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Surface Tension and Viscosity Studies of Molten Resins for Thermoplastic Recording*

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Synopsis

Analytical and experimental studies of surface tension and viscosity properties of Dow resins PS-2 and 276V-2 are described. This investigation was undertaken to provide information on materials of interest for thermoplastic recording. It was found that external plasticization lowered the surface tension of the polystyrene while greatly decreasing the viscosity. Typical values for a 25% mixture of PS-2 in 276V-2 are $\gamma = 35$ dynes/cm. and $\eta = 20$ poise at 80°C.

Introduction

Thermoplastic recording of electrical charge patterns has been reported by Glenn and Wolfe[1] to be a relatively simple, dry method utilizing optical readout. Recordings in black and white and color of television and radar displays have been demonstrated. However, the lack of information on surface tension and viscosity for thermoplastics useful in this application limited the value of analytical studies of surface deformation. The work reported here was initiated to correct partially this condition.

Surface Tension of Thermoplastic Melts

In this investigation, the surface tension of thermoplastic melts was measured by means of a precision Jolly balance. A wire frame, as in Figure 1, was immersed in the melt to be tested. The method is described in many basic texts.

The surface tension of the thermoplastic melt decreased with increasing temperature, as shown in Figure 2. Values for water, and carnauba and opal wax are included for comparison.[2]

The data obtained on molten resins by the tensiometer method can only be considered as approximate because of errors introduced by stickiness of the melt, especially as the temperature approaches solidification. Other errors are introduced, because the film is relatively cooler than the melt due to lack of temperature control, although a crude aluminum foil enclosure was used to insure against very large temperature gradients. The

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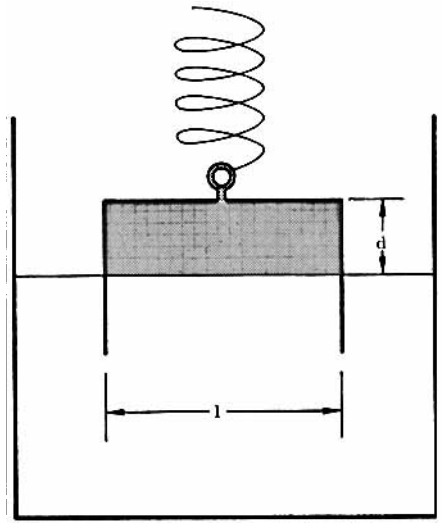

Fig. 1. A method for measuring surface tension.

weight of the wire pulled from the surface is also uncertain due to drops of adhering melt.

The surface tension of binary mixtures (75/25 and 50/50 ratios) of molten Dow resins 276V-2 and PS-2 becomes constant at higher temperatures, as shown in Figure 2. This leveling effect of surface tension with increasing temperature indicates the change of molecular compositions above those temperatures and is apparently due to evaporation or decomposition of the lower molecular weight resin 276V-2.

Viscosity Measurements

The melt viscosities were measured in a No. 600 Fenske type viscometer at 80°C. and are given in Table I. Viscosities of the solvent and the dilute

TABLE I
Approximate Absolute Melt Viscosity of Binary Mixture of Resins PS-2 and 276V-2

Composition		Average flow time at 80.0°C., sec.	Specific gravity	Absolute viscosity, poise
276V-2, wt. %	PS-2, wt. %			
100	—	2.5	1.0[a]	0.10–0.20[a]
75	25	37.4	1.0[a]	15–30[b]
50	50			30–60[c]
25	75			45–90[c]
—	100			60–120[c]

[a] Value from Dow Chemical Co.
[b] Calculated value from eq. (1).
[c] Extrapolated value from Figure 3.

TABLE II

Viscosity, Molecular Weight, and Second-Order Transition Temperature Relationship of Binary Mixtures of Resins PS-2 and 276V-2

Composition, wt.-%		Concentration, g./100 ml. benzene	Average flow time at 29.0°C., sec.	η_r	η_{sp}	η_{sp}/C	$[\eta]$	Molecular weight[a] $\times 10^{-4}$	Second-order transition temp., °C.	
276V-2	PS-2								Calculated[b]	Observed
—	—	0.0000	24.4							
100	—	0.3530	24.4	1.0000	0.0000	0.0000				
		0.8260	24.6	1.0082	0.0082	0.0099				
		1.0290	24.7	1.0123	0.0123	0.0119	0.000			
75	25	0.5660	25.0	1.0246	0.0246	0.0434				
		0.9860	25.4	1.0410	0.0410	0.0416				
		1.3785	25.9	1.0614	0.0614	0.0445	0.445	0.342	44.5	Tacky solid
50	50	0.4220	25.0	1.0285	0.0285	0.0675				
		1.1320	26.6	1.0901	0.0901	0.0796				
		2.5450	29.8	1.2213	0.2213	0.0969	0.069	0.715	73.5	35–70
25	75	0.4120	25.4	1.0410	0.0410	0.0995				
		0.8680	26.8	1.0983	0.0983	0.1132				
		1.7820	29.7	1.2172	0.2172	0.1219	0.098	1.15	83.5	50–80
—	100	0.1865	25.0	1.0250	0.0250	0.1340				
		0.5220	26.2	1.0737	0.0737	0.1412				
		0.9255	27.8	1.1393	0.1393	0.1505	0.130	1.68	88.7	76–87

[a] $[\eta] = K'M^a$, where constants for polystyrene, $K' = 0.97 \times 10^{-4}$ and $a = 0.74$, are used.

[b] $T_s = 100 - (1.9 \times 10^5/M_n)$.

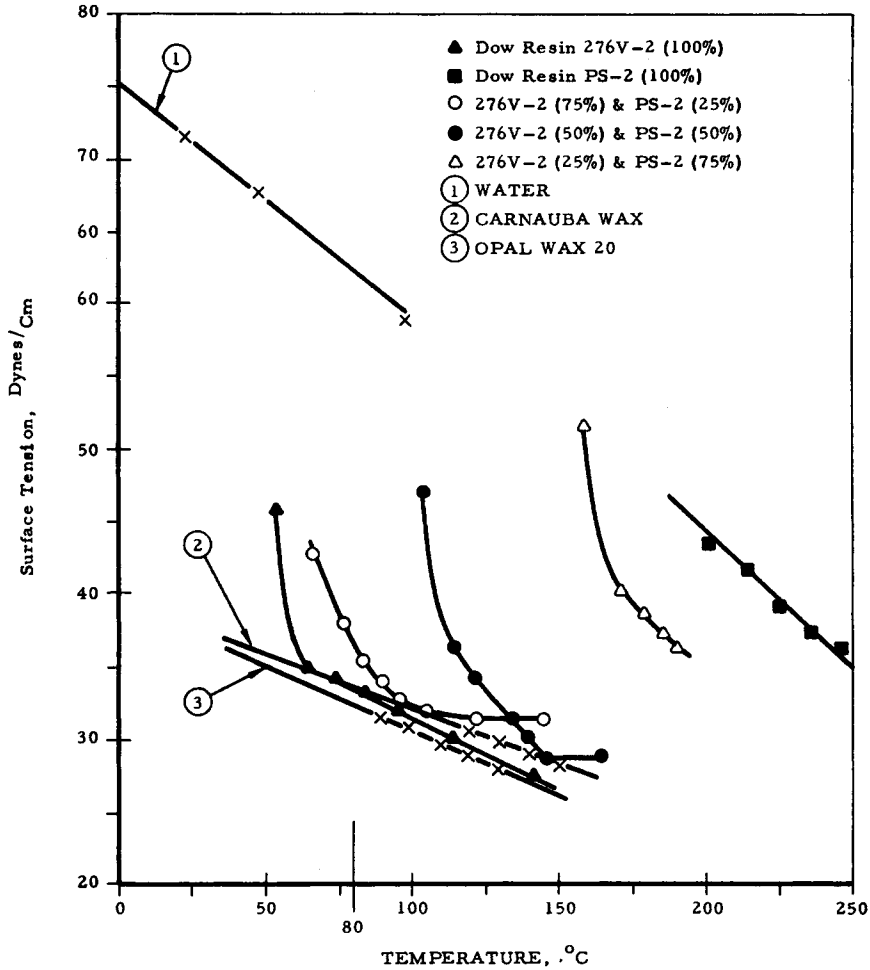

Fig. 2. Effect of temperature upon surface tensions of molten resins.

solutions were measured in a No. 150 Fenske viscometer at 29.0°C. with the results shown in Table II.

The absolute melt viscosity η, of the 75/25 binary mixture molten resin 276V-2 and PS-2 was calculated from eq. (1):

$$\eta_1/\eta_2 = d_1t_1/d_2t_2 \tag{1}$$

where t is the flow time, and data on specific gravities of resin 276V-2 (d_2) and PS-2 (d_1) and absolute viscosity η_2 of resin 276V-2 at 60°C. were available from the Dow Chemical Company. The approximate absolute viscosities of other compositions were graphically estimated from Figure 3.

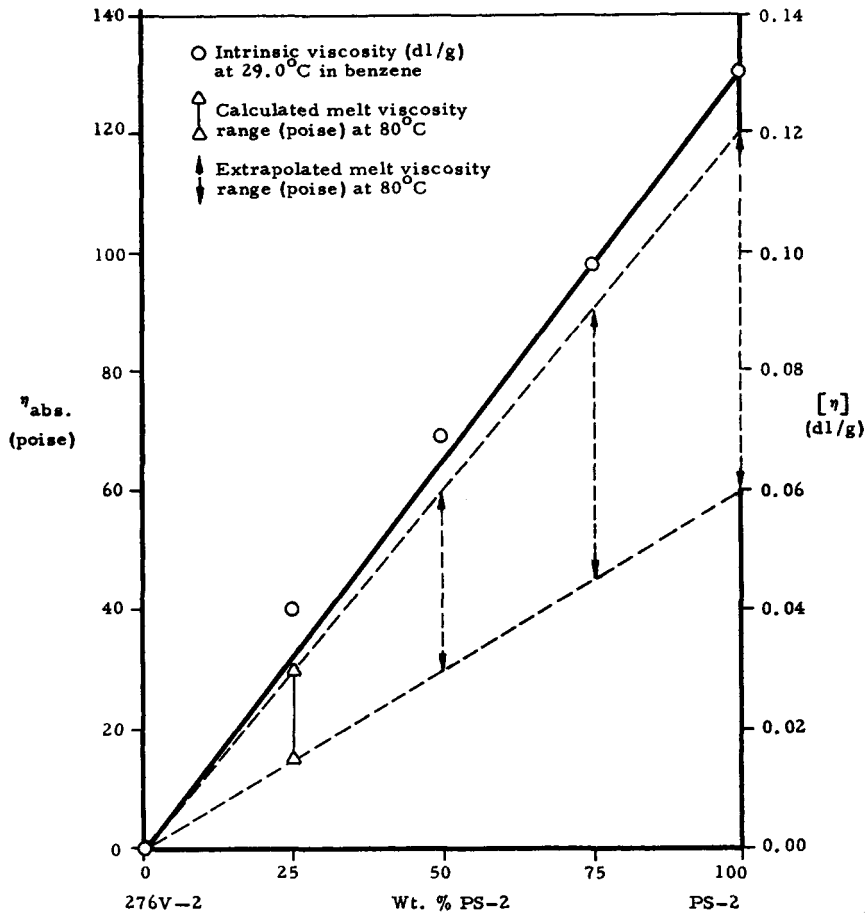

Fig. 3. Viscosity and composition relationship for binary mixture of resins PS-2 and 276V-2.

Molecular weights of the various compositions of binary mixtures in Table II were not determined, but calculated from eq. (2), where the

$$[\eta] = K'M^a \tag{2}$$

constants $K' = 0.97 \times 10^{-4}$ and $a = 0.74$ used were those determined osmotically for polystyrene at 30°C. in benzene.[3]

The second-order transition temperatures T_s of the same binary mixtures were calculated from eq. (3), based on work by Fox and Flory.[4] The observed values were determined by Fischer-Johns melting point apparatus (see Table II).

$$T_s = 100 - (1.9 \times 10^5/M_n) \tag{3}$$

Conclusion

The values of surface tension and viscosity of thermoplastics are useful guides in selecting materials of interest for thermoplastic recording. The addition of plasticizers to the thermoplastic not only lowers the second-order transition temperature, but also viscosity and surface tension.

The plasticized PS-2 resin with 276V-2 represents one example of a material useful for thermoplastic recording. Internal plasticization may provide even better performances than the external plasticized resin mentioned.

References

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Résumé

On décrit des études analytiques et expérimentales sur les propriétés de tension superficielle et de viscosité des résines Dow PS-2 et 276V-2. Cette étude a été entreprise afin d'obtenir des informations sur des matériaux qui sont intéressants pour l'enrégistrement thermoplastique. On a trouvé qu'une plastification externe diminue la tension superficielle du polystyrène, tandis que la viscosité diminue fortement. Des valeurs typiques pour un mélange de 25% de PS-2 dans le 276V-2 sont $\gamma = 35$ dynes/cm et $\eta = 20$ poises à 80°C.

Zusammenfassung

Es werden analytische und experimentelle Untersuchungen der Oberflächenspannung und Viskositätsiegenschaften der Dow-Harze PS-2 und 276V-2 beschrieben. Die Untersuchung sollte Informationen über für thermoplastisches Aufzeichnen interessante Stoffe liefern. Es wurde gefunden, dass eine äussere Weichmachung die Oberflächenspannung von Polystyrol erniedrigt und zu einer starken Herabsetzung der Virkosität führt. Typische Werte für eine Mischung von 25% PS-2 in 276V-2 sind $\gamma = 35$ dyn/cm und $\eta = 20$ Poise bei 80°C.

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