

**ISOCHRONE VISCOELASTIC FUNCTIONS VIA ACTIVATION ENERGY OF
FLOW – CHARGE TRANSFER COMPATIBILIZED POLYBLENDS**

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SYNOPSIS

It is shown that charge transfer interaction in polymer systems enlarges the rubber plateau and contributes to stabilization of incompatible polymer blends.

**1. BACKGROUND TO THE ACTIVATION ENERGY OF
FLOW**

Based on Boltzmann's superposition principle viscoelastic functions are expressed in terms of the relaxation

time distribution function – relaxation time spectrum – $H(\tau)$, which is normalized by the zero shear viscosity

$$\eta_0 = \int_0^{\infty} H(\tau) d\tau = \int_0^{\infty} \tau H(\tau) \ln \tau \quad (1)$$

Because of the time scale involved the logarithmic formalism is preferred.

The temperature invariance of the relaxation time spectrum is the main condition of the time-temperature superposition principle which governs the shift procedures for getting composite curves of viscoelastic functions. Taking into account the temperature function of the zero shear viscosity predicted by Eyring's transition state theory

$$\eta_0 = A \exp(E/RT) \quad (2)$$

the temperature invariance of $H(\tau)$ implies identical temperature dependence for all relaxation times.

The shift factor of isotherms, $a_T = \tau(T)/\tau(T_0)$, can then be expressed:

$$\begin{aligned} \log a_T &= (\log \tau - \log \tau_0) = (\log \omega_0 - \log \omega) = \\ &= \frac{E}{2.3R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \end{aligned} \quad (3)$$

It is evident that a logarithmic time difference – $\log a_T$ – for isotherms, IT, is equivalent to a reciprocal temperature difference – $a_F = \Delta(T)^{-1}$ – for isochrones, IC^{1,2}.

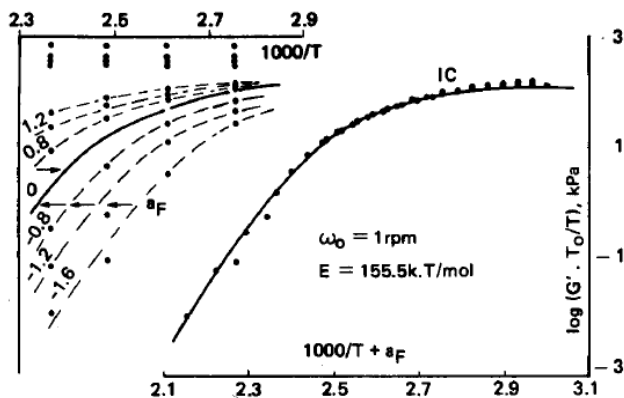
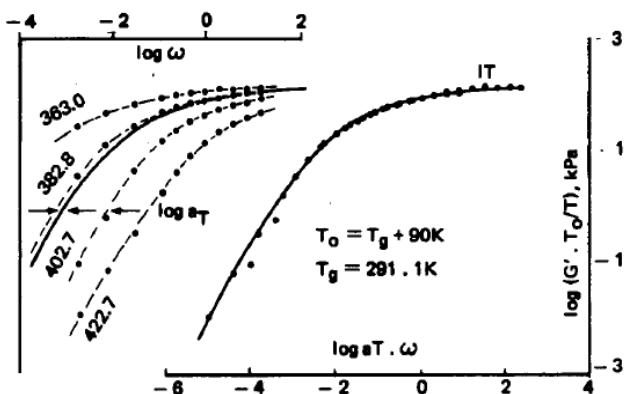


Fig. 1 Composite curves of the storage modulus G' of PMBA-A_{10%}

This is demonstrated in Fig. 1 for the storage modulus, G' , in the terminal zone of an acceptor group containing poly (butylmethacrylate). Both the shifts are performed assuming constant activation energy as predicted by the Eyring model of viscous flow.

Starting with the observation that in accordance with (3) the activation energy of flow is given by the ratio of the two shift factors, $\log a_T/a_F$, it can be easily shown (Fig. 2) that this corresponds also to the slopes in a given point of the crossing isochrone and isotherm viscoelastic curves, respectively³

$$\frac{(\delta \log G' / \delta (1/T))_{\omega}}{(\delta \log G' / \delta \log \omega)_T} = \frac{E(T)}{2.3 R} \quad (4)$$

Temperature invariant activation energy is not imposed by relation (4), and taking into account that approaching T_g temperature dependent activation energy is predicted by the WLF relation

$$E(T) = 2.3RT_0 c_1^0 T / (c_2^0 + T - T_0) \quad (5)$$

equation (4) is formulated correspondingly.

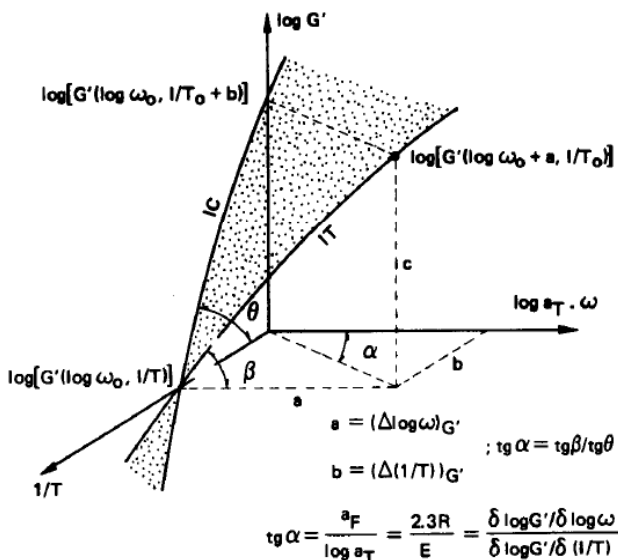


Fig. 2 Interrelation between IT and IC curves of viscoelastic functions.

In the terminal zone of constant activation energy a smooth surface of the viscoelastic functions in the log frequency – reciprocal temperature space is obtained³. Approaching T_g the surfaces become wavy as evidenced in Fig. 3 for a head-to-head PVC of $M_w = 30,000$.

Although the WLF relation predicts, in accordance with (5), a steady increase only of the activation energy, a decrease of $E(T)$ is observed near T_g^2 . This is in accordance with suggestions of failure of the WLF relation very near T_g^4 .

As it has been shown, $E(T)$ relates also the relaxation time spectrum with a corresponding reciprocal relaxation – temperature spectrum⁵.

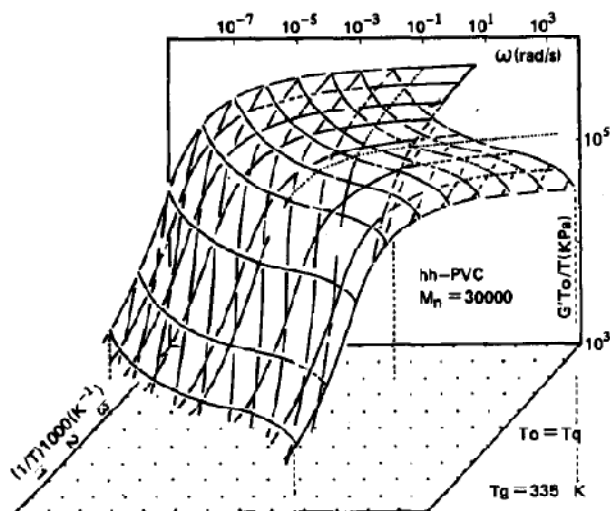


Fig. 3 Viscoelastic surface of hh-PVC in the T_g range

2. RESULTS AND DISCUSSION

2.1 Compatible blends

Data concerning the rheological behaviour of a compatible polyblend, illustrated for the storage modulus, are shown in Fig. 4 for a 1:3 w/w blend of Polystyrene (PS, $M_w = 75,000$, $T_g = 373K$) and Poly (vinylmethylether) (PVME, $M_w = 73,000$, $T_g = 237K$). It is demonstrating that the isochrone composite curve of the blend is situated in the temperature range between the two components. Analogous the isotherm composite curve is situated in a frequency range between the components, with a tendency towards PVME.

If the IT composite curves are shifted to contact at the same G_N -value, (Fig. 5), the flatter slope of the blend suggests an increase of the polydispersity of the relaxation

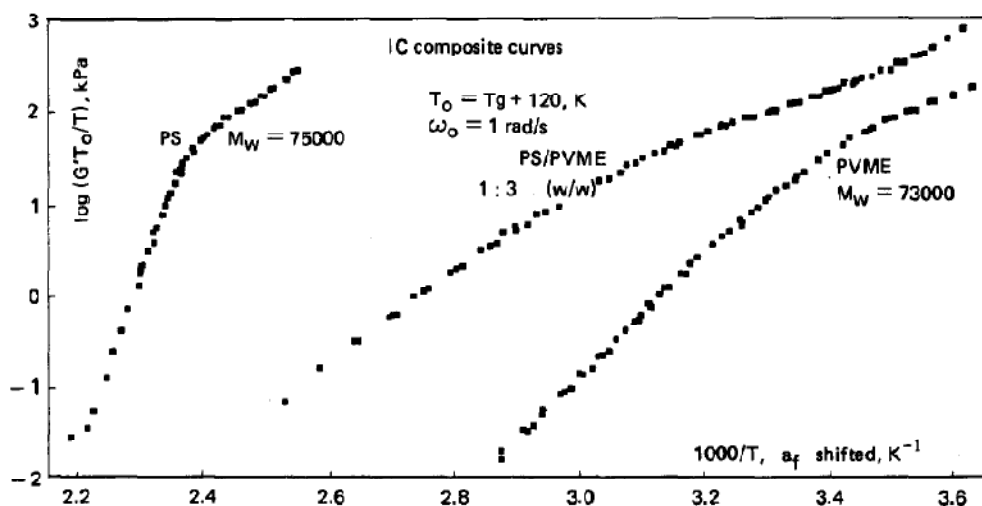


Fig. 4 IC composite curves of the compatible PS/PVME blend

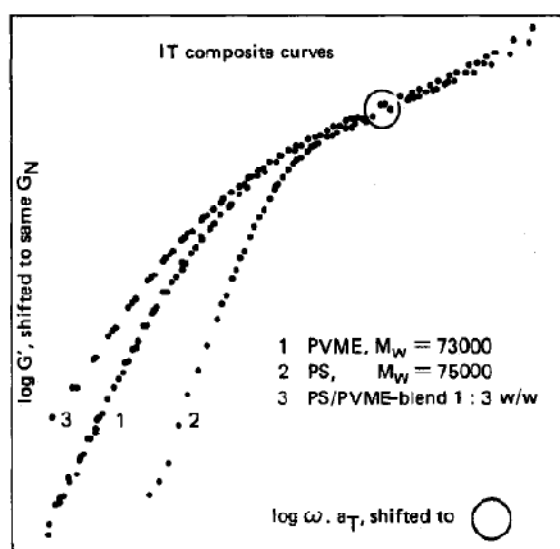


Fig. 5 IT composite curves of the PS/PVME system shifted to contact at same G_N -value.

process in the compatible blend. The respective characteristic $\log(J_e^0 G_N)$ values are 0.02 for the PS, 1.27 for the PVME and 2.86 for the blend.

Charge transfer (CT) – interaction of electron donor (D) and electron acceptor (A) groups generally extends the rubber plateau in compatible blends⁶.

For illustration data of the 1:1 mole blend of random copolymers of Poly (butylmethacrylate) – PBMA – with 10% mole of D 2-(3,5-dinitrobenzoyl) ethyl methacrylate and A 2-(9-carbazolyl) ethylmethacrylate, respectively, are presented in Fig. 6.

2.2 CT-compatibilization

CT-interaction may be applied also for stabilization of incompatible polyblends. This is demonstrated for both the blends of PBMA with Poly (methylmethacrylate) -PMMA- and Poly-(dimethylsiloxane) -PDMS⁷. Comparison

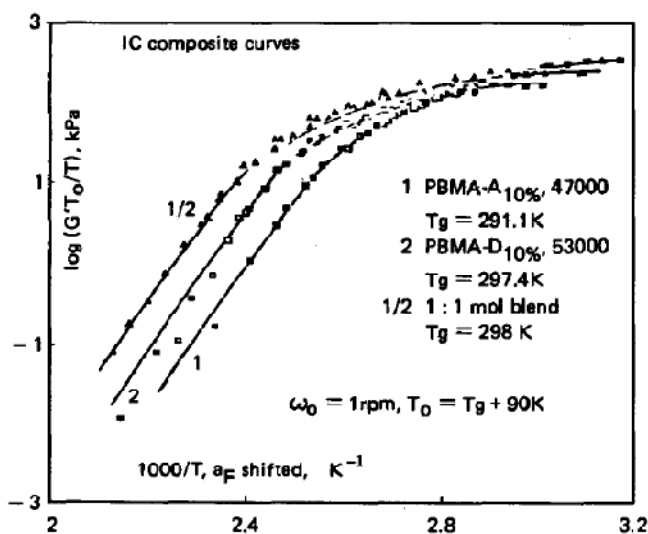


Fig. 6 IC composite curves of the PBMA-system in the terminal zone

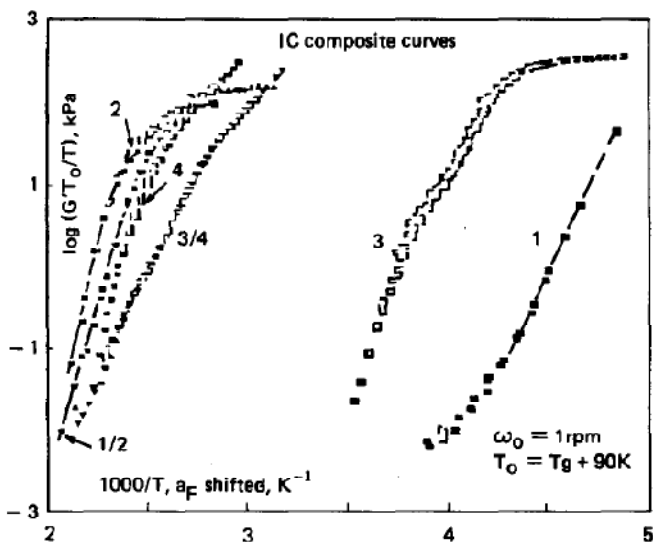


Fig. 7 IC composite curves of the incompatible PBMA/PDMS system.

of the rheological behaviour of incompatible polyblends of random and blockcopolymers containing D and A groups respectively, suggests a stronger CT-effect in the blend of random copolymers as seen in Fig. 7. The notations stand for:

- 1 - random PDMS-A₁₀%, $M_n = 7,500$, $T_g = 157.5K$,
- 2 - PBMA-D₁₀%, $M_w = 53,000$, $T_g = 291.1K$,
- 3 - $\frac{A}{A}$ PDMS $\frac{A}{A}$ a PDMS, $M_w = 30,000$ with two A-endgroups on both the chainends and 4- a triblock (D)₁₅-PBMA-(D)₁₅ M_w of the PBMA of about 50,000. Both the blends 1/2 and 3/4 are of 1:1 A/D-ratio.

ACKNOWLEDGEMENTS

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