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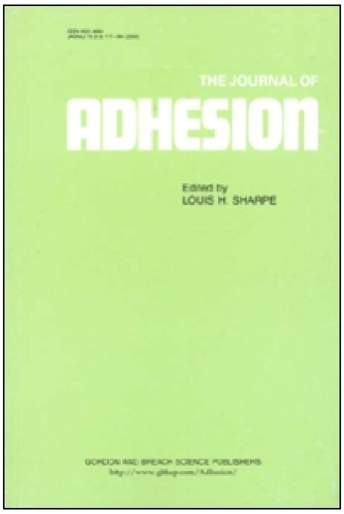

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A Physical Model to Predict the Thermomechanical Behaviour of Hot-Melt Adhesives

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A Physical Model to Predict the Thermomechanical Behaviour of Hot-Melt Adhesives

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The paper presents a model that allows one to calculate the linear viscoelastic behaviour (complex shear modulus as a function of frequency) and thermomechanical behaviour (complex shear modulus as a function of temperature) of various formulations of hot-melt adhesives containing a polymeric base, a tackifying resin and a crystalline wax. The model takes into account the nature and molecular weight distribution of the polymer, the glass transition temperatures of the polymer and the resin, and the crystallinity of the added wax. A computer program has been derived from the model to simulate the thermomechanical behaviour of the formulations from their composition. It fits, with a reasonable accuracy, the experimental data. The model has been tested for two polymeric bases (EVA and EBA) and two different tackifying resins.

KEY WORDS adhesion; rheology; thermomechanical analysis; hot-melt adhesives; formulation; resin; polymers; glass transition temperature.

1. INTRODUCTION

Hot-melt adhesives (HMAs) are essentially made of blends of a rubbery polymer base, a tackifying resin that is (at least partially) compatible with the polymer and, in most cases, a crystalline wax that essentially sets the crystallization temperature of the adhesive. 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, the elasticity in the melt and rubbery states (which may be related to Dahlquist criterion),[1] the open time, the setting time and the temperature range of use. In the past few years, there has been a strong tendency to link the basic, fundamental material properties of the blends to the practical parameters of product use. The properties most commonly referred to are the visco-

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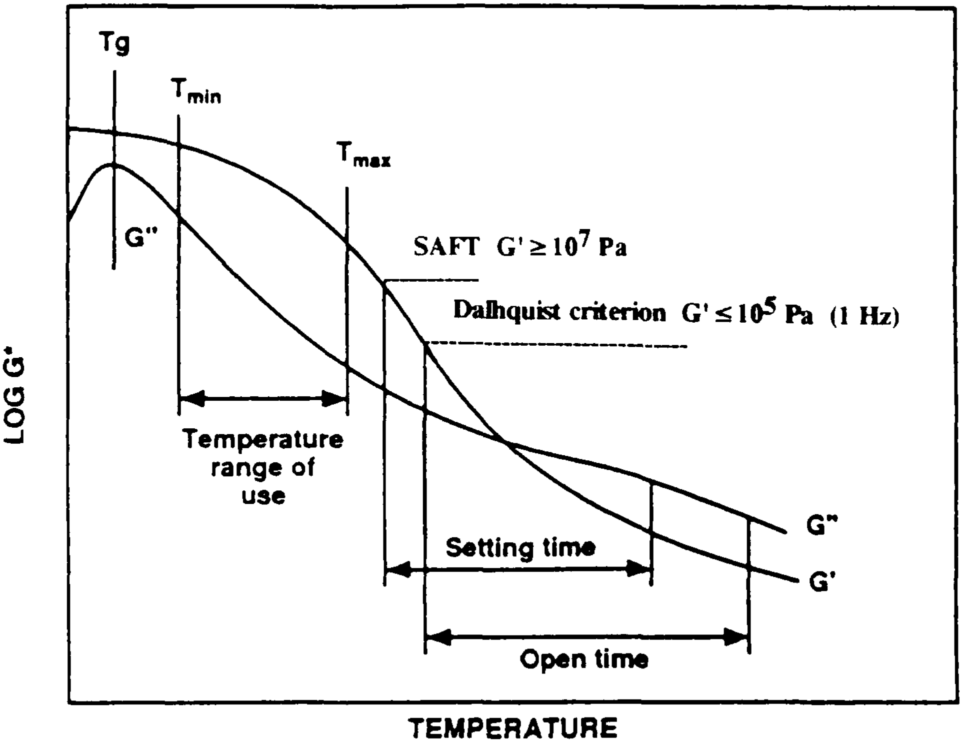

FIGURE 1 Applications windows concept: schematic variations of the thermomechanical behaviour of an HMA formulation.

elastic properties, that govern the processability and, to a large extent, the adhesion properties of HMAs. The temperature dependence of the storage modulus, G′, and the loss modulus, G″, at a fixed frequency (referred to as thermomechanical analysis, TMA) may be directly related to the industrial process of HMAs.[2,3] We have reported on Figure 1 the schematic variations of the complex shear modulus as a function of temperature for a typical HMA; the correlated parameters of the processing of HMA are reported on the same curve.

We propose in this paper a physical model based on a previous study on the effect of resin content on the rheological properties of polymer/resin blends.[4] The present model takes into account the addition of a crystalline wax and allows one to calculate the thermomechanical curves (G′ and G″ as a function of temperature) given the blend composition and the chemical and physical characteristics of the components of a given formulation.

2. EXPERIMENTAL

2.1 Samples

We have studied polymer/resin binary blends and polymer/resin/wax ternary blends. The blends are detailed in Table I. The polymeric bases were (1) an ethylene

TABLE I
Blend compositions and glass temperatures

Samples	T_α (°C)	T_g (°C)	Polymer weight fraction
EVA + resin A	−27	−36	1
	−11	−24	0.75
	−10	−22	0.625
	5	−14	0.50
	10	−10	0.375
	30	9	0.25
	65	38	0
EBA + resin A	−42	−50	1
	−22	−36	0.75
	3	−13	0.375
EVA + resin B	−23	−33	0.75
	−16	−26	0.375
	−7	−18	0
EVA + resin A + wax	11	−12	$\Phi_{EVA} = 0.33$ $\Phi_{resin} = 0.56$

vinyl acetate (EVA) copolymer (28% VA content), (2) an ethylene butyl acrylate (EBA) copolymer (33% butyl acrylate) from the Elf-AtoChem Co. The tackifying resins were (1) a terpene-phenolic resin (Dertophène T from the DRT Company, France) (resin A) and (2) a liquid resin (Staybelite Ester 3E from Hercules) (resin B). The added wax was a microcrystalline wax (saturated alkane in C58 with no aromatic functionality) from Société Française de Pétrochimie.

The blends were prepared by mechanical blending at 170°C and stabilized with 0.3% Irganox 1010 from Ciba-Geigy. Compositions of the blends are listed in Table I.

2.2 Rheology

The rheological measurements were performed with a Rheometrics RDA 700 rotary rheometer in parallel plate geometry. Plate diameters were 1 or 2 cm depending on the modulus range in order to avoid large instrument compliance corrections. Low temperature measurements were made using a liquid nitrogen cooling device.

Mechanical spectroscopy measurements (variations of the real (G′) and imaginary (G″) parts of the complex shear modulus as a function of frequency) were performed at various temperatures (0°C to 130°C) in the frequency range 10^{-2} to 10^2 rd/s. The thermomechanical analysis (TMA) measurements (variations of G′ and G″ at a circular frequency of 10 rd/s as a function of temperature) were performed in the temperature range of −60 to +130°C; the heating rate was 2°C/min.

2.3 Thermal Analysis

Differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer DSC II calorimeter. For every blend, a fresh sample was first heated up to 150°C from room temperature (heating rate: 10°C/min), then cooled down to −50°C (cooling rate: 40°C/min). After being held 10 min at this temperature, the sample was at last heated up to 150°C at 10°C/min. The T_g values were determined on this last scan.

3. RESULTS AND DISCUSSION

3.1 Thermal Properties

3.1.1 Pure Components The EVA copolymers are semi-crystalline polymers with a melting range of 0°C to 75°C, having a maximum located at 55°C. The degree of crystallinity is 12%.

The EBA copolymer is also a semi-crystalline copolymer having a melting range of −25 to 95°C with a maximum at 72°C, the degree of crystallinity being 15%.

Resins A and B are amorphous with T_gs of 40°C and −18°C, respectively, measured by DSC.

The microcrystalline wax is a highly crystalline wax with a melting range of 63 to 120°C and a maximum at 105°C.

We have reported in Figure 2 the T_gs measured by DSC for the two blend series: EVA/resin A and EBA/resin A. On Figure 3 the T_gs measured by DSC have been compared with the T_α temperatures measured by TMA (maximum of G″(T)) for

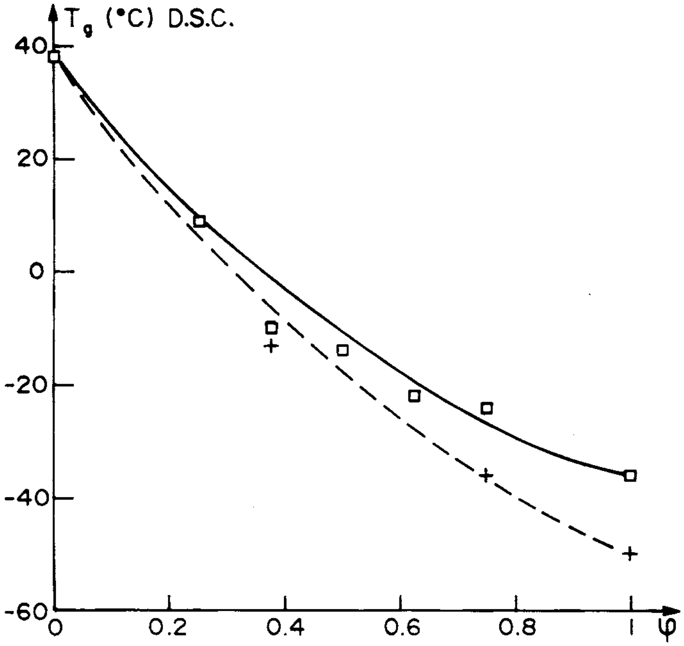

FIGURE 2 Glass transition temperatures as a function of polymer volume fraction, determined by DSC: EVA + resin A (□); EBA + resin A (+); full and dotted line: theory.[4]

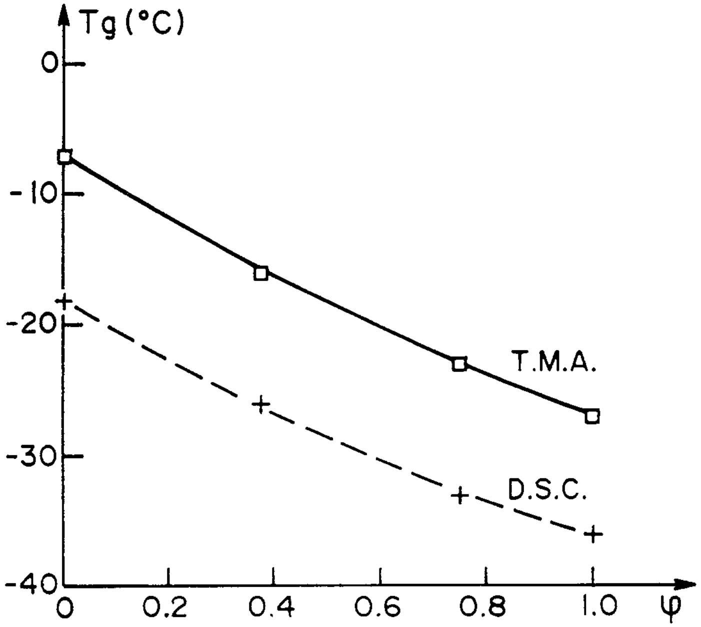

FIGURE 3 Glass transition temperatures (DSC: (+)) as a function of polymer volume fraction, compared with T_α temperatures (TMA: (□)) for the EVA + resin B series; lines: theory.[4]

the EVA/resin A blend series; the lines on the two figures have been calculated from a blending law for T_gs proposed in previous papers[4] for compatible or partially-compatible polymeric blends. The variations of T_g as a function of polymer volume fraction in the blends determined by DSC and the T_α temperatures follow reasonably well that blending law based on additivity of free volumes, so all the blends studied in the present paper are compatible in the sense defined in Ref. 4.

3.1.2 Polymer/Resin Blends

- EVA + resin A: at high resin content ($\phi < 0.375$; in the following discussion ϕ will denote the polymer volume fraction) the blend is monophasic in the whole temperature range, *i.e.* there is only one amorphous phase: the resin "kills" the polymer crystallinity. At higher polymer content, crystallinity is recovered and a quasi-unimodal (in shape) distribution of spherulites is observed, the diameter of which increases linearly with EVA content.
- EBA + resin A and EVA + resin B: all blends are semi-crystalline at room temperature with an amorphous polymer/resin phase and a crystalline phase.

3.1.3 Full Formulation: Polymer/Resin/Wax For an EVA/RESIN ratio of 30/50 by weight, corresponding to a typical industrial formulation, addition of wax leads to an EVA/wax co-crystallisation with a full crystallisation of wax and a maximum on the thermogram at 100°C.

3.2 Rheological Model and Properties

3.2.1 The Case of Non-crystalline Samples

- **monodisperse case**

The rheological model is based on previous studies[5] by mechanical spectroscopy of the melt properties of linear and star-branched monodisperse samples, in a time (or frequency) range covering relaxation domains from the terminal region of relaxation to the glassy behaviour. It has been shown[5] that the complex compliance $J^*(\omega)$ (that is, the reciprocal of the complex shear modulus $G^*(\omega)$) of a monodisperse material could be fitted in a very broad frequency range by the equation:

$$J^*(\omega)=\frac{1}{j\omega\eta_0}+J_p^*(\omega)+J_t^*(\omega)+J_\infty \qquad (1)$$

The first term $(1/j\omega\eta_0)$ is a purely viscous term; the $J_p^*(\omega)$ complex function characterizes the terminal relaxation domain, and the rest of the equation characterizes the rubber-to-glass transition region. In the limiting case of a monodisperse linear polymer sample, the complex compliance may be expressed as:

$$J^*(\omega)=\frac{1}{j\omega\eta_0}+\frac{J_n^0}{(1+j\omega\tau_p(M))}+\frac{J_n^0}{(1+j\omega\tau_t)^{1-\alpha}}+J_\infty \qquad (2)$$

where η_0 is the zero-shear viscosity,
J_∞ is the reciprocal of the glassy modulus, G_∞ ($G_\infty \approx 10^9$ Pascals),
J_n^0 is the reciprocal of the plateau modulus, G_n^0,
$\tau_p=\eta_0(M)/G_n^0=\eta_0(M)\,J_n^0$ scales as the maximum (reptation) relaxation time with molecular weight,
τ_t is the characteristic time of the transition from the rubbery plateau to glassy behaviour (10^{-3} to 10^{-6} s depending on the polymer),
α is a Cole-Cole parameter characterizing the distribution of retardation times in the transition region that has the same value for all linear polymers (0.3).

The variations of all these parameters with molecular weight are known:

$$\eta_0 \propto M^{3.4} \qquad (3)$$

$$J_n^0 \text{ or } G_n^0 \propto M^0 \qquad (4)$$

as well as the variations with polymer volume fractions in the case of polymer solutions:

$$G_n^0 \propto \phi^2 \text{ and } J_n^0 \propto \phi^{-2} \qquad (5)$$

$$\eta_0 \propto \phi^{3.4} \qquad (6)$$

It is, therefore, possible to predict the behaviour of a monodisperse sample (or concentrated solution) knowing its molecular weight (and volume fraction).

As far as temperature is concerned, it is also possible to determine the temperature dependence of viscosities and relaxation times of concentrated polymer solutions, knowing the glass transition temperatures (T_g) of the polymer and solvent (as far as HMAs are concerned, the resin may be considered as an "antiplasticizing" solvent).[4] All these features have already been explained for polymers[5] (and specifically for hot-melts)[2] in previous articles.

At this point we have to specify that the rheological model presented here is valid only for temperatures above the glass transition temperature: below that temperature, the physical concepts we used in our model (WLF temperature dependence, free volume concept, Davidson-Cole relaxation, etc.) are no longer valid, but the glassy behaviour is beyond the scope of the present paper.

- **polydisperse case**

One may start from the blending law for zero-shear viscosities:

$$\eta_0 = A(T)\, M_w^{3.4} \tag{7}$$

M_w being the weight-average molecular weight:

$$M_w = \int_0^\infty M\, W(M)\, dM; \quad \text{hence:} \tag{8}$$

$$\eta_0 = \left[\int_0^\infty [\eta_0(M)]^{1/3.4}\, W(M)\, dM\right]^{3.4} \tag{9}$$

and A(T) the mobility factor depending on temperature, T. One may extend this equation to complex viscosities $\eta^*(\omega)$:[4]

$$\eta^*(\omega) = \left[\int_0^\infty [\eta^*(\omega;M)]^{1/3.4}\, W(M)\, dM\right]^{3.4} \tag{10}$$

$$\text{with } \eta^*(\omega) = G^*(\omega)/j\omega$$

In the case of concentrated solutions of technical polydisperse polymers (that is, the case of HMA formulations), the variations of the plateau modulus, limiting compliance and zero-shear viscosities with polymer volume fraction are the same as for model polymers (eq. (5) and (6)). We have reported on Figure 4 the variations of the plateau modulus of EVA/resin A, EVA/resin B and EBA/resin A blends as a function of polymer volume fraction: the variations give a power law dependence with an exponent close to 2, in agreement with the theoretical exponent (2 to 2.3).[5] This is a further argument for blend compatibility; in that case, the variations of the elastic parameters depend only on the polymer concentration and are independent of the resin nature, so it is possible to adjust the T_gs and concentrations in choosing among the large number of resins available to get the desired values of "viscosity" and "elasticity." As described in Ref. 4, we may hence compute the linear viscoelastic behaviour of a commercial bulk polymer or a polymer/resin formulation, given (i) the molecular weight distribution of the polymer (GPC data, for example), (ii) the resin content and its T_g. This powerful simulation tool allows also to compute the thermomechanical curves (G' and G'' as a function of temperature) for polymer/resin blends. The general validity of the model has been extended here to formulations made of various polymers and resins.

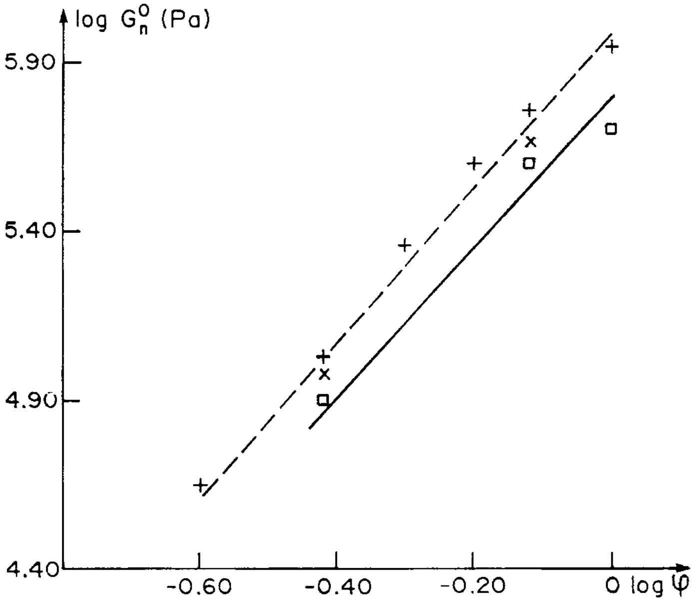

FIGURE 4 Plateau modulus as a function of polymer volume fraction: EVA+resin A (+); EVA+resin B (×); EBA+resin A (□).

3.2.2 Case of a Full Formulation Polymer/Resin/Wax

A full formulation is a semi-crystalline blend at room temperature, with an amorphous EVA (or EBA)/resin phase and a PE/wax crystalline phase. The crystalline phase increases the modulus value at intermediate (plateau region) frequencies, whereas the modulus increase in the transition and glassy region is small and may be regarded as negligible.[6,7] It is then necessary, in that case, to take into account the crystallinity effects on the rheological (hence adhesive) properties of an adhesive formulation. If we can introduce into the above rheological model the effects of crystallinity on the complex shear modulus, it should then be possible to compute numerically (i) the isothermal viscoelastic properties (for example: complex shear modulus, complex viscosity, relaxation function, creep function) above and below the melting temperature, (ii) the thermomechanical properties from the glass transition up to the processing temperatures. This would be of great help to the formulator.

- **Elastic modulus of a semi-crystalline blend:**

The complete formulations being biphasic below the melting point, the rheological properties of the system are related to the individual properties of the amorphous and crystalline phases; the high modulus of the crystalline part increases the overall modulus of the blend. We have chosen to consider the crystalline part within a blend as a hard filler; this has the advantage of simplicity and allows us to use the viscoelastic models derived for polymer blends or filled polymers. The drawback of that choice is that these models are phenomenological to a large extent, so the more complete treatment we present here is a more "engineering" and less "physical" model than what was presented above and in Ref. 4 in the case of purely amorphous blends. The simplest way to combine the properties of a polymer matrix and a filler, or dispersed phase, is to use a parallel model to describe the elastic modulus of the blend:

$$G^0_p = (1 - \chi(T))\, G^0_n + \chi(T)\, G_c \qquad (11)$$

where G^0_p denotes the computed elastic modulus corresponding to the "parallel" model, $\chi(T)$ is in our case the volume fraction of the crystalline phase (that is a function of temperature within the crystallisation peak), G_c is its elastic modulus ($\sim 10^9$ Pa) and G^0_n is the plateau modulus of the amorphous (elastic liquid) phase. This equation would be, in fact, a physically reasonable representation of the behaviour of a compatible (*i.e.* monophasic or intimate) blend.

The equivalent series combination of moduli is:

$$(G^0_s)^{-1} = (1 - \chi(T))/G^0_n + \chi(T)/G_c \qquad (12)$$

where G^0_s denotes the computed elastic modulus corresponding to the "series" model. That equation would be the simplest to describe the modulus of a biphasic system. In fact, most of the theoretical or phenomenological rheological models of polymeric blends are based on parallel and series combinations of the properties of the components.[8,9,10] In order to reduce the number of "ad-hoc" parameters, we have selected a hybrid model[11] of parallel and series combination of the moduli of the crystalline and amorphous phases as:

$$G^0 = \chi(T)\, [(1 - \chi(T))]\, [G^0_p - G^0_s] + G^0_s \qquad (13)$$

$\chi(T)$ is approximated in our computations to the crystallinity ratio derived from the DSC curves. The thermal analysis data (crystallinity as a function of temperature) may be introduced into the model either directly (experimental thermograms) or analytically (as a curve fitting of the thermogram) with a very small difference between the thermoviscoelastic curves calculated by the two methods.

- **Viscosity of a semi-crystalline blend:**

The variations of viscosity as a function of blend composition and temperature in the melt state are well described by the models presented before.[4,7] In the vicinity of the crystallisation zone the viscosity diverges as temperature decreases; as the crystallisation zone extends to a broad range of temperatures in the case of these polymeric blends, there is no viscosity discontinuity at a given temperature, but the viscosity rather diverges very rapidly in a limited temperature range during the crystallisation process. We write the viscosity, η, within the crystallisation peak as the product of the melt viscosity and a term that diverges as the degree of crystallinity, $\chi(T)$, increases:

$$\eta = \eta_0\, (1 - \chi_0/\chi(T))^{-m} \qquad (14)$$

The value of the parameter, m, corresponds to a best fit of the experimental thermomechanical curves (a single value, m = 13, has been selected for all calculations).

In the case of semi-crystalline blends, these values of plateau moduli and viscosities (equations (13) and (14), respectively) may be included in the basic equation of the rheological model of section 3.2.1 (eq. (2)), leading to a complete thermorheological model taking into account the blend crystallinity. As an example, a comparison of the thermorheological model predictions with the experimental data is presented in Figures 5 through 8 for a series of various formulations. The input data introduced to calculate each thermomechanical curve is: GPC data (molecular weight distribution) of the polymer, blend composition, T_gs of the components. So it is easy to simulate what would be the effects of changing the resin and/or the molecular weight distribution of the polymeric base. There is a reasonable agreement between the model predictions and experimental data, but the discrepancy between experimental and theoretical values increases at moderate temperatures (*i.e.* in the plateau region) when the amount of crystalline phase increases (see Fig. 8, corresponding to the full formulation). This indicates that the way of handling the crystallinity effects on mechanical properties in the model is oversimplified, and this aspect of the model could eventually be refined following a more fundamental approach, using physical models of polymer blends or filled polymers.

Another important application of the model is the calculation of the mechanical spectroscopy data, $G^*(\omega)$, of a formulation at a given temperature, from the blend

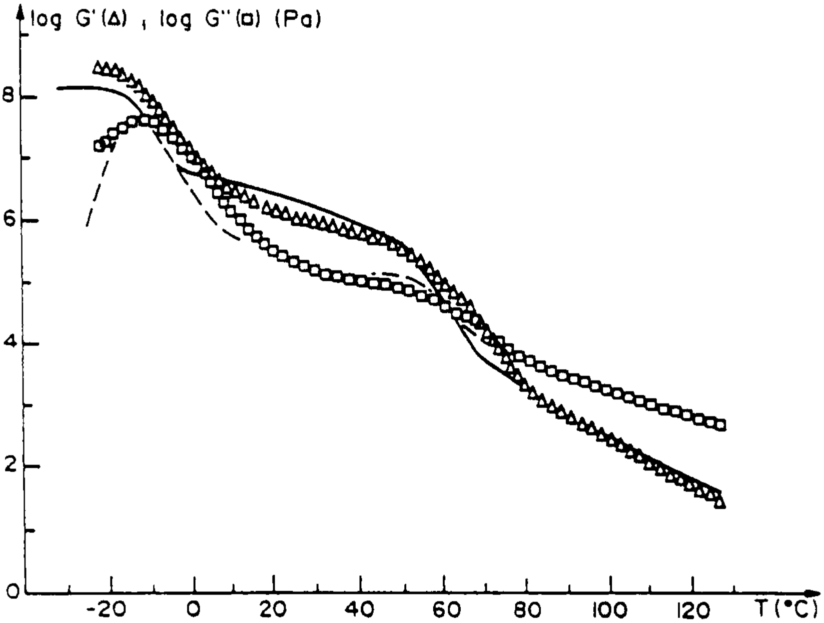

FIGURE 5 Comparison between the experimental TMA ($G^*(T)$) curves and model predictions (full line: G'; dotted line: G''): EVA + resin A ($\Phi = 0.75$).

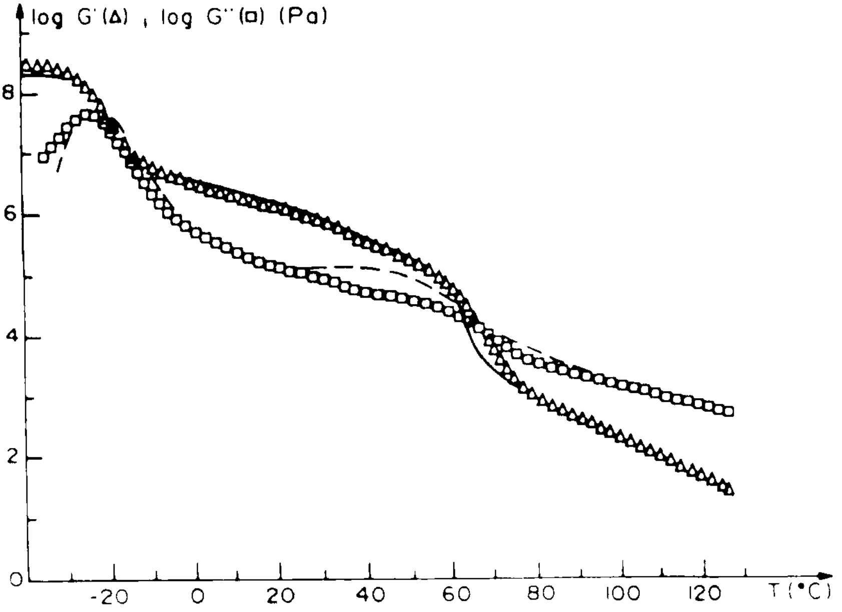

FIGURE 6 Comparison between the experimental TMA (G*(T)) curves and model predictions (full line: G'; dotted line: G''): EVA + resin B (Φ = 0.75).

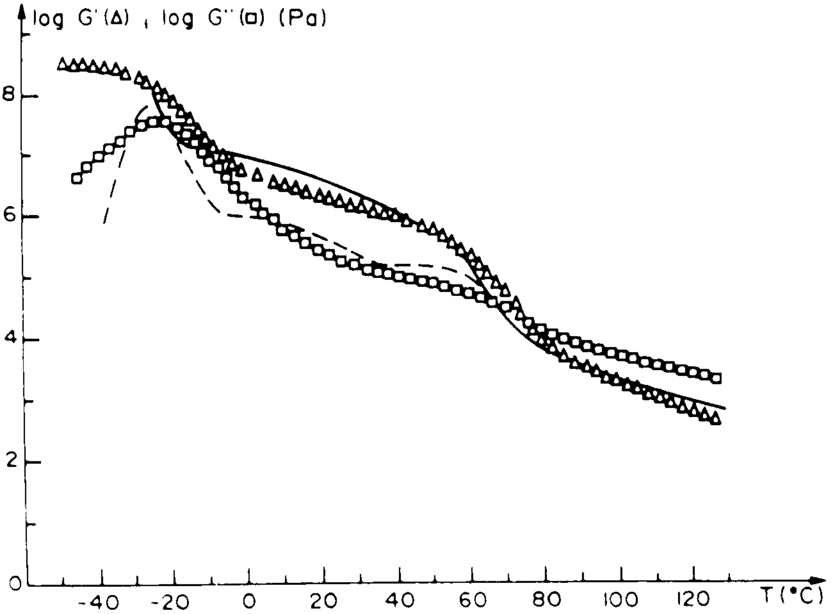

FIGURE 7 Comparison between the experimental TMA (G*(T)) curves and model predictions (full line: G'; dotted line: G''): EBA + resin A (Φ = 0.75).

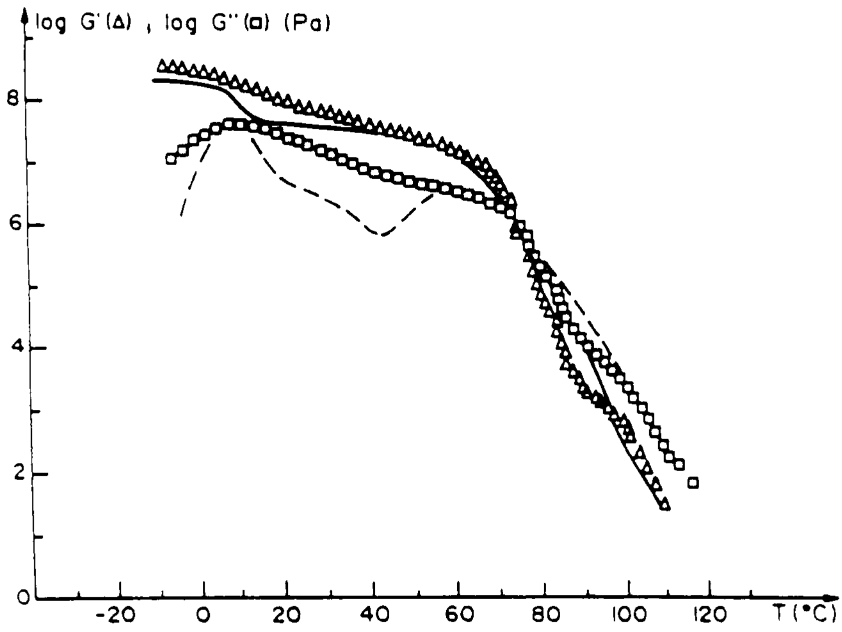

FIGURE 8 Comparison between the experimental TMA ($G^*(T)$) curves and model predictions (full line: G'; dotted line: G''): full formulation EVA + resin A + wax ($\Phi_{EVA} = 0.56$ and $\Phi_{resin} = 0.33$).

composition. We have reported in Figures 9 and 10 the variations of $G'(\omega)$ and $G''(\omega)$ at room temperature for four different formulations of the same EVA copolymer: the experimental data are compared with the computer simulation. The first important point is that it is possible to "guess," with a reasonable accuracy, the rheological behaviour and the glass transition location in the frequency scale when it is not available experimentally. Furthermore, that simulation is done here in the most difficult case, due to the vicinity of the glass transition: a small error in the T_g calculated by the model has a dramatic effect on the viscoelastic curves, hence agreement is much better when the calculation is done at temperatures not too close to the T_g of the formulation.

Finally, it is well known that the rheological curves are directly related to the peeling behaviour of hot-melt and pressure-sensitive adhesives.[12,13,14] If the peeling rate corresponds to times (or frequencies) within the terminal zone of the rheological behaviour, failure will be mostly cohesive. At higher peeling rates, corresponding to the plateau region, a transition to interfacial failure appears; when one gets into the transition (plateau to glassy) region, instabilities referred to as "stick-slip" will generally occur followed by very low values of peeling energy at higher rates (glassy behaviour). The study of the correlation between peeling and rheological properties is beyond the scope of the present paper, but we wish to present, as an illustration of another application of our model, a comparison between the rheological and experimental peeling behaviour of some formulations studied above. The peeling curves on aluminium foils at 25°C are presented in Figure 11; the peeling

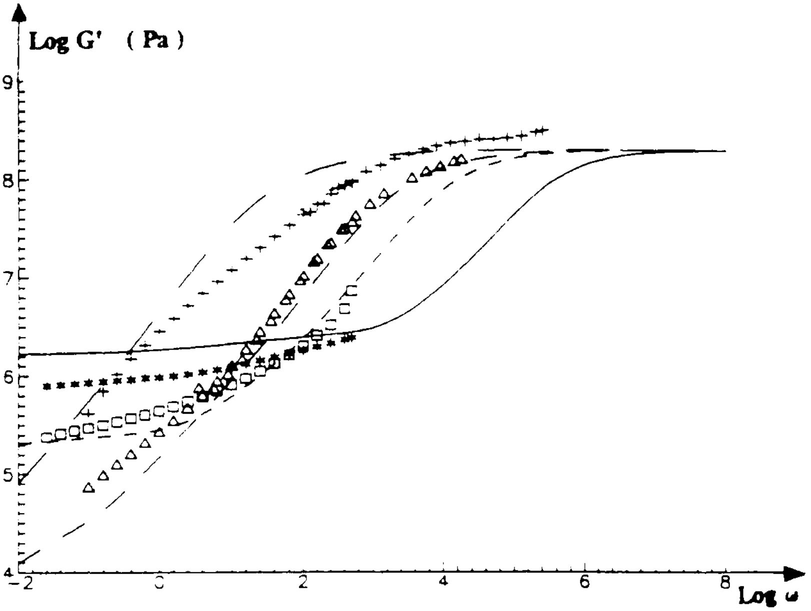

FIGURE 9 Elastic modulus as a function of frequency for four (EVA + resin A) formulations; T = 25°C. (+): Φ = 0.25; (Δ): Φ = 0.375; (□): Φ = 0.50; (*): Φ = 0.75; lines = model.

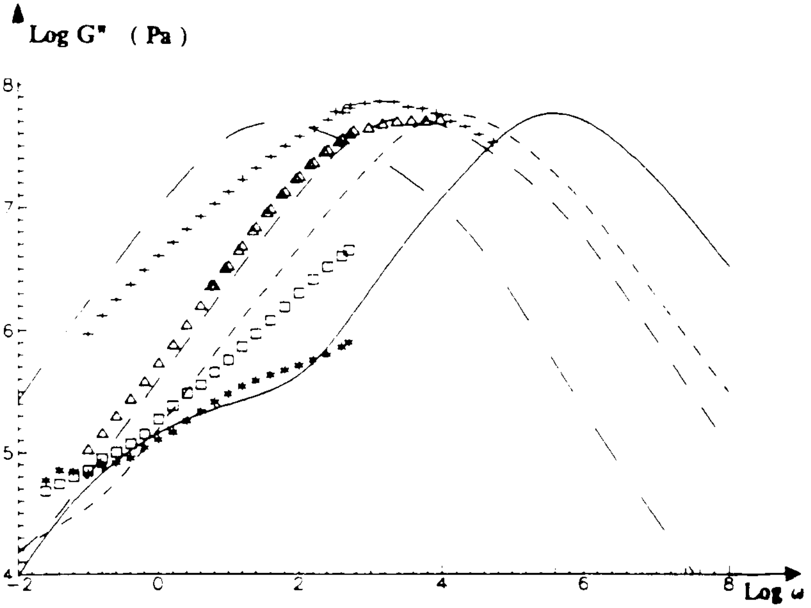

FIGURE 10 Loss modulus as a function of frequency for four (EVA + resin A) formulations; T = 25°C. (+): Φ = 0.25; (Δ): Φ = 0.375; (□): Φ = 0.50; (*): Φ = 0.75; lines = model.

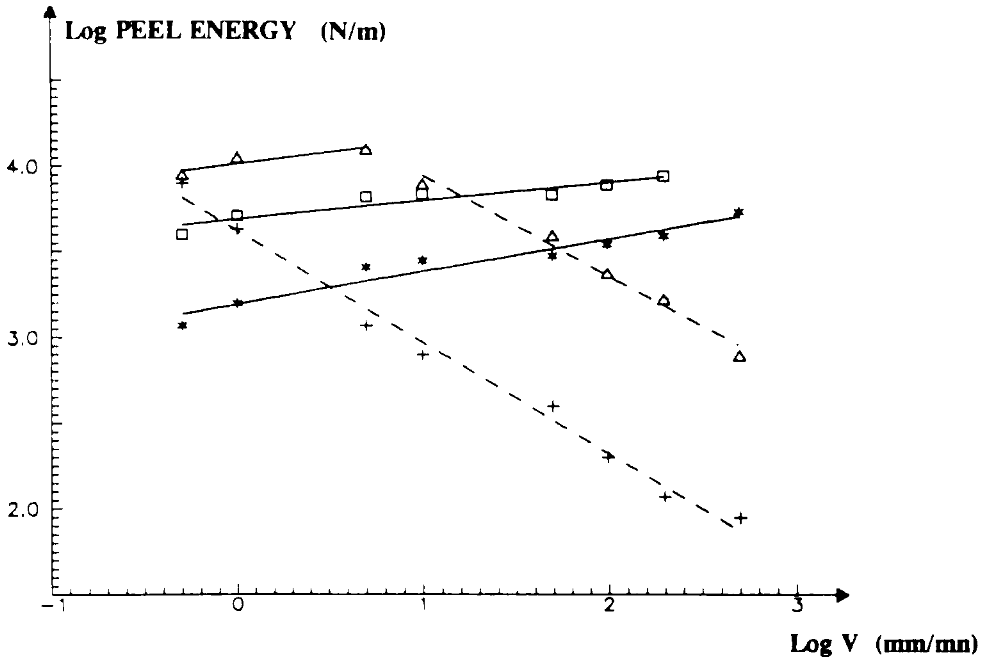

FIGURE 11 Peeling energy as a function of peeling rate at 25°C (EVA + resin A blends). (+): $\Phi = 0.25$; (Δ): $\Phi = 0.375$; (□): $\Phi = 0.50$; (*): $\Phi = 0.75$. Full line: interfacial failure; dotted line: stick-slip.

conditions and experimental setup had been reported before.[7] The corresponding rheological curves are Figures 9 and 10. As expected, there is a direct correlation between the two sets of curves:

- for a polymer volume fraction $\Phi = 0.25$, the viscoelastic behaviour is located in the vicinity of the glassy region, and a "stick-slip" peeling mode is observed.
- for $\Phi = 0.375$, one enters the transition region and a transition of interfacial to instable (stick-slip) failure is observed.
- for $\Phi = 0.5$ and 0.75, the rheological behaviour is rubbery and one obtains interfacial failure with a steady increase of peeling energy with peeling rate.

One observes also that increasing resin content lowers the elastic plateau values and increases the peeling energy values in the stable zone. Therefore, on the one hand, adhesion properties will be improved with resin addition by lowering the plateau modulus; on the other hand, the temperature range of use is strongly reduced because of the increase of T_g. An industrial formulation will hence be a compromise between these two effects. It is clear, however, that rheology is not the whole story as far as adhesion properties are concerned, and that interfacial interactions have to be developed for the bulk and surface rheological properties to play their role. One may assume, however, that when interfacial interactions are of the same order of magnitude (that could be a good approximation for homologous blend series in a limited range of concentrations), the rheological properties will reflect, quantitatively, the differences between adhesion properties. All these features will be developed in a forthcoming paper dedicated specifically to adhesion properties.

CONCLUSION

The physical models of concentrated polymer solutions and melts, as well as polymer blends, can be used to predict such important parameters as the T_g, the melt viscosity and the elastic parameters of HMAs. These parameters are related to the processing and adhesion properties of these materials, and the use of "applications windows" concept gives a direct relationship between thermomechanical curves and product specifications.

The model presented in this paper can be translated into a computation tool to simulate, with a good accuracy, the thermorheological behaviour of a given HMA formulation, given its composition. Furthermore, this model takes into account the content of a crystalline wax and is general enough to be applied to different polymeric bases and different resins.

The next step will be to include this approach in a model of adhesion to describe the peeling behaviour of a given family of HMAs as a function of their composition. It is the feeling of the authors that such simulation tools derived from polymer physics may be of great help to adapt HMA formulations to industrial specifications, avoiding, on the one hand, the approximations of "rule of thumb" methods and, on the other hand, time-consuming, trial-and-error methods to design formulations.

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