried out under conditions close to those in which the product is used. These tests include determinations of the shear adhesion failure temperature, peeling tests, measurements of open and setting times, and tack tests. (The open time is that period after the adhesive has been deposited during which the adhesive is tacky enough to accept the substrate. After the open time, it is not possible to apply the substrate.) Trial-and-errors methods or more sophisticated statistical methods coupled with these tests may lead to the proper HMA formulation. Suppliers provide useful guidelines regarding the basic components of the HMA, such as the melt flow index of the polymers, the R&B (ring and ball) temperature of the resin, the cloud point temperature of the blends, and the melt temperature of the waxes.

Nevertheless, in the past few years, there has been a strong tendency to link the basic fundamental properties of the blends to the practical parameters of product use. The properties most commonly referred to are the viscoelastic properties, especially the temperature dependence of the storage modulus G' and the loss modulus G'' at a fixed frequency. This relationship is studied through thermomechanical analysis (TMA). Some authors have popularized this relationship through the concept of "application windows" in a plot of G' against the temperature of the maximum of the loss tangent. Using the same TMA curves, some have proposed some quantitative or semiqualitative criteria related to open and setting time, flexibility, and so forth (*1*, *2*).

We believe that this approach is quite a good guide. One objection, however, is that no clear link has been established between the composition of the blend and its viscoelastic properties. In other words, how can we compute the viscoelastic properties of the blend starting from the properties of the ingredients?

Here, we present highlights of computation methods that may be

helpful, illustrating how some simple rules drawn from these computations can be used to tune a formulation.

The basic principles

The hot-melt process may be perceived in terms of a plot of G' and G'' as a function of temperature at a fixed frequency. A frequency of around 1 Hz may serve as the reference frequency, since the time constants of the HMA processes are about 1 s. On such a plot, we can set up some criteria to define the "open time" and "setting time" temperatures, as illustrated in **Fig. 1.** (Criteria for open and setting times are based on values of the storage modulus G'. Above a certain degree of "solidity," no more tack exists, which ends the open time. Below a certain degree of "solidity," the mechanical strength is too low, which is the state before the setting time begins.)

Another important parameter, the melt viscosity, cannot be seen on this plot, but it can be computed from the blend composition.

The viscoelastic response in dynamic conditions at 1 Hz (an oscillatory experiment) gives a good idea of the response after 1 s (= 1/frequency) in static conditions (e.g., the "finger" test for tack). In the curves in Fig. 1, the frequency is fixed at 1 Hz, and the temperature is varied.

The glass transition temperature

A more basic property that defines the location of the curve on the temperature scale is the glass transition temperature, Tg. The glass transition temperature may be defined as the temperature corresponding to the maximum of G'', or the loss tangent, as illustrated in Fig. 1. As opposed to being calculated, the value of Tg may be measured directly by differential scanning calorimetry (DSC).

The glass transition temperature will more or less define the lowest temperature of use. A material tested even slightly above this temperature is likely to have a glassy behavior, provided it is tested at an appropriate deformation rate. This effect is the consequence of the time-temperature superposition principle, which has been considered for rubber-based hot-melt adhesives (*3, 4*).

In other words, if a material is tested above its Tg, at low frequencies it will appear soft or liquid. Above some high temperature, it will behave as a glossy material. The same phenomena will be observed with peeling rates or with mechanical testing rates in general.

Let us consider how to compute the glass transition temperature starting from the basic materials.

Table I presents the Tg values for various blends of an EVA copolymer (EVATANE 28420) and a phenolic polyterpene resin (Dertophene T). According to the DSC data, the Tg of the polymer is lower (-38°C) than the Tg of the resin (+38°C). The binary blends have intermediate, single values for Tg. A single Tg is a sign of good compatibility. More fundamentally, it means that the small resin molecules swell the entangled network of the polymer, affecting its viscoelastic behavior.

Figure 2 is a plot of the Tg of the blends against the polymer volume fraction. The curves can be fitted by the following equation (*5*):

$$Tg = [\phi\alpha_{1f} Tg_1 + (1-\phi)\alpha_{2f} Tg_2 - k\phi(1-\phi)] / [\phi\alpha_{1f} + (1-\phi)\alpha_{2f}] \quad (1)$$

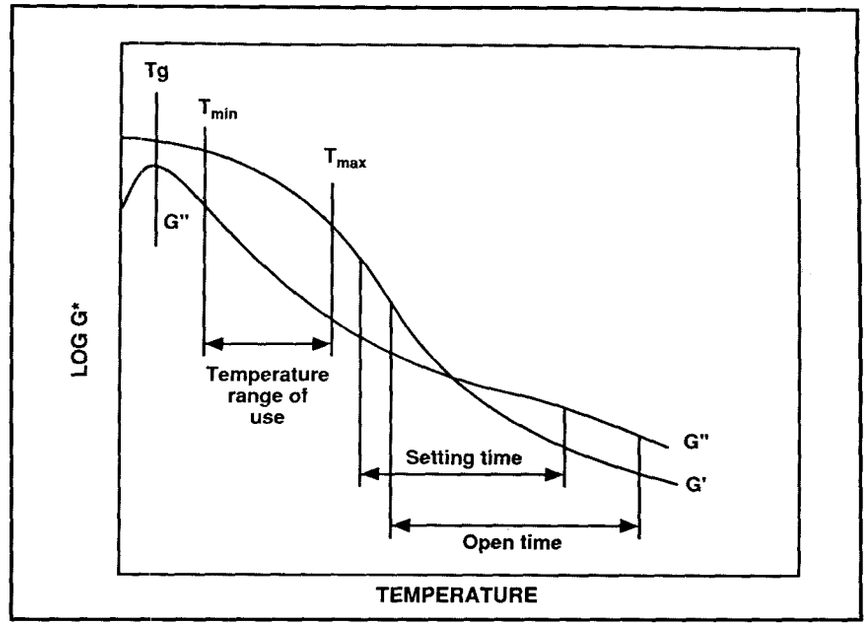
where

ϕ = polymer volume fraction

α_{1f} = free volume expansion coefficient of the polymer

α_{2f} = free volume expansion coefficient of the solvent.

1. Basic TMA curve related to product use properties



In our case, we have assumed that the free volume expansion of the polymer and solvent are the same, which is a reasonable approximation for highly concentrated polymer solutions. Therefore, as shown elsewhere (*5*):

$$\alpha_{1f} = \alpha_{2f} = \alpha_f$$

Hence, Tg can be computed from the composition of the blend, given the Tg of the resin and the polymer. Generally, the model can be used for blends of polymers with compatible additives. More details are given elsewhere (*5*).

Effect of wax content on Tg

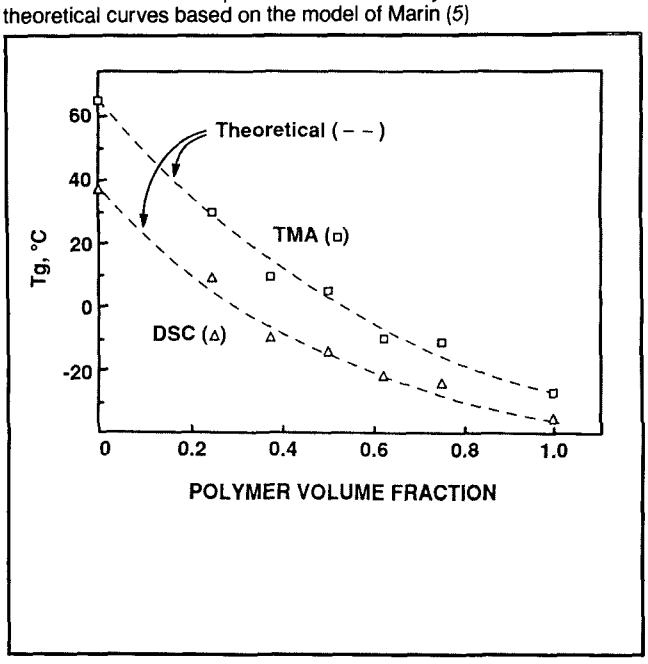
EVA-based formulations with increasing levels of wax display the same Tg, whatever the wax content, as shown in **Table II.** The wax acts just like a filler, and its main purpose is to tune the open and setting times.

The curves in **Fig. 3** show that a high content of wax induces a sharp increase in the modulus. This increase depends on the degree of crystallinity of the wax, as demonstrated elsewhere (*2, 6*).

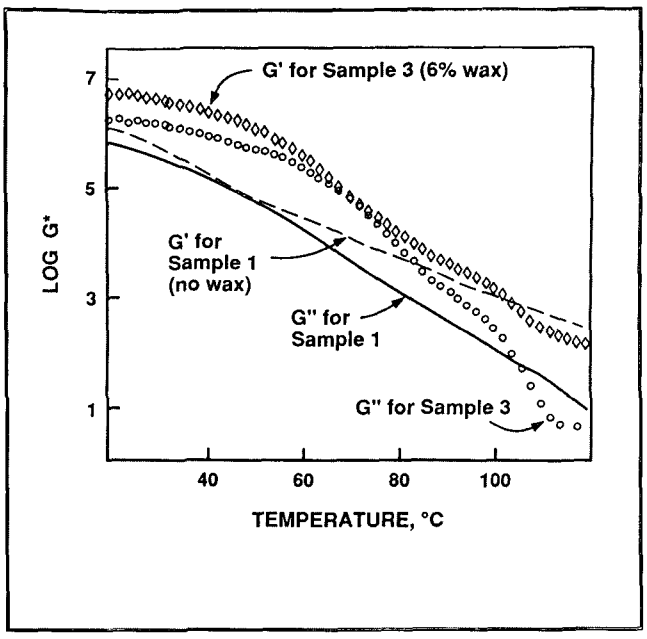
The lowest temperature of use

Since the Tg of the formulation is not affected by wax content, we can also expect the minimum temperature of use not to be affected. In effect, this is what is observed.

2. Glass transition temperatures measured by DSC and TMA, with theoretical curves based on the model of Marin (5)



3. TMA curves for Samples 1 and 3 from Table II



I. Influence of EVA content on Tg, binary blends

Sample	EVA, % by volume	Tg, °C TMA	Tg, °C DSC
1	100	-27	-38
2	75	-11	-24
3	62.5	-10	-22
4	50	5	-14
5	37.5	10	-10
6	25	30	9
7	0	65	38

Evatane 28420: 28% vinyl acetate, melt index = 420.
Dertophene T: R&B temp. = 95°C.

II. Influence of wax content on Tg, ternary blends

Sample	Wax, % by weight	Tg by TMA, °C	Symbol in Fig. 4
1	0	10	○
2	2.4	11	■
3	5.9	13	▷
4	11	12	●
5	16	11	□

Wax: Sasolwax H2 (Sasol Co.), melting point = 100°C.
Blend: Evatane 28420, Dertophene T, Sasolwax H2.
EVA: resin ratio = 0.375 EVA to 0.625 resin.

Figure 4 shows the peeling energy as a function of peeling rate for formulations with increasing amounts of wax as listed in Table II. At the highest peeling rates, a stick-slip mode (S-S) is observed in all cases at 23°C, with the exception of a low-peeling-energy adhesive mode (A-G for adhesive-glassy). This A-G mode of failure reflects the glassy behavior of the hot melt at high peeling rates, not far above the Tg (here 13°C). [This phenomenon arises from the time-temperature equivalence principle (*3, 4*).] Practically speaking, the A-G mode of failure means that the adhesive assembly can be separated by a simple, sudden hand-pulling.

Nevertheless, whereas the lowest temperature of use is not affected by the wax content, the general level of peeling energy is lowered as wax content increases. We can illustrate this fact in Fig. 4 with the peeling behavior at 40°C, which is far above the Tg. An interesting feature is that the mode of failure is shifted from the cohesive mode to the adhesive mode as wax content is increased. These facts are correlated with the liquid-like (low wax contents) or solid-like (high wax contents) behavior of the formulations, as detailed elsewhere (*6*).

Regarding general purpose applications like packaging, the level of adhesion is often less important than that the lowest temperature of use be close to Tg. In other words, Tg is the limiting parameter, and the ratio of polymer to resin must be considered carefully.

The highest temperature of use

The shear adhesion failure temperature (SAFT) is often referred to as the highest temperature of use. In this test, the adhesive is in fact experiencing a creep deformation (deformation under constant stress). Hence, the relevant viscoelastic function is the creep function $J(t)$, which can be expressed as:

$$J(t) = J e_0 + [\Sigma Ji (1 - \exp(-t/\tau_i))] + t/\eta_0 \quad (2)$$

where

Je_0 = limiting compliance

Ji = compliance associated with relaxation time

t = time

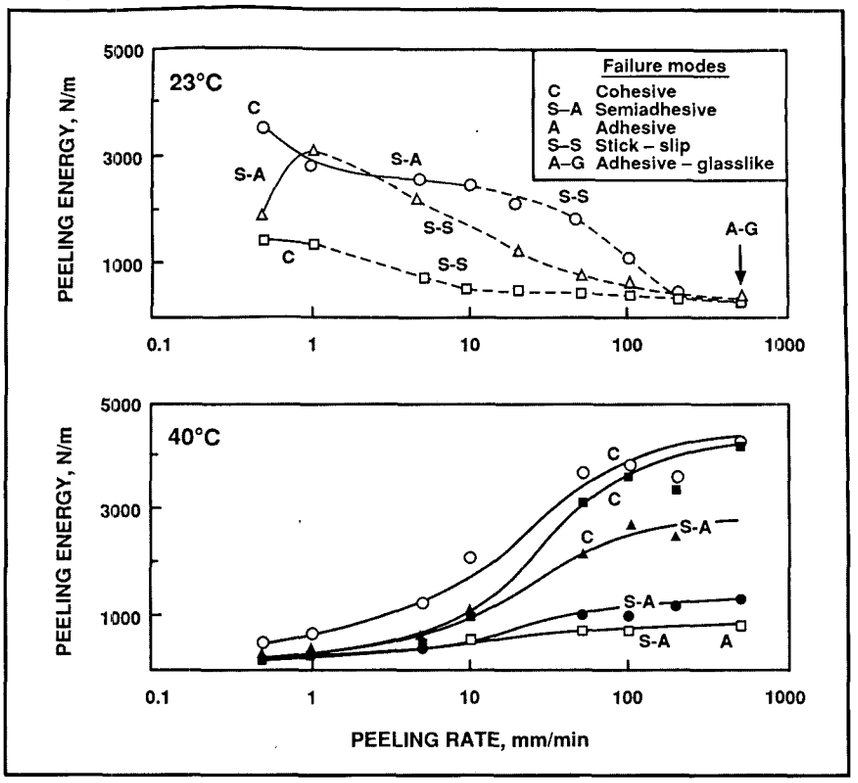
τ_i = relaxation time i

η_0 = zero-shear viscosity.

The first two terms pertain to elastic compliance (instantaneous and retarded). The last term, t/η_0, is a viscosity term. The elastic terms reflect the behavior over short durations, whereas the viscous term is dominant at longer times. Since the SAFT test proceeds at low heating rates (0.4°C/min), it is a lengthy process, and its rate is controlled by viscosity.

Figure 5 bears out this statement. In this figure, we have reported the SAFTs of various formulations (having the same composition of 30% EVA, 50% resin, and 10% wax) in which the EVA melt index is varied from 5 to 800. The SAFT is inversely related to the melt index. In other words, the higher the melt index, the lower the SAFT.

4. Peeling energy as a function of peeling rate for Samples 1-5 from Table II at 23°C and at 40°C



Melt viscosity

The melt viscosity at temperatures such as 170°C governs the ease of dispensing the adhesive in a given process. In some cases, very low viscosities are needed, whereas higher viscosities are needed for some other dispensing devices. In the high temperatures range, the wax and the resin may be considered to be solvents of the polymer. The viscosity can be expressed as:

$$\eta_0 = \eta_r(T - T_g)(\Phi\, Mw)^n \qquad (3)$$

where

η_r = a reference viscosity

Φ = volume fraction of the polymer

Mw = average molecular weight (determined by gel permeation chromatography)

n = an exponent theoretically close to 3.4 (*7*).

In **Fig. 6**, we have plotted on a logarithmic scale the melt viscosity of EVA-based formulations against the weight average molecular weight of the EVA, the EVA volume fraction being held constant. This line has a slope of 3.3., which is close to the theoretical value. Given the adhesive composition, then, it is possible to compute the viscosity rather precisely.

Practical use of the computation tools

The resin we used acts as an antiplasticizing solvent of the EVA polymers. That is, it will increase the Tg of the polymer while decreasing the melt viscosity. In fact, we can theoretically predict the full viscoelastic behavior of the binary blends of EVA and resin (*5*). Of special interest is the effect of the resin on the plateau modulus of the polymer: the resin will decrease the plateau modulus. This effect is the "tackifying" effect (*3*). The need to add a wax to comply with the process conditions (open and setting times especially) means that this tackifying effect is of less interest, but it would be important in the case of a pressure-sensitive adhesive.

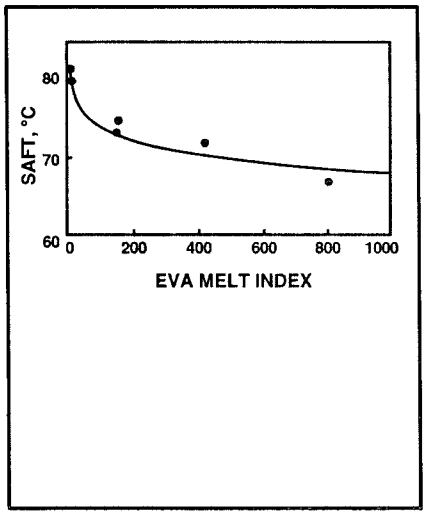
Let us see how we can profit from the basic computation concepts presented here for a typical packaging HMA. The Tg is essentially determined by the polymer-resin ratio, and the viscosity is determined by ($\Phi\, Mw$) (provided we are well above Tg, as we are in this case). We want to tune simultaneously the melt viscosity and the Tg. Let's take an example.

The two formulations given in **Table III** are based on EVA with the same vinyl acetate contents but quite different melt indexes (150 and 800). By using the EVA with the highest melt index, it is possible to increase the polymer volume fraction, while keeping the viscosity constant. In other words, we will increase the EVA-resin ratio while keeping the same wax content such that ($\Phi\, Mw$) remains the same.

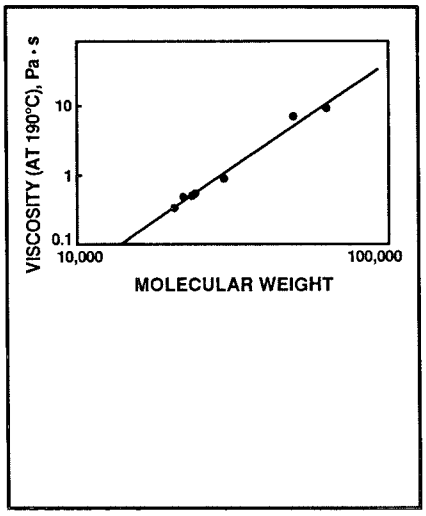
This is what we observe for the two HMA formulations presented in Table III. When the ratio of polymer to resin is increased, Tg is decreased. Hence, the lowest temperature of use is lowered, without sacrificing the viscosity. Furthermore, the peeling behavior at 23°C is improved with the highest EVA-resin ratio, because the Tg is decreased from 18°C to 10°C.

Another way to decrease the Tg could be to use an ethylene copolymer with a lower Tg like a butyl acrylate ethylene copolymer, or another resin or oil could be used. However, we have reached the goal more simply by changing the type and amount of EVA.

5. SAFTs of various ternary blends for different melt indexes of EVA



6. Melt viscosity of EVA-based HMAs with same polymer, resin, and wax composition (slope = 3.3)



III. Tuning Tg and viscosity by adjusting the EVA melt index and the ratio of EVA and resin

	Formulation A	Formulation B
Type of EVATANE	28150	28420
Melt index	150	800
Vinyl acetate, %	28	28
Composition, %		
EVATANE	30	43
Dertophene T	50	37
Sasolwax H2	10	10
Tg, °C	18	10
Peeling energy, J/m² (at 23°C)	Stick-slip	3000
Viscosity, Pa • s (at 190°C)	2.2	2.1

Conclusions

Computation tools based on solvent-polymer interaction models can be used to predict such important parameters as the Tg, the melt viscosity, and possibly the elastic parameters of HMAs. All these parameters can be related to product specifications by applying the "application windows" concept, for instance. Some physical data on the basic components of the formulations are needed: the Tg of the resin and the Tg and *Mw* of the polymer.

This approach can be profitable in helping to choose the proper resin (according to its Tg) and the proper ratio of polymer to resin. These tools are also useful for a comprehensive description of the way the resin and the wax affect the processing and adhesion behavior of the polymer.

Materials and methods

The experiments were performed on blends of ethylene vinyl acetate (EVA) copolymers, a terpene phenolic resin, and a synthetic wax. These components, especially the EVA copolymers, are extensively used for HMAs in bookbinding and packaging.

Peeling samples

Peeling samples were prepared according to ASTM D-3167, Floating Roller Peeling. The rigid part of the assembly was a 2-mm-thick plate of AU4G aluminum alloy, and the aluminum flexible foil was 100 mm thick.

Viscoelastic measurements

The TMA measurements were performed with a Rheometrics RDA 700 rotary rheometer. The variations of the real (G') and imaginary (G'') parts of the complex shear modulus at a fixed frequency (10 radians/s) were measured as a function of temperature in the temperature range of -50°C to +130°C. The experiments were performed in parallel plates geometry (2 cm diameter, 2 mm thickness).

Differential scanning calorimetry

DSC measurements have been performed on a Perkin-Elmer DSC II instrument. For every blend, a fresh sample was first cooled to -50°C then heated to 120°C at a rate of 10°C/min (first scan). The sample was then cooled to -50°C at -40°C/min, held 10 min at this temperature, and finally last heated to 120°C at a rate of 10°C/min (second scan).□

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