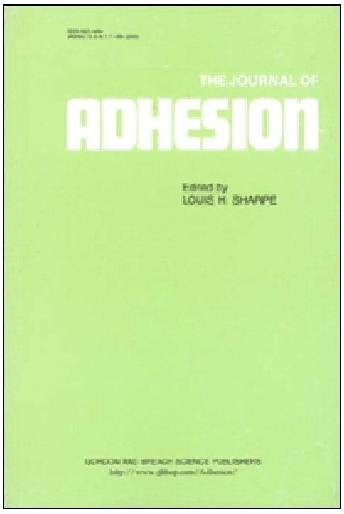

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Rheological Properties of Hot-Melt Adhesives: A Model for Describing the Effects of Resin Content

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Rheological Properties of Hot-Melt Adhesives: A Model for Describing the Effects of Resin Content

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The complex shear modulus of a series of EVA/resin blends has been measured in a broad range of frequencies and temperatures. The variations of the viscoelastic parameters (plateau modulus, limiting compliance, zero-shear viscosity) have been studied as a function of resin content. The addition of small compatible molecules to the polymer has two effects: a topological effect due to the swelling of the entanglement network and a thermodynamic effect due to the increase of the glass transition temperature. It is possible to play on both effects to get the wanted elastic and viscous behavior, as far as process and adhesive properties are concerned. As a consequence, a viscoelastic model is given, allowing one to calculate in a wide range of frequencies (or times) the behavior of these bases of hot melt adhesives, given the composition of the blend and its temperature.

KEY WORDS Ethylene vinyl acetate (EVA)/resin blends; viscoelastic parameters (plateau modulus, limiting compliance, zero-shear viscosity); glass transition temperature; tackifier; plasticization; time-temperature superposition.

INTRODUCTION

The mechanical behavior of non-reactive, polymer-based, hot-melt adhesive joints is strongly influenced by the rheological properties of the adhesive formulation, as widely shown in the literature.[1-5]

In the melt state, the viscoelastic behavior governs the processability of these materials: the viscoelastic parameters determine the ability to allow high production rates, good adhesion properties at short times ("tack", for example), and good creep properties. Each process necessitates a specific range of values for the rheolog-

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ical parameters (viscosity, limiting compliance, plateau modulus, relaxation times), and this may be obtained by a "fine tuning" of the formulation.

In the solid state, besides interfacial interactions, adhesion is also largely governed by the rheological properties of these materials: the peeling energy as a function of peeling rate is a viscoelastic function that roughly obeys the time-temperature superposition principle. For the same family of materials, the rheological properties directly reflect the differences in the adhesion properties.[6]

In the case of hot-melt adhesives, the building-up of cohesion as a function of temperature may be characterized by thermomechanical analysis; this technique leads to practical parameters and criteria[7,8] that may be more pertinent than those derived from thermal analysis (DSC), as far as processing is concerned.

These adhesives are essentially made of blends of a (rubbery) polymer and a tackifying resin that is (at least partially) compatible with the polymeric base. The "art of formulation" proceeds mainly from a practical know-how but also from trial-and-error methods that are time consuming and not efficient in the long-term. This paper applies, to hot-melt adhesives, some methods and models used in the field of polymer rheology. The main idea is to build a rheological model that describes the rheological (topological) and thermodynamic effects of adding a compatible solvent made of small molecules to a polymer. The model has to be predictive, in order to become a useful tool for the formulator: it has to predict the rheological behavior of a formulation from its composition, taking into account the temperature effects. Furthermore, the behavior has to be characterized in a very broad range of times (or frequencies), owing to the very different time scales involved in the processing and adhesion conditions for these materials.

The present paper deals with the effects of resin content on the viscoelastic properties of hot-melts made from an ethylenevinylacetate (EVA) polymer base. The model, derived from previous studies on model (monodisperse) polymers[9] is, however, much more general and may be readily applied to other similar systems.

1. EXPERIMENTAL

1.1 Samples

We have studied a series of 7 samples (including the bulk polymer). The polymer base is an ethylene vinyl acetate copolymer (EVATANE 28420) from the ATOCHEM company; its weight-average molecular weight M_w is 24300 and polydispersity index 2.9. The tackifying resin is a terpene-phenolic resin (Dertophene T) from DRT company. The compositions of the blends are listed in Table I.

1.2 Rheology

Dynamic mechanical experiments were performed with a Rheometrics RDA 700 rheometer in a parallel plate geometry. Platen diameter was 2 cm and sample gap 2mm. Experiments were performed in a temperature range from 0°C to 120°C (above the glass transition temperature of the sample) and a frequency range

TABLE I
Composition and glass transition temperatures of the blends (DSC and TMA)

Sample	Φ EVA Vol. Frac	Tg °C meas. TMA	Tg °C calc. TMA (eq 12)	Tg °C meas. DSC	Tg °C calc. DSC (eq 12)
1	1	-27	-27	-36	-36
2	0.75	-11	-16	-24	-28
3	0.625	-10	-8	-22	-23
4	0.5	5	3	-14	-25
5	0.375	10	16	-10	-6
6	0.25	30	30	9	6
7	0	65	65	38	38

between 10^{-2} and 10^2 rd/s. The experimental data were corrected for instrument compliance that has to be taken into account in the high moduli range.

1.3 Thermomechanical Analysis

The variations of the real (G′) and imaginary (G″) parts of the complex shear modulus at a fixed frequency (10 rd/s) were measured as a function of temperature in the temperature range −50 to +130°C. The experiments were performed in the same geometry as in 1.2, above. The low temperature measurements were made using a liquid nitrogen controller, and sample temperature upon heating was precalibrated at the selected heating rate (5°C/m) locating a thermocouple within a test sample. Temperature uncertainties may be estimated to less than 1°C, taking into account the temperature gradient within the sample. The T_α temperature, corresponding to the maximum of G″(T) is a good thermomechanical image of the glass transition temperature (at the low frequency used here); the "glass transition temperatures" measured by thermomechanical analysis have been listed in Table I.

1.4 Thermal Analysis

Thermal analysis measurements were performed with a Perkin-Elmer DSC-II differential calorimeter. At first, a temperature scan was made on each sample from room temperature up to 150°C at 10°C/m; the sample was cooled down from 150°C to −50°C at a cooling rate of −40°C/mn, then heated up to 150°C at 10°C/mn. The Tg values listed in Table I correspond to values determined upon heating on that last scan.

2. DISCUSSION

2.1 Rheology

The bulk polymer (EVA) is partly crystalline at room temperature and presents a melting temperature of *ca* 68°C.[8] The polymer is thus a viscoelastic solid at room temperature, with a crystallinity ratio of about 20%, and a viscoelastic liquid above the melting temperature. A schematic of the variations of the complex shear modulus of a monodisperse polymer is given on Figure 1 for both cases. In the liquid state, one may observe three regions:[11]

- At the lowest frequencies, the flow region gives the limiting behaviour characterized by three parameters:

—the zero-shear viscosity $$\eta_0 = \lim_{\omega \to 0} \frac{G''(\omega)}{\omega} \tag{1}$$

—the limiting compliance $$J_0^e = \lim_{\omega \to 0} \frac{G'(\omega)}{(G''(\omega))^2} \tag{2}$$

—the terminal relaxation time $$\tau_0 = \eta_0 J_0^e \tag{3}$$

The viscosity and terminal relaxation time values of the referenced samples determined from the above equations are given in Table II; the reference temperature is 110°C. The corresponding compliance values may easily be derived from equation (3).

- At intermediate frequencies the "plateau region" is spanned, where the real part of the modulus changes very slowly with frequency for quasi-monodisperse polymers ($G'(\omega) \simeq G_0^n$). For polymers having a broad distribution of molecular weights, the real part of the complex shear modulus increases steadily with frequency, and a direct determination of G_0^n is difficult to achieve: the experimental variations of $G'(\omega)$ reported on Figure 2 are typical of commercial polymers having a broad distribution of molecular weights. The recent studies on the effects of molec-

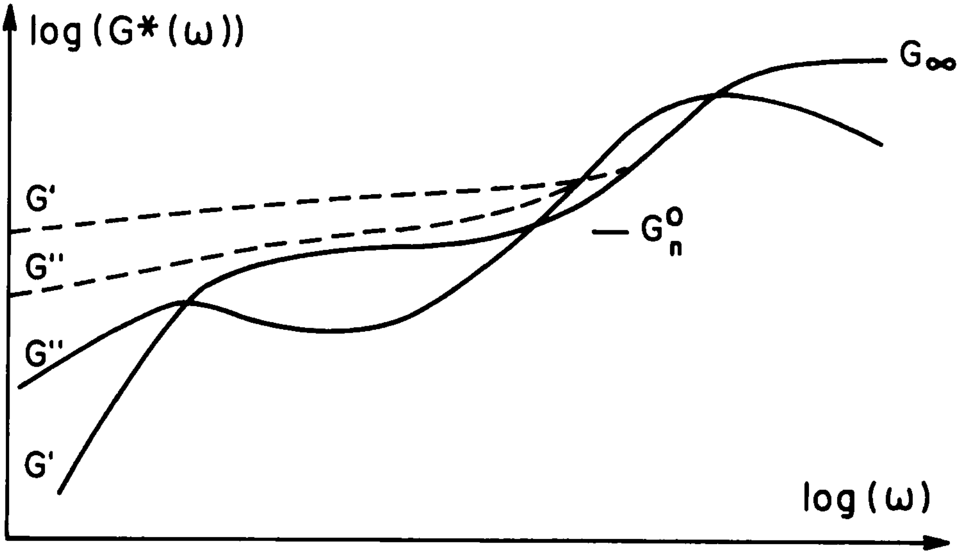

FIGURE 1 Schematic of the variations of the complex shear modulus of a hot-melt adhesive below and above the melting temperature (———: liquid; — — —: solid).

TABLE II
Zero-shear viscosity, average retardation time, terminal relaxation time and plateau modulus of the samples (T = 110°C)

Sample	η_0 (Pa s) 110°C	τ_p (s) 110°C	$\tau_0=\eta_0 J_0^e$ (s)	G_0^n (Pa)
1	226	8.3 10^{-3}	15 10^{-3}	6.28 10^5
2	174	5.8 10^{-3}	10 10^{-3}	5.73 10^5
3	120	4.4 10^{-3}	7.7 10^{-3}	4.07 10^5
4	87.1	3.4 10^{-3}	6.0 10^{-3}	2.28 10^5
5	53.8	2.8 10^{-3}	4.8 10^{-3}	1.07 10^5
6	38.9	2.4 10^{-3}	4.2 10^{-3}	0.45 10^5

ular weight distribution on the viscoelastic properties of linear polymers, using models of molecular dynamics,[12,13] show however that the shapes of the $G'(\omega)$ and $G''(\omega)$ curves in the terminal region of relaxation depend essentially on the shape of the molecular weight distribution (*i.e.* the polydispersity index as a first approximation). In particular, the value G_0 defined as the crossover modulus value at which $G'(\omega)=G''(\omega)=G_0$ (by prolongating the limiting lines with slopes of 2 and 1) is a function of the polydispersity index P only, as a first approximation:

$$G_0=G_0^n\ f(P) \tag{4}$$

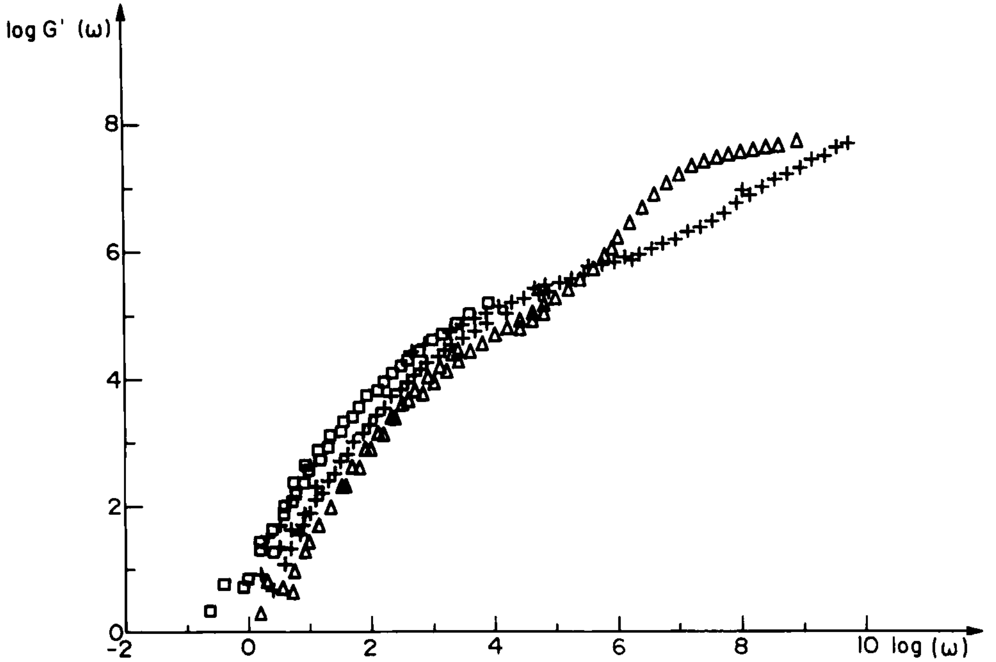

FIGURE 2 Storage modulus G′ as a function of circular frequency for the various blends: master curves at 110°C. (□: $\Phi=1$; +: $\Phi=0.5$; Δ: $\Phi=0.25$).

A compilation of the data related to studies on the rheological properties of linear polymers of various species leads to a "master curve" for the f(P) function. In our case: P = 2.9 and f(P) = 0.15 for the EVA sample, so the plateau modulus of this polymer can be estimated to be $G_0^n = 6.3 \times 10^5$ Pa with a good approximation. The values of the plateau modulus of the various samples are given in Table II.

- The viscoelastic behavior in the "transition region" between the rubbery (plateau) region and the glassy region has been experimentally measured for the three samples having the highest resin content: in that case the glassy relaxation gets closer to the terminal relaxation, because of the increase of the glass transition temperature, Tg. Whereas the viscoelastic behavior in the terminal and plateau regions differs in the liquid (high temperatures) and solid (low temperatures) states, the behavior in the transition region is poorly affected by the small amount of crystallinity when going from a liquid to a solid (because the glassy modulus G_∞ is 2 to 4 orders of magnitude higher than the elastic modulus of the polymer in the melt or elastic state above Tg (see Fig. 1), so the time-temperature superposition principle may be approximately applied in the transition region within the whole experimental temperature range above Tg for all samples.

We have reported on Figures 2 and 3 the master curves of G′(ω) and G″(ω) characterizing the liquid state (T>Tg, and no crystallinity) for all samples. The reference temperature is 110°C, and the horizontal (frequency) shift factors log

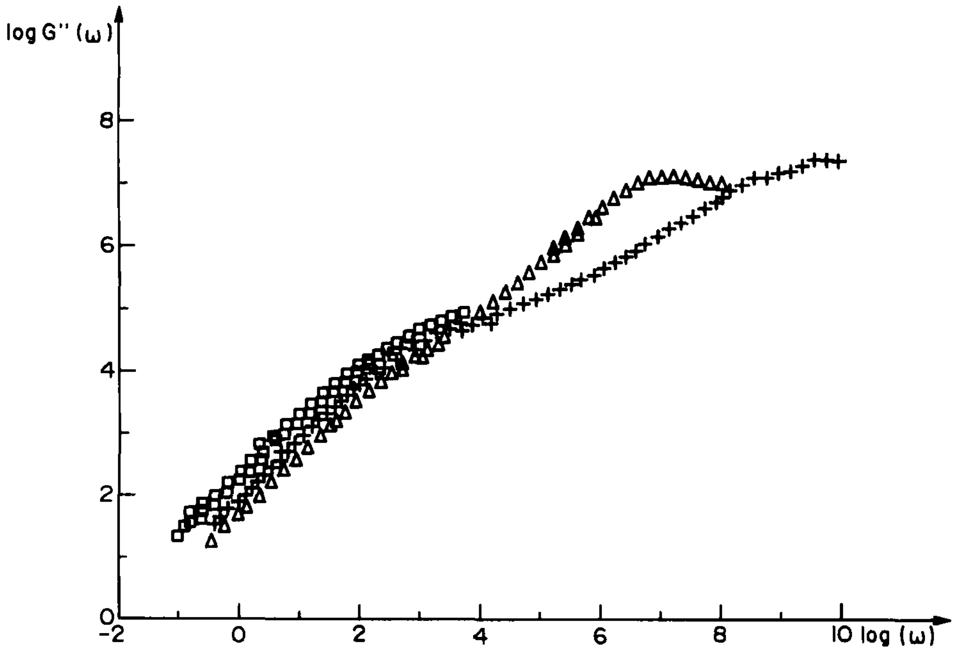

FIGURE 3 Loss modulus G″ as a function of circular frequency for the various blends: master curves at 110°C. (□: Φ = 1; +: Φ = 0.5; Δ: Φ = 0.25).

a_T[11,15] may be fitted by the WLF parameters reported in Table III and determined by a least squares method:

$$\log a_T = (B_T/2.303)\,(1/(T_0 - T_\infty) - 1/(T - T_\infty)) \qquad (5)$$

T_0 is the reference temperature (here 110°C).

The master curves have been drawn using the experimental data obtained (i) in the transition region at all temperatures; (ii) in the terminal region only above the melting temperature. No vertical shift has been made, so the plateau modulus and limiting compliance may be considered as independent of temperature within the temperature range of the study. One may observe that the plateau modulus is decreased as resin content increases, whereas viscosity is lowered at high resin content. The polymer viscosity is decreased with resin addition at high temperatures, but the viscosity of the polymer/resin blends may be higher than the viscosity of the bulk polymer at lower temperatures, because of the Tg increase (see § 3, below). Because of the same (Tg) effect, the transition region shifts towards lower frequencies as resin content increases, and the resulting higher coupling between the transition and terminal relaxations results in an increase of $G'(\omega)$ at intermediate frequencies; that effect may counteract the plateau lowering due to the swelling of the entanglement network in that frequency range, and good adhesion at small and intermediate times will be a compromise between both effects. In other words, the "tackifying" effect of the resin may be affected if its content is too high.

2.2 Thermal and Thermomechanical Analysis

The glass transition temperatures determined by DSC and the T_α temperature obtained from thermomechanical analysis are reported in Table I. The corresponding values are plotted as a function of polymer volume fraction on Figure 4. There is a good correlation between both determinations of Tg for the pure EVA sample as well as for the blends, taking into account the arbitrary definition of the glass transition temperature and its dependence on the time scale of measurement. The discrepancy between the mechanical and thermal measurements is known to be greater for small molecules, as evidenced for the pure resin studied here.

3. DATA ANALYSIS AND MODEL

3.1 Topological and Thermodynamic Effects

We have to take into account two types of effects due to the addition of small molecules to a polymer. On the one hand there will be topological effects of the solventlike additive that will "swell" the entanglement network; this effect may be accounted for by the models of molecular dynamics.[12,13,14,15] In the tube model and its derivatives, the concentration dependence of the plateau modulus, limiting compliance and zero-shear viscosity due to the tube enlargement are precisely described. On the other hand, the Tg of the resin being higher than the Tg of the polymer, the resin acts as an "antiplasticizer" and shifts the glass transition of the

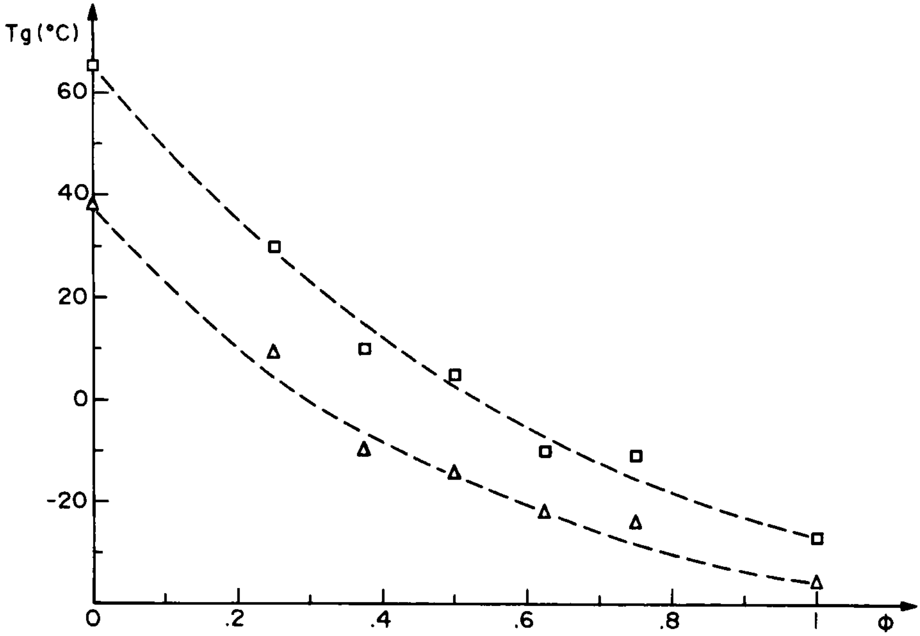

FIGURE 4 Glass transition temperatures measured by DSC (Δ) and TMA (□); (dotted line -----: theory, eq 12).

blend to values above the Tg of the polymer. This thermodynamic effect will lead to higher values of the friction coefficient at the same temperature. These two counteracting effects may be illustrated by writing the zero-shear viscosity as:

$$\eta_0 = S(P(M); \Phi)\ \mathrm{Mob}(T - Tg(\Phi)) \qquad (6)$$

The S term is a structure factor depending on the molecular weight distribution of the sample P(M)[12,13] and on the polymer volume fraction in the blend Φ. The Mob term is a mobility factor that describes the temperature dependence on the friction factor and hence the viscosity. In the case of glassy polymers, equation 6 is equivalent to the WLF equation:[11]

$$\log \eta_0 = A_\eta/2.303 + B_\eta/(2.303(T - T_\infty)) \qquad (7)$$

$$\text{with:}\quad \mathrm{Mob} = \exp(B_\eta/(T - T_\infty)) \qquad (8)$$

$$\text{and}\quad S = \exp(A_\eta)$$

T_∞ may be related to Tg by the approximate relation: $Tg - T_\infty = 60°C$, that holds true for a very large number of polymers.[11] The B ($B = B_\eta = B_\tau$) factor may be related to the free volume expansion factor α_f of the glass transition theories:[9,11]

$$B = 1/\alpha_f \qquad (9)$$

$$\text{and}\quad f(T) = f_g - \alpha_f\ (T - Tg)$$

f(T) being the free volume at temperature T, and f_g the free volume at $T = Tg$. The free volume expansion factor α_f (hence the WLF B factor) may be assumed to be independent of Φ in the case of concentrated polymer solutions, so the T_∞ (Φ) function contains all the information on the plasticizing effect of the small molecules.

We have calculated by a least squares method the B and T_∞ values from the temperature dependence of the viscosities and frequency shift factors, and the results obtained are reported in Table III. As there is a strong coupling between the values of B and T_∞ determined by a least squares method for each sample, an average value of B has been first estimated from all the samples data, then a least squares value of T_∞ has been estimated for each sample using that average B value in order to reduce the numerical scatter on T_∞. The B and T_∞ values calculated from the viscosity and frequency shift factors are the same within experimental uncertainty and the same observation could be made for the temperature shift factors of the relaxation times τ_p and τ_0. Besides, the hypothesis that the B factor does not depend on Φ in that concentration range seems reasonable (its average value is $B_{av}/2.303 = 672$). Taking into account the T_∞ values obtained by both methods, one may observe that the rule:

$$Tg - T_\infty = 60°C \tag{10}$$

is approximately obeyed in the case of these EVA/resin blends (see Table III), and this relation may be used to predict the temperature dependence of viscosities and relaxation times from a Tg value determined by DSC. Furthermore, if one assumes additivity of the free volume of the polymer and resin, including a coupling term:[9]

$$f_{blend} = \phi\, f_1 + (1-\phi)\, f_2 + k\phi(1-\phi) \tag{11}$$

one ends up with the following blending law for Tg:[9]

$$T_g = \frac{\phi\, \alpha_{1f} T_{g1} + (1-\phi)\, \alpha_{2f} T_{g2} - k\phi(1-\phi)}{\phi\, \alpha_{1f} + (1-\phi)\, \alpha_{2f}} \tag{12}$$

where f_1 and f_2 are the free volumes, α_{1f} and α_{2f} the free volume expansion coefficients, of the polymer (index 1) and solvent. In our case, we assumed that the free

TABLE III

WLF parameters for shift factors and viscosities obtained by least square fitting of experimental viscosities and frequency shift factors (eq. 5 and 7)

Sample	$B_\eta/2.303$	$B_\tau/2.303$	T_∞ (°C) from viscosity	T_∞ (°C) from shift factor	$T_g - 60°C$
1	747	715	−82	−78	−87
2	730	721	−74	−66	−76
3	635	630	−81	−76	−68
4	706	617	−58	−59	−57
5	711	607	−44	−46	−45
6	680	564	−32	−34	−30

volume expansion of the polymer and solvent are the same, which is a reasonable approximation for highly concentrated polymer solutions. So $\alpha_{1f} = \alpha_{2f} = \alpha_f = 1/B$.

This law had been applied earlier to the case of the study of rheological properties of model anionic polybutadienes in various solvents,[9] and gives for our EVA/resin blends a good fit with the experimental data as seen on Figure 4, with the same coupling factor k ($k = 3 \times 10^{-2}$) as for polybutadiene in an aromatic oil. The dotted lines on Figure 4 have been calculated from equation (12). As we can calculate from the model the concentration dependence of the glass transition temperature (hence of T_∞), the concentration and temperature dependences of the mobility factor (or friction factor) are now defined.

The calculation of the mobility factor allows the derivation of the true structure factor, that it is not possible to evaluate from isothermal measurements (the structure factor S(Φ) should be calculated at the same segmental mobility or "iso free volume", *i.e.* at the same values of Mob(Φ)). We have reported on Figure 6 the variations of the structure factor η_0/Mob as a function of polymer volume fraction: the experimental power law exponent of 3.42 is to be compared with the theoretical exponent of 3–3.4 and the experimental exponents of 3 to 4 obtained from previous studies on the rheological properties of concentrated polymer solutions.[9–13]

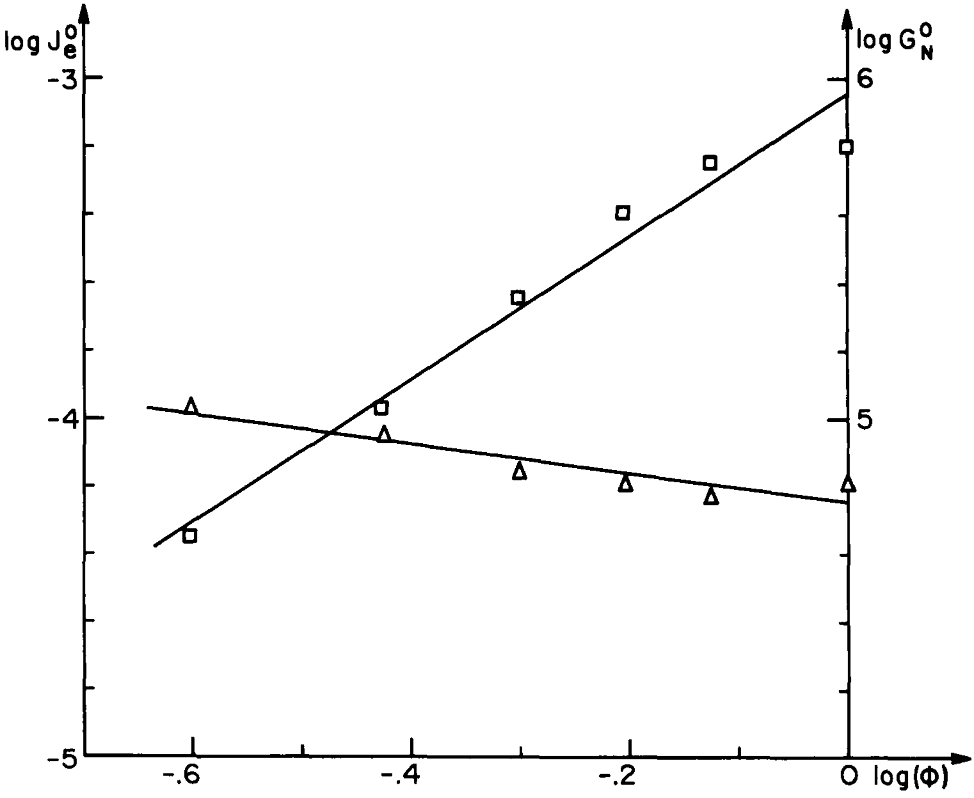

FIGURE 5 Plateau modulus (□) and limiting compliance (Δ) as a function of polymer volume fraction.

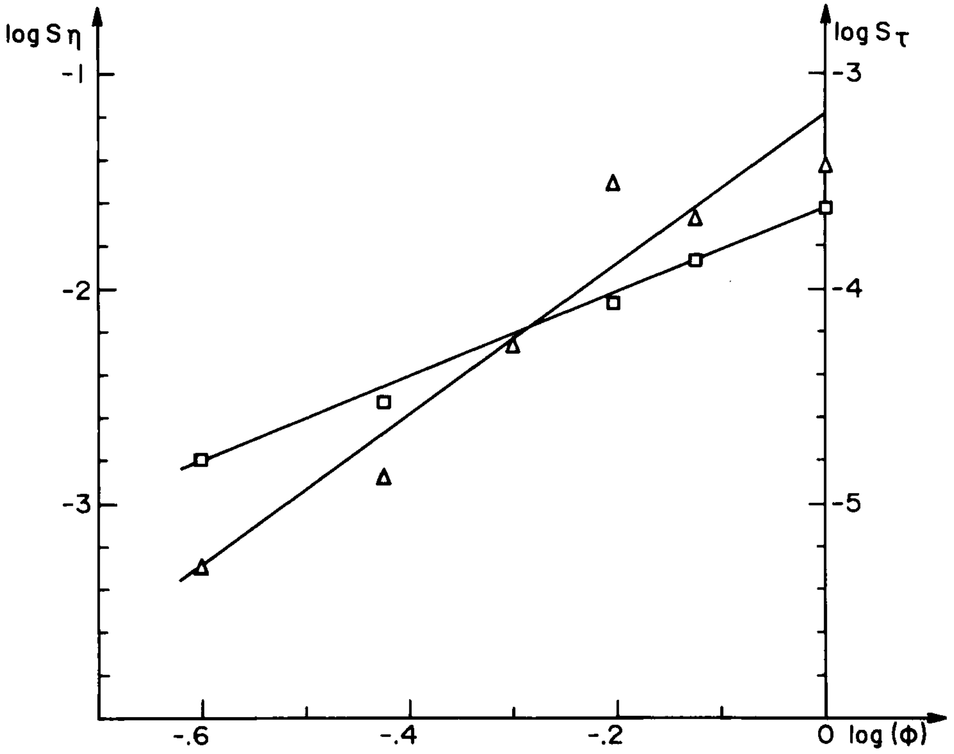

FIGURE 6 Structure factors S_η (Δ) and S_τ (□) for the viscosity and terminal relaxation time τ_0 ($= \eta_0 J_0^e$) as a function of polymer volume fraction.

The variations of the plateau modulus and limiting compliance as a function of polymer volume fraction are reported on Figure 5 as a log-log plot. The exponent of 2.06 of the power law obtained for the plateau modulus is close to the theoretical values of 2/2.25.[9,10,13] The experimental slope of -0.43 obtained for the limiting compliance J_0^e is far from the expected value (-2), but the experimental determination of the limiting compliance is very difficult: the limiting slope of 2 on the log-log plot of $G'(\omega)$ is reached at very low levels of moduli, where experimental errors are large (Fig. 2 and 3), and one is not sure that one is truly in the limiting behavior range. Furthermore, the determination of J_0^e involves uncertainties in both G' and G'' values (eq. 2).

One may say, as a conclusion of this part, that rheological and thermal measurements demonstrate the topological and thermodynamic miscibility to a large extent for the resin and the polymer studied here.

3.1 Rheological Model

The rheological model is based on previous studies of the rheological properties of model linear polymers.[14] The experimental data from mechanical spectroscopy may be fitted in a very large frequency range from the terminal region up to the glassy region by an equation giving the complex compliance (reciprocal of the complex shear modulus: $J^*(\omega) = 1/G^*(\omega)$) as a function of frequency:

$$J^*(\omega) = \frac{1}{j\omega\eta_0} + J_p^*(\omega) + J_t^*(\omega) + J_\infty \qquad (13)$$

$$J^*(\omega) = \frac{1}{j\omega\eta_0} + \frac{J_p}{(1+j\omega\tau_p)^{1-\alpha}} + \frac{J_t}{(1+j\omega\tau_t)^{1-\beta}} + J_\infty$$

The first term of the right hand side of eq. (13) is a flow term that disappears for viscoelastic solids, $J_p^*(\omega)$ represents the terminal retardation domain (low frequencies) and $J_t^*(\omega)$ the retardational behavior in the transition and plateau regions. η_0 is the zero-shear viscosity, τ_p the average relaxation time of the terminal region, τ_t the retardation time of the transition region; J_t is the reciprocal of the plateau modulus (J_n^0) in the case of monodisperse samples, and J_∞ the reciprocal of the glassy modulus ($J_\infty \approx 10^{-9}$ Pa for all organic glasses). The limiting compliance is related to J_t and J_p by the equation:

$$J_0^e = J_p + J_t \qquad (14)$$

The characteristic retardation times τ_p and τ_t are given by the reciprocal of the frequencies corresponding to the maxima of the retardational compliance ($J''(\omega) - 1/\omega\eta_0$) in, respectively, the terminal and transition regions;[14] the variations of τ_t describe how the glass transition shifts as a function of resin content, and the average retardation time of the terminal region τ_p is simply proportional to the longest relaxation time τ_0 (see Table II). The α and β parameters describe the dispersion of retardation times in the two domains, and their values are independent of temperature and blend composition ($\alpha = 0.13$ and $\beta = 0.25$; a single retardation time would correspond to $\alpha = 0$). The Cole-Cole analysis of the complex compliance and the numerical determination of the parameters of equations (13) proceed from a classical analysis of complex functions in the complex plane in physics (in exactly the same way as for dielectric studies, for example) and have been described earlier.[13,14] The Cole-Cole domains of the initial model[14] have been replaced here by Davidson-Cole equations that give a better fit in the transition region and allow an analytical derivation of the creep function J(t). These features will be developed in a further article.

As an example, a comparison between model predictions and experimental data is given in Figures 7 and 8 for samples having 25% and 38% resin.

The important point here is that the elastic parameters (compliance, plateau modulus) depend only on the polymer/resin ratio in the high polymer concentration range (that is always the case for PSA and hot-melt adhesives), whereas the viscosity and relaxation times are strongly influenced by the shift of the glass transition temperature. As the variations of all parameters in equation (13) are known, it is possible to predict with a good accuracy the rheological behavior of a formulation, given its composition. The only data used to calculate the theoretical lines of Figures 7 and 8 are the temperature and resin content. This should allow one to get the desired thermomechanical and viscoelastic properties of hot-melt or PSA formula-

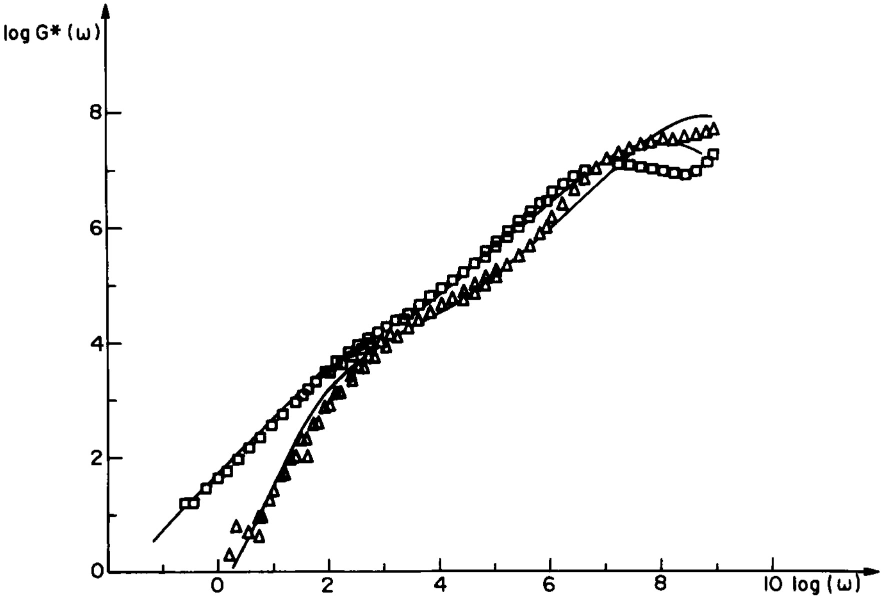

FIGURE 7 Comparison between the experimental shear modulus and model predictions for the sample with Φ = 25% polymer content (T = 110°C) (Δ: G′, experimental; □: G″, experimental; ——: model, eq 13).

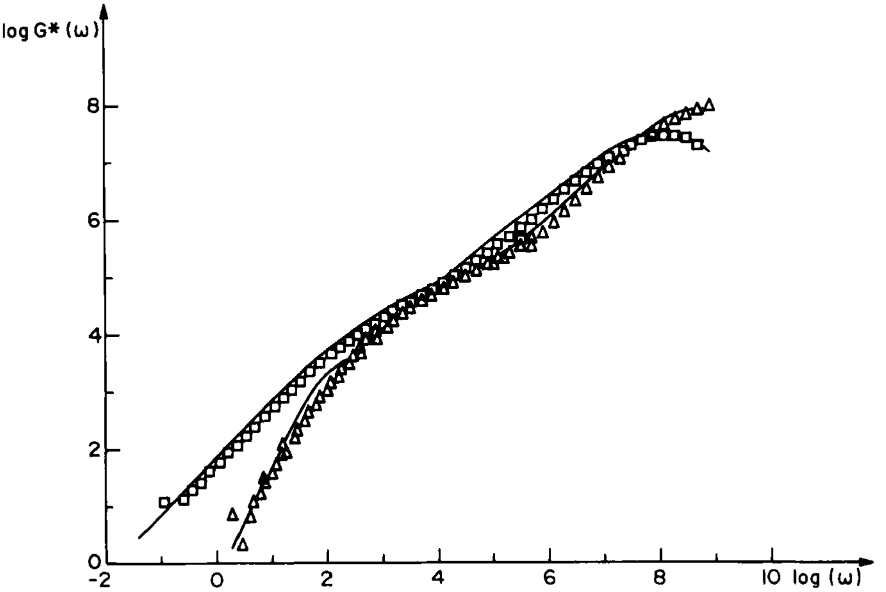

FIGURE 8 Comparison between the experimental shear modulus and model predictions for the sample with Φ = 37.5% polymer content (T = 110°C) (Δ: G′, experimental; □: G″, experimental; ——: model, eq 13).

tions, by varying the contents of resin and plasticizer, in particular to get the desired plateau modulus level along with an adequate glass transition temperature.

Industrial formulations do also include plasticizers (and their effects may be readily explained and calculated using the thermodynamic model given in this paper) and crystalline waxes that mainly control the setting temperature and increase the elastic modulus. These particular effects of waxes will be studied in a future paper.

CONCLUSION

The linear viscoelastic properties of hot melt adhesives in the melt state depend on the nature of the polymer base and the nature and concentration of the tackifying resin. The elastic properties (plateau modulus, limiting compliance) depend only on the polymer concentration, independently of the resin nature, at high polymer content, provided the system is compatible to a large extent. On the other hand, the effect of adding resin changes the viscosity and relaxation times in two aspects: on the one hand, the topological effects may be characterized by the concentration parameter only (structure factor), but the change of the glass transition temperature can increase or decrease the viscosity (plasticizing or antiplasticizing effect), depending on whether the Tg of the resin is, respectively, below or above the Tg of the polymer. In the antiplasticizing case, the topological and thermodynamic effects have a counteracting effect as far as viscosity is concerned. So it is possible to play on both sides to have the desired values of viscosity and elasticity. The rheological model presented here integrates all these aspects in a predictive approach that may be a useful tool for the adhesive industry. Furthermore, the equation given here for the complex compliance or modulus may be used to derive easily the viscoelastic functions in the time domain (creep function J(t) or relaxation modulus G(t)) from the integral relations of linear viscoelasticity. All these viscoelastic functions may also be included in various models of adhesion (peeling, tack), and this will be the topic of later publications.

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References

1. A. N. Gent, R. P. Petrich, *Proc. Roy. Soc.* **A310,** 433 (1969).
2. D. H. Kaelble, *J. Coll. Sci.* **19,** 433 (1964).
3. D. H. Kaelble, *J Adhesion* **1,** 102 (1969).
4. G. Kraus, K. W. Rollman, C. A. Gray, *J. Adhesion* **10,** 221 (1979).
5. J. Schultz, A. Gent, *J. Chimie Physique* **5,** 708 (1973).
6. A. Zosel, *Colloid and Polymer Science* **263,** 541 (1985).
7. D. W. Bamborough and P. M. Dunckley, *Adhesives Age* **33**(12), 20 (1990).
8. J. Komornicki, M. Bourrel, G. Marin, M. Brogly, "Rheology as a support to formulation of EVA based Hot-Melt adhesives." Submitted to *J. Adhesion Sci. & Technol.* (1991).

9. G. Marin, E. Menezes, V. R. Raju and W. W. Graessley, *Rheol. Acta* **19,** 462 (1980).
10. V. R. Raju, E. V. Menezes, G. Marin, W. W. Graessley and L. Fetters, *Macromolecules* **14,** 1668 (1980).
11. J. D. Ferry, *Viscoelastic Properties of Polymers, 3rd Ed.* (Wiley, New York, 1980).
12. J. P. Montfort, G. Marin and Ph. Monge, *Macromolecules* **19,** 1979 (1986).
13. G. Marin, "Polymer Rheology: recent developments in molecular dynamics" in *Research Trends* (in press).
14. G. Marin and W. W. Graessley, *Rheol. Acta* **16,** 527 (1977).
15. G. Marin, J. P. Montfort and Ph. Monge, *Rheol. Acta* **21,** 449 (1982).