

Mechanism for the Action of Tackifying Resins in Pressure-Sensitive Adhesives

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Synopsis

In a study of pressure-sensitive adhesives prepared from mixtures of natural rubber and three different tackifying resins, it was shown that a tackifying resin may form either one- or two-phase systems with natural rubber. Measurements of the viscoelastic properties of the adhesives show that the effect of tackifying resins is to modify the viscoelastic properties so that the adhesive performance in bonding and unbonding is improved. It is suggested that a two-phase system is not necessary for good tack, and a theory based on a two-phase system cannot adequately explain the rate dependence of tack tests. Tack measured by the probe test is shown to be dependent upon a balance between the viscoelastic properties and the transition temperature of the adhesives. This theory is used to explain the effect of contact time, withdrawal speed, and resin softening point on the tack of adhesives.

INTRODUCTION

The phenomenon of tack can be divided into three separate cases. Rubbers and elastomers have the ability to adhere to themselves on the application of light pressure—this is rubber tack or autohesion. Tack of viscous liquids such as printing ink is the resistance of separating the printing surface from the paper surface. The ink is split and remains on both surfaces as thin layers. Pressure-sensitive adhesives show tack when applied to a surface under light load and short time. This paper is concerned with pressure-sensitive tack.

Tack is a subjective property of pressure-sensitive adhesives which is defined by ASTM D1878-61T as "the property of a material which enables it to form a bond of measurable strength immediately upon contact with another surface." It is subjective in that tack values vary with the method and conditions of measurement. In order to increase the tack of raw polymers, compounding ingredients known as tackifying resins are blended with the polymers. The mechanism of action of these resins has been the subject of a great deal of research, and the most widely accepted theory is due to Wetzels.^{1,2,3}

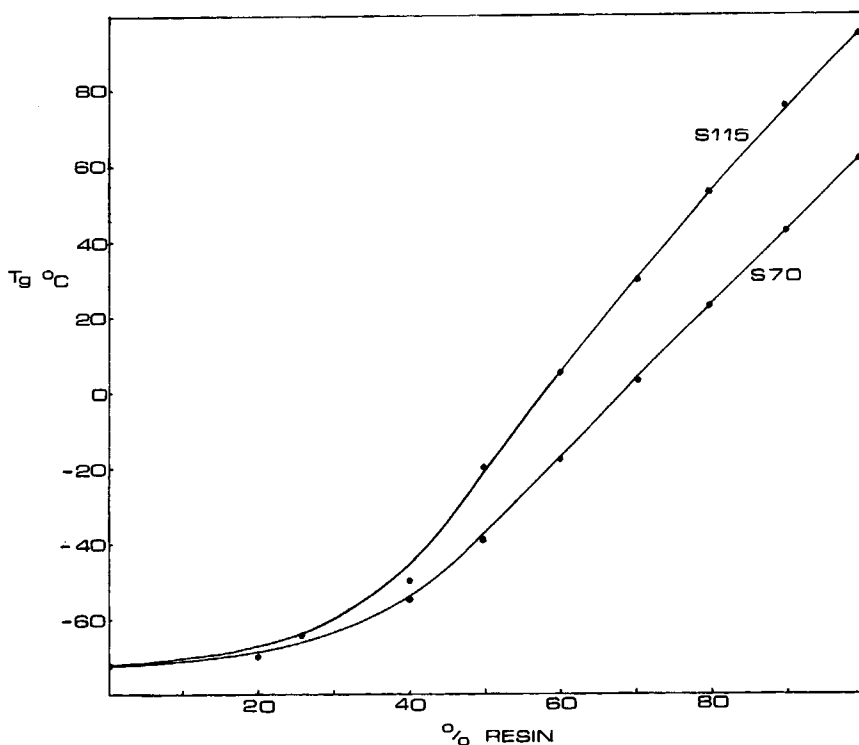


Fig. 1. Variation of transition temperatures with resin concentration for Piccolyte S.115 and S.70/natural rubber mixtures as measured by dilatometry.

Wetzel investigated natural and synthetic rubber with rosin ester tackifiers and explained the characteristic variation of tack with resin concentration by assuming the development of a two-phase system. At low resin concentration, less than 40%, tack is only raised slightly over that of the rubber; this is due to the resin being completely soluble in the rubber. The rapid rise in tack after 40% resin concentration is, according to Wetzel, due to the rubber being saturated with resin and the development of a disperse second phase consisting of resin and low molecular weight rubber. This disperse phase is assumed to have a much lower viscosity than the continuous phase and is thus able to give faster wetting of the adherend and can accommodate irregularities in the adherend topography, i.e., it effectively increases the bond area. The second phase continues to develop until the maximum amount of low molecular weight rubber has dissolved in the disperse resin phase—this is the point of maximum tack. Further increase in resin concentration results in the resin phase increasing in brittleness and a phase inversion occurs, the resin phase becoming continuous. The adhesive, now being glassy in nature, is unable to wet the adherend, with the result that the tack value falls to zero. Replica electron micrographs have been obtained by Hock and Abbott^{4,5} to substantiate this two-phase theory.

Wetzel² observed that the resin content for maximum tack increased with decreasing resin softening point. This was explained by assuming that more low molecular weight rubber can dissolve in lower softening point resin, thus increasing the amount of disperse phase before phase inversion.

Although this theory appears to explain the variation of tack with resin concentration, it fails when rate effects are considered. It has been shown in the literature⁷ that the maximum in the tack curve can be shifted to dif-

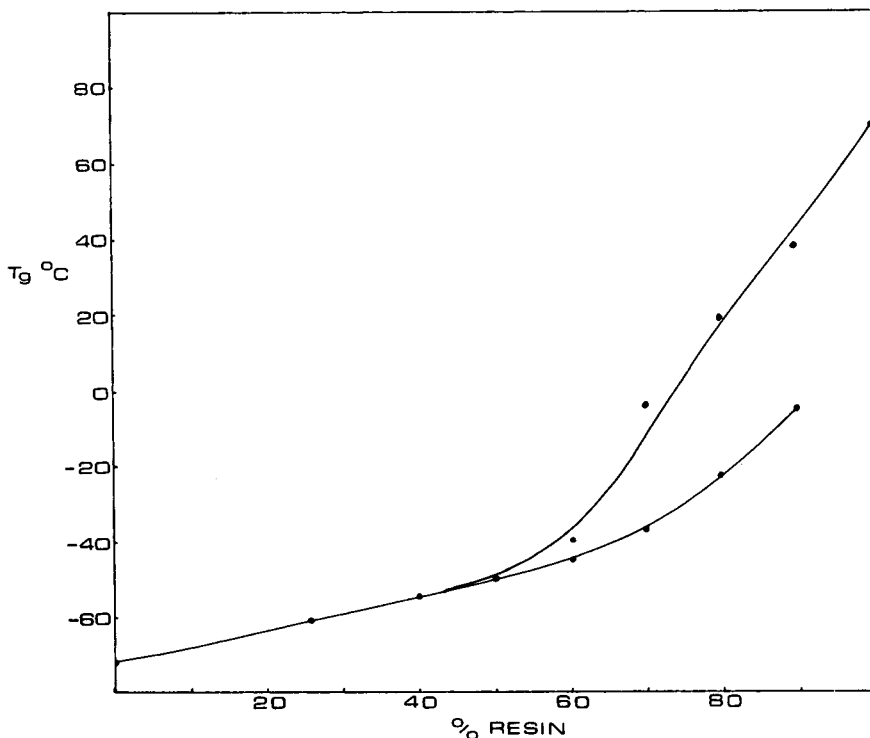


Fig. 2. Variation of transition temperatures with resin concentration for Pentalyne H/natural rubber mixtures as measured by dilatometry.

ferent resin concentrations by altering the stress rate. The two-phase theory cannot explain this result.

Dahlquist^{6,7} has shown that the tackifier has an effect on the adhesive moduli. He has also shown by photographs of the probe during the unbonding process that separation during a probe tack test is by low-angle peel.

Recent work has firmly established the viscoelastic nature of peel adhesion,^{8,9} and for this reason it was decided to investigate the effect of the tackifier resin on the viscoelastic properties of the adhesive.

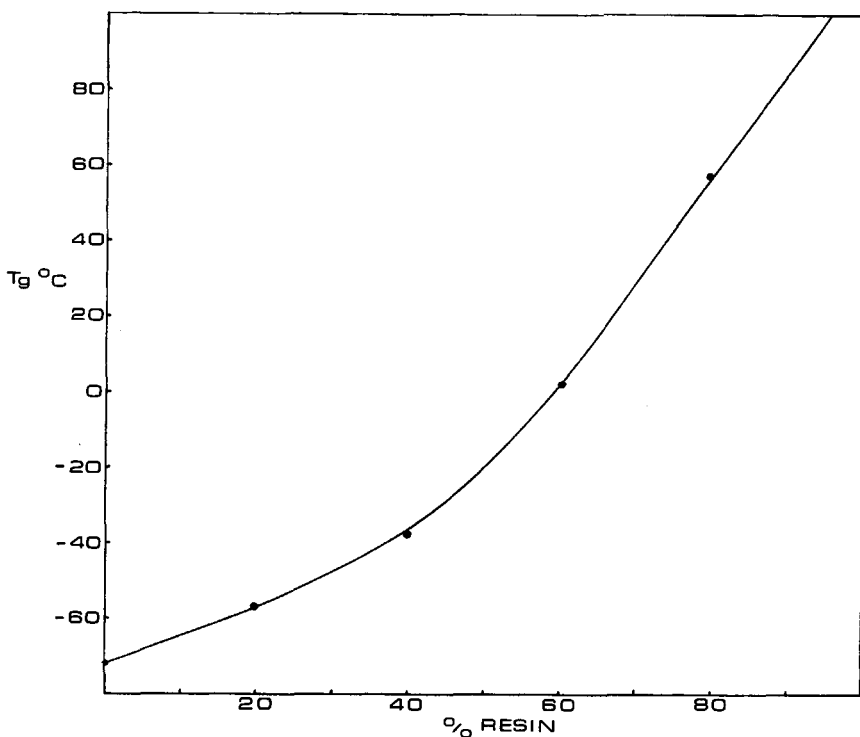


Fig. 3. Variation of transition temperatures with resin concentration for Arkon P.125/natural rubber mixtures as measured by dilatometry.

EXPERIMENTAL

All adhesives were based on pale crepe natural rubber, with a number-average molecular weight of 4.5×10^6 by high-speed membrane osmometry. Four commercial tackifying resins were investigated: (i) Pentalyn H (Hercules Powder Co. Ltd.), a pentaerythritol ester of hydrogenated rosin; (ii) Piccolyte S.115 (Pennsylvania Industrial Chemical Corporation), a poly- β -pinene; (iii) Piccolyte S.70 (Pennsylvania Industrial Chemical Corporation), a poly- β -pinene; and (iv) Arkon P.125 (Arakawa Forest Chemical Industries Ltd.), reported to be a polymerized dicyclopentadiene.

All adhesive mixtures were prepared as 20% solutions in toluene. The solutions were spread by a doctor blade method. The toluene was allowed to evaporate completely at room temperature.

Glass transition temperatures were determined dilatometrically according to the method of Bekkedahl.¹⁰ The presence of a two-phase system is indicated by two inflections in the volume-temperature plot. This results in two lines in the T_g -versus-resin concentration graph. Methanol/water, 60/40, was used as the confining fluid; preliminary experiments showed that this mixture neither leached out the resin nor caused the adhesive to swell.

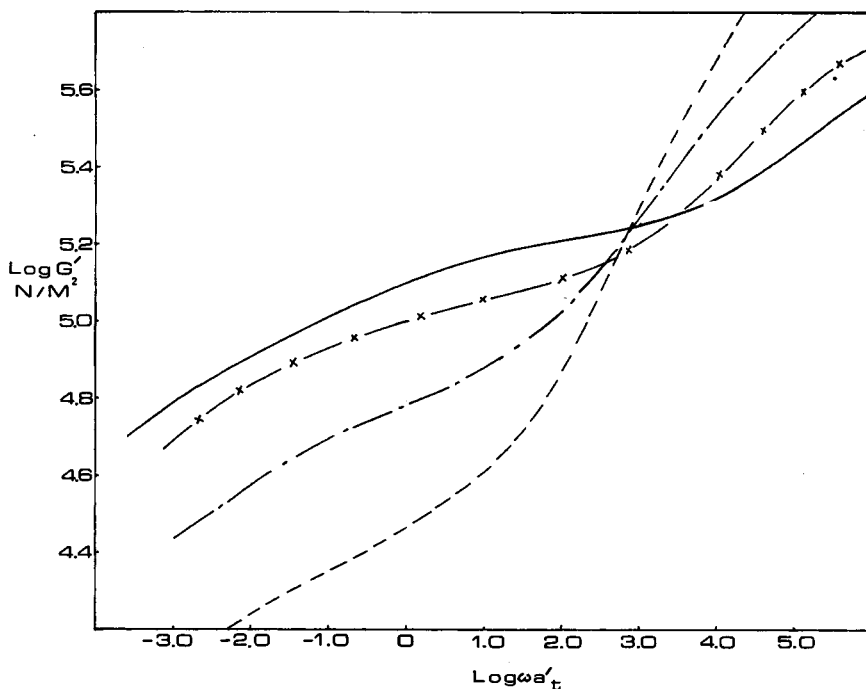


Fig. 4. Master curves of in-phase shear modulus (G') vs. $\log \omega a_t'$ for Piccolyte S.115/natural rubber mixtures reduced to 296°K: (—) natural rubber; (x-x-x) 25% Piccolyte S.115 resin; (---) 40% Piccolyte S.115 resin; (- - - -) 50% Piccolyte S.115 resin. (Note: In Figures 4-9, each curve is constructed from 104 values which for the sake of clarity are omitted.)

Viscoelastic properties were determined on a Weissenberg rheogoniometer in oscillatory mode using parallel plates in conjunction with a digital transfer function analyzer (Solartron). Measurements were made at 13 frequencies in the 0.01-25 Hz range and at eight temperatures between -48°C and 50°C. Preliminary experiments showed that the rubber-resin mixtures exhibited linear viscoelastic behavior at all resin concentrations investigated, i.e., the modulus was independent of the input amplitude. This enabled the results to be treated in accordance with the theory of Walters and Kemp¹¹ to give values for in-phase shear modulus (G'), out-of-phase shear modulus (G''), complex shear modulus (G^*), $\tan \delta$, and in-phase component of the dynamic viscosity (η').

All results were reduced to 296°K and shifted to form master curves by applying the time-temperature superposition principle.¹² It was found that all experimental shift factors, $\log a_t$, were in agreement with the predicted values from the general W.L.F. equation:

$$\log a_t = \frac{-8.86 (T - T_s)}{101.6 + T - T_s}$$

Thus, each curve in Figures 4-9 is constructed from 104 values.

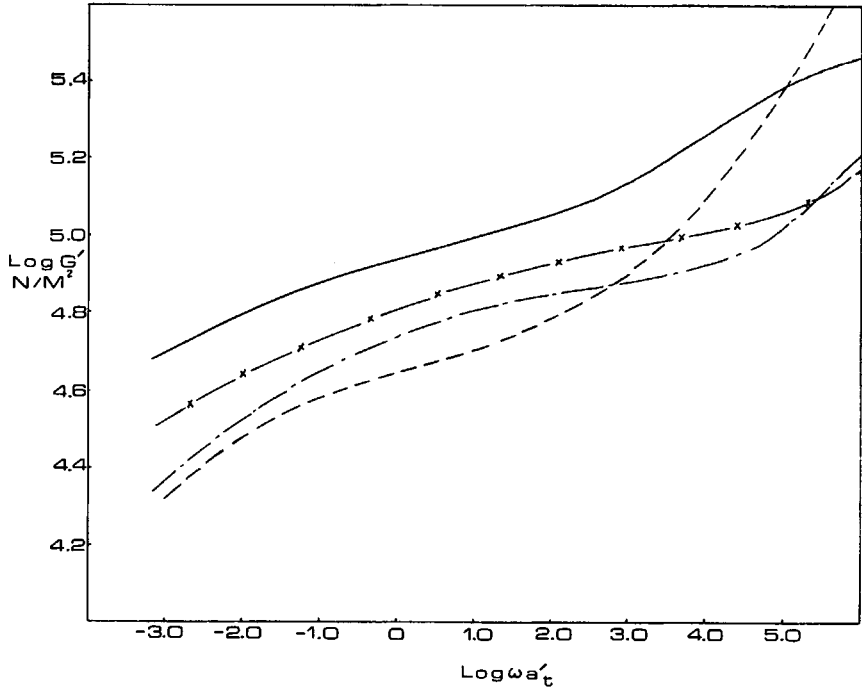


Fig. 5. Master curves of in-phase shear modulus (G') vs. $\log \omega a_1'$ for Pentalyn H/natural rubber mixtures reduced to 296°K: (—) natural rubber; (x-x-x) 25% Pentalyn H resin; (---) 40% Pentalyn H resin; (- - - -) 50% Pentalyn H resin.

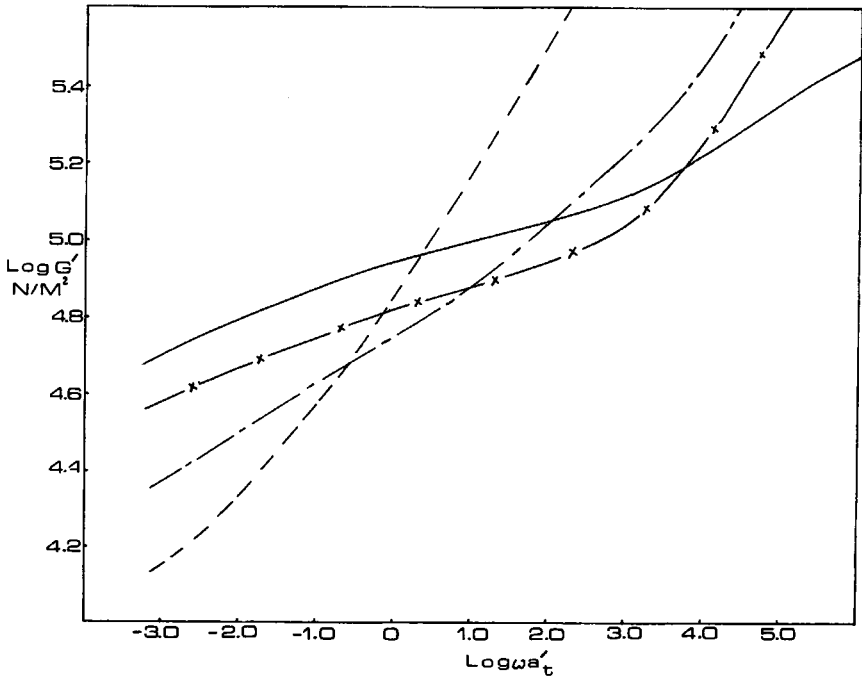


Fig. 6. Master curves of in-phase shear modulus (G') vs. $\log \omega a_1'$ for Arkon P.125/natural rubber mixtures reduced to 296°K: (—) natural rubber; (x-x-x) 25% Arkon P.125 resin; (---) 40% Arkon P.125 resin; (- - - -) 50% Arkon P.125 resin.

TABLE I
Liquids Used to Determine Critical Surface Energy of Adhesives

Liquid	Surface tension, ergs/sq cm
Water	72.8
Glycerol	63.4
Methylene iodide	50.8
Ethylene glycol	46.5
Nitrobenzene	43.3
Anisole	45.2
Chlorobenzene	33.3

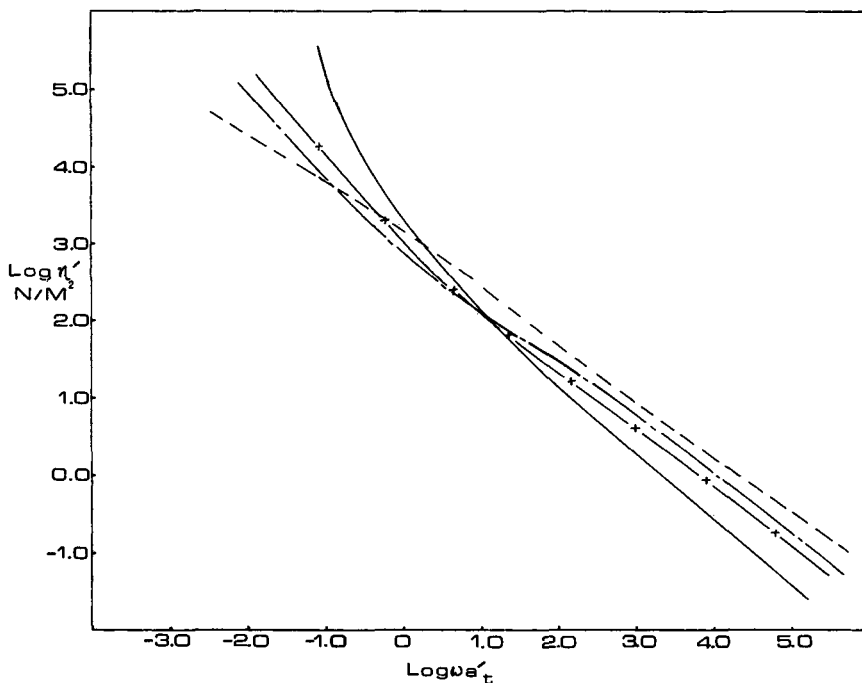


Fig. 7. Master curves of the in-phase component of the dynamic viscosity (η') vs. $\log \omega a_i'$ for Piccolyte S.115/natural rubber mixtures reduced to 296°K: (—) natural rubber; (x-x-x) 25% Piccolyte S.115 resin; (---) 41% Piccolyte S.115 resin; (- - - -) 50% Piccolyte S.115 resin.

A probe test similar to that of Wetzel¹ was used to measure the tack of the adhesives. A stainless steel probe $\frac{1}{4}$ in. in diameter and 45 g in weight was attached to the load cell of an Instron tensile testing machine. The end of the probe was machined flat so that it made an angle of 90° with the longitudinal axis. The probe passed through a PTFE-lined guide and made contact with the adhesive surface. The adhesive was spread on a glass slide to give it a rigid backing. By use of the Instron controls, the contact time and withdrawal speed could be varied. All measurements were carried out in a constant temperature room at 20°C.

TABLE II
Surface Energy of Probe Materials

Material	Surface energy, ergs/sq cm
Polytetrafluoroethylene	18.5
Polypropylene	34.1
Poly(methyl methacrylate)	41.2
Phenolic resin	42.1

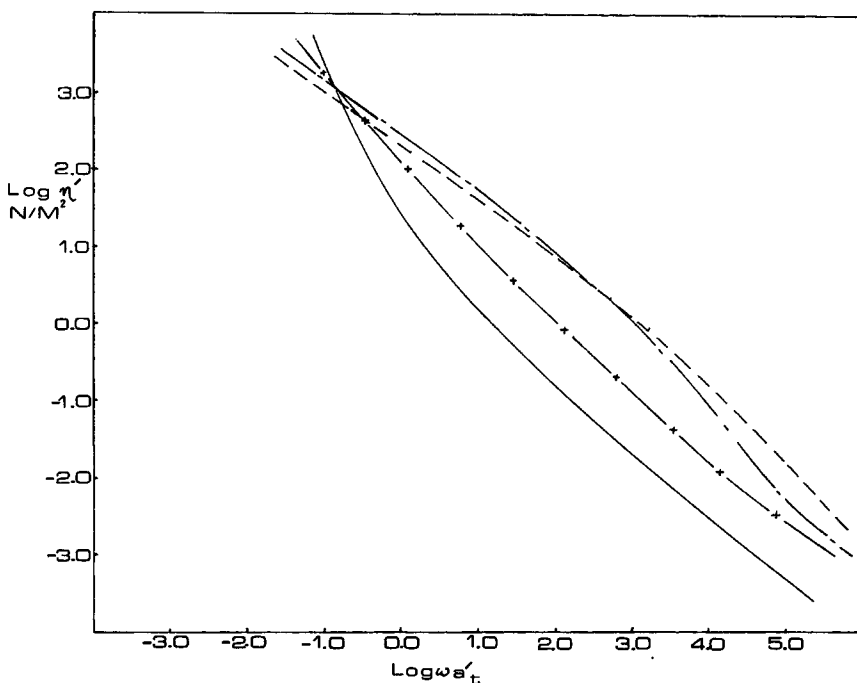


Fig. 8. Master curves of the in-phase component of the dynamic viscosity (η') vs. $\log \omega a'_t$ for Pentalyn H/natural rubber mixtures reduced to 296°K: (—) natural rubber; (x-x-x) 25% Pentalyn H resin; (---) 40% Pentalyn H resin; (- - - -) 50% Pentalyn H resin.

The contact angles of liquids on the adhesive surface were measured by the sessile drop method. The drops were viewed through a microscope fitted with a goniometer eyepiece. The liquids used to determine the critical surface energy of the adhesives are shown in Table I.

A graph of the cosine of the contact angle against the liquid surface tension is a straight line. The critical surface energy (γ_c) of the adhesive is taken as the surface tension at which the cosine of the contact angle equals 1.

The effect of the surface energy of the probe material was investigated by constructing probes of different materials each having the same diameter

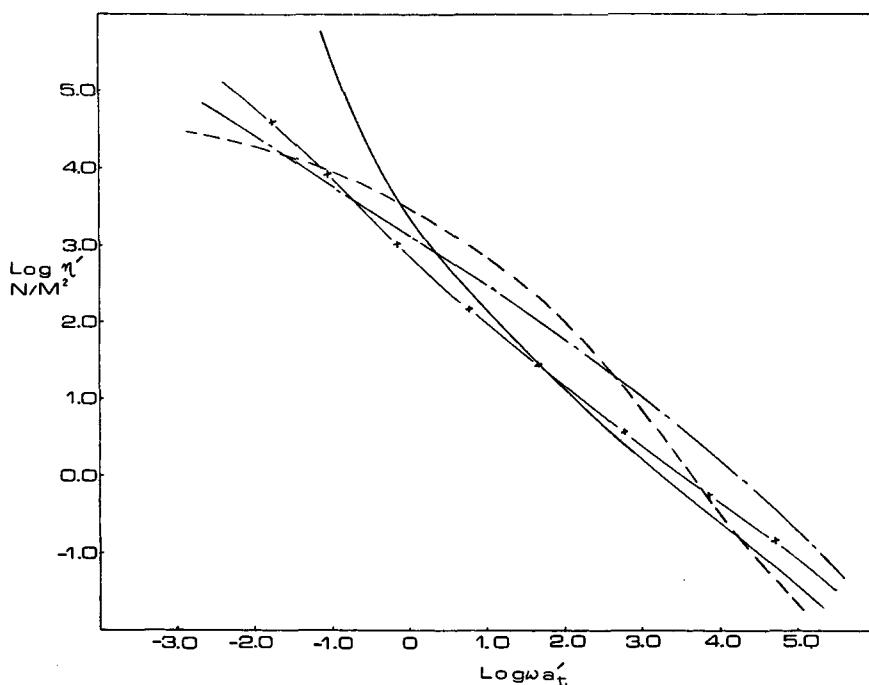


Fig. 9. Master curves of the in-phase component of the dynamic viscosity (η') vs. $\log \omega a'$ for Arkon P.125/natural rubber mixtures reduced to 296°K: (—) natural rubber; (x-x-x) 25% Arkon P.125 resin; (---) 40% Arkon P.125 resin; (- - - -) 50% Arkon P.125 resin.

and weight as the stainless steel probe. The materials are shown in Table II.

DISCUSSION

Figures 1 and 3 show that three of the resins studied, Piccolyte S115, Piccolyte S70, and Arkon P.125, are compatible with natural rubber at all resin concentrations. These data, which confirm the earlier dynamic measurements of Fukuzawa et al.,¹³ contradict Wetzel's theory for tackification. However, Figure 2 confirms Wetzel's findings in that Pentalyn H forms two phases as shown by the development of two T_g 's for resin concentration in excess of 60%, although it should be noted that Wetzel stated that the two phases develop at approximately 40% resin concentration. As the T_g of both phases continues to rise with increased resin, one phase cannot become saturated, as was suggested by Wetzel.

The variation of tack with resin concentration can be explained by the effect of the resin on the viscoelastic properties of the adhesive mass. In a typical probe tack test, the bonding time is long compared with the unbonding time. At long times the addition of resin causes a reduction in both the in-phase shear modulus (G') and the in-phase component of the dynamic viscosity (η') of the adhesive mass relative to that of the rubber (Figs. 4-9).

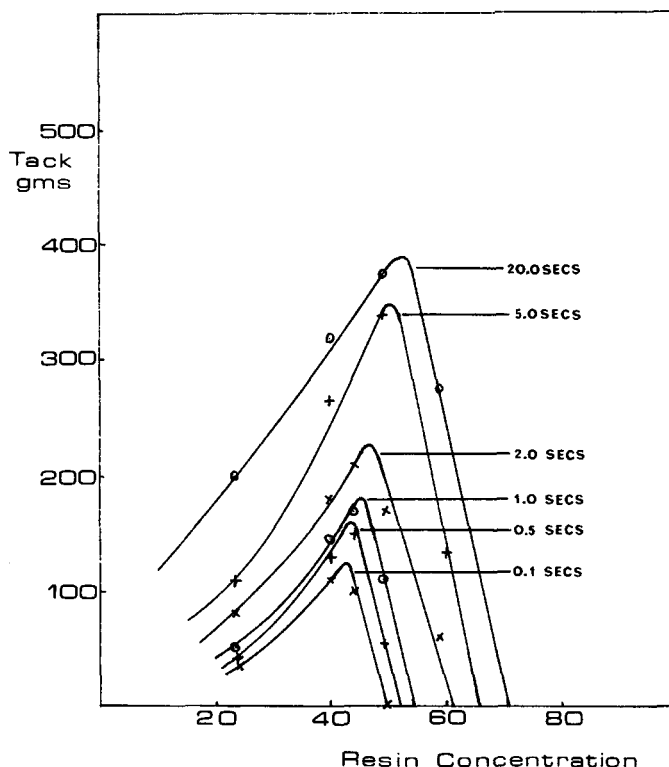


Fig. 10. Effect of varying contact time on the tack of Piccolyte S.115/natural rubber mixtures (withdrawal speed = 20 in./min).

This reduced viscosity will give a faster and more intimate wetting of the adherend and the resulting increased bond area will lead to higher tack values. The magnitude of this reaction is small at low resin concentrations and rapidly increases as the resin approaches and exceeds 40%. At short times, G' is increased over that of the rubber. Aubrey and Sherriff¹⁴ have shown that the 90° peel strength of these rubber-resin mixtures increases with G' , i.e., tack values will increase with increasing G' values.

The viscosity-lowering mechanism continues until the effect of the resin is to raise the adhesive mass T_g above room temperature. At this resin concentration and stress rate, the adhesive is glassy and unable to wet the adherend, and thus the tack value falls rapidly away to zero.

Consideration of the two curves in Figure 1 (the lower curve being for a similar β -pinene resin of lower softening point Piccolyte S70) provides an explanation for the variation of the resin concentration at maximum tack with resin softening point. As the resin softening point decreases, the resin concentration at which the T_g of the adhesive mass exceeds room temperature increases, i.e., the resin concentration at maximum tack will increase with decreasing softening point.

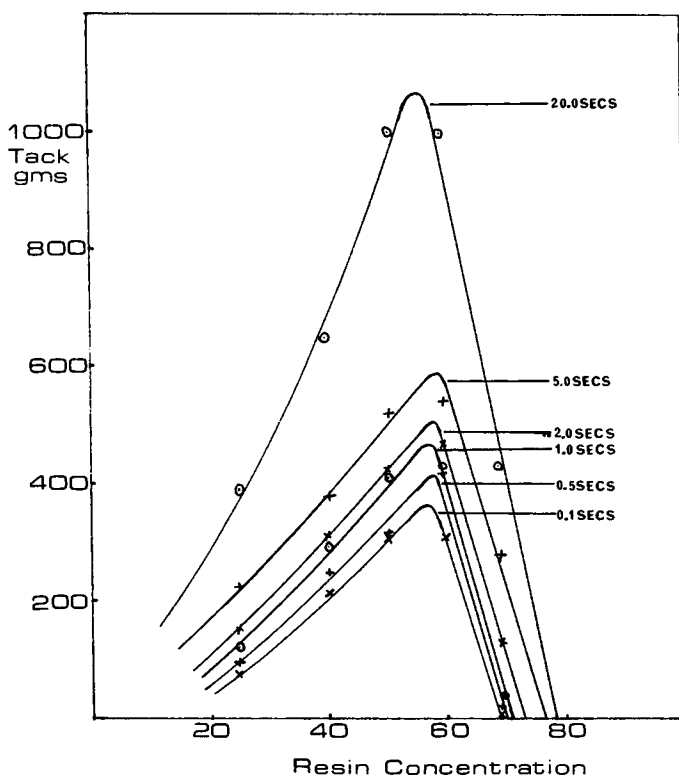


Fig. 11. Effect of varying contact time on the tack of Pentalyne H/natural rubber mixtures (withdrawal speed = 20 in./min).

Increase of the contact time (Figs. 10-12) increases the tack value; the adhesive is allowed longer time to flow and to make greater contact with the probe surface. This greater contact area causes an increase in the measured value of tack. Increase in the contact time also causes an increase in the resin concentration at which maximum tack occurs. The position of maximum tack is controlled by the T_g of the mixture. At resin concentrations at which the T_g of the mixture approaches room temperature, the adhesive will have difficulty in making contact with the adherend at very short contact times. At longer times, the adhesive will have made appreciably more contact. The increase of contact time will shift the maximum tack closer to the resin concentration at which the T_g of the mixture is in excess of room temperature, i.e., at higher resin concentration.

Variation of the withdrawal speed (Figs. 13-15) has two effects on tack. It causes the resin concentration at which maximum tack occurs, and the value of the maximum tack itself, to vary. Increase of the withdrawal speed or stress rate decreases the resin concentration at which T_g of the mixture becomes greater than room temperature since T_g is dependent upon stress rate, and so the resin concentration at which maximum tack occurs

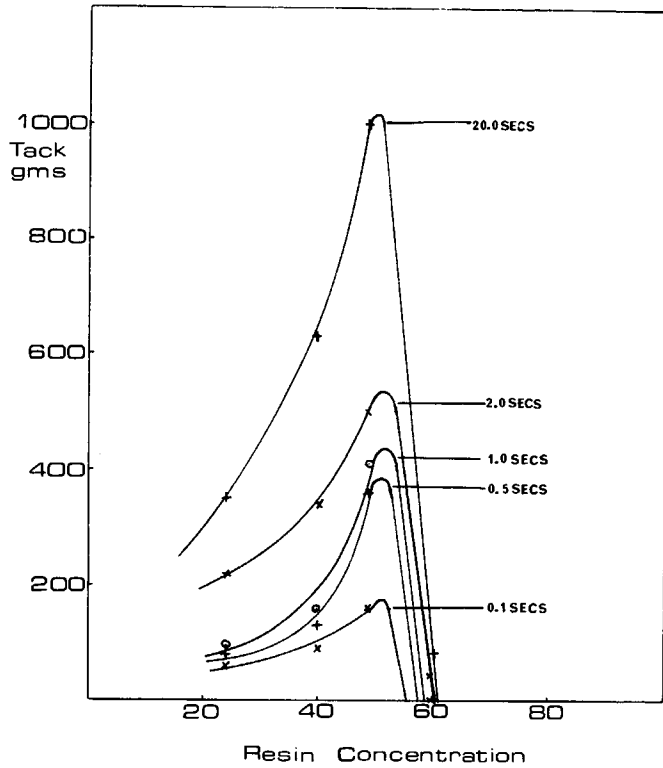


Fig. 12. Effect of varying contact time on the tack of Arkon P.125/natural rubber mixtures (withdrawal speed = 20 in./min).

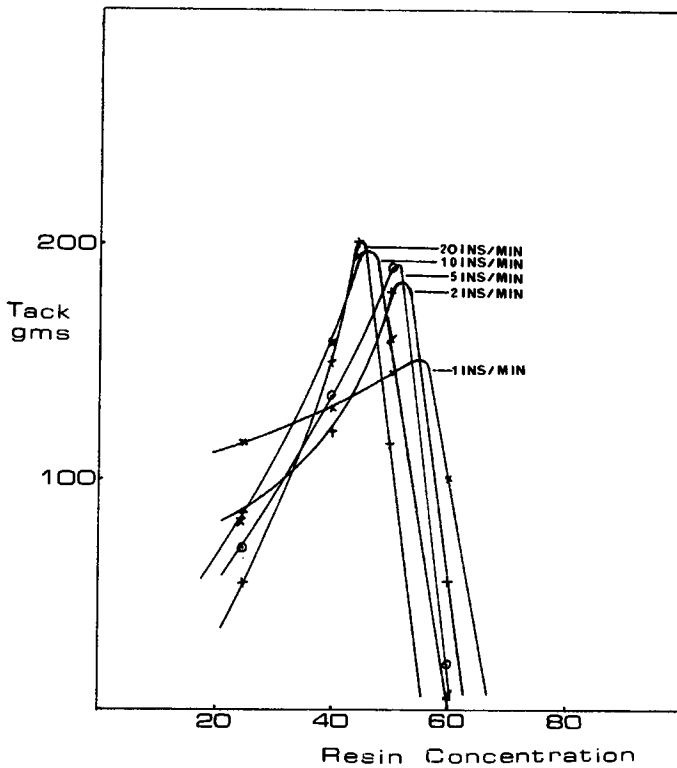


Fig. 13. Effect of varying withdrawal speed on the tack of Piccolyte S.115/natural rubber mixtures (contact time = 0.5 sec).

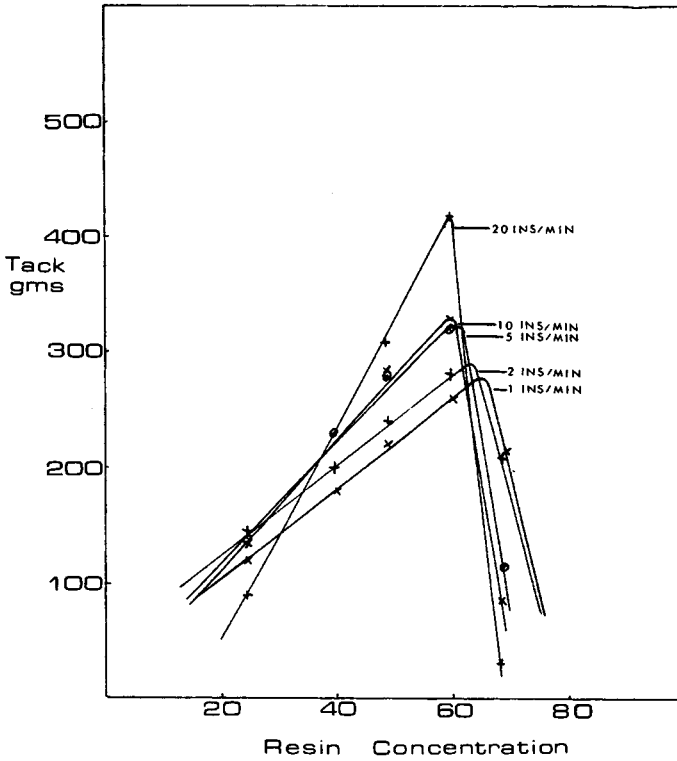


Fig. 14. Effect of varying withdrawal speed on the tack of Pentalyne H/natural rubber mixtures (contact time = 0.5 sec).

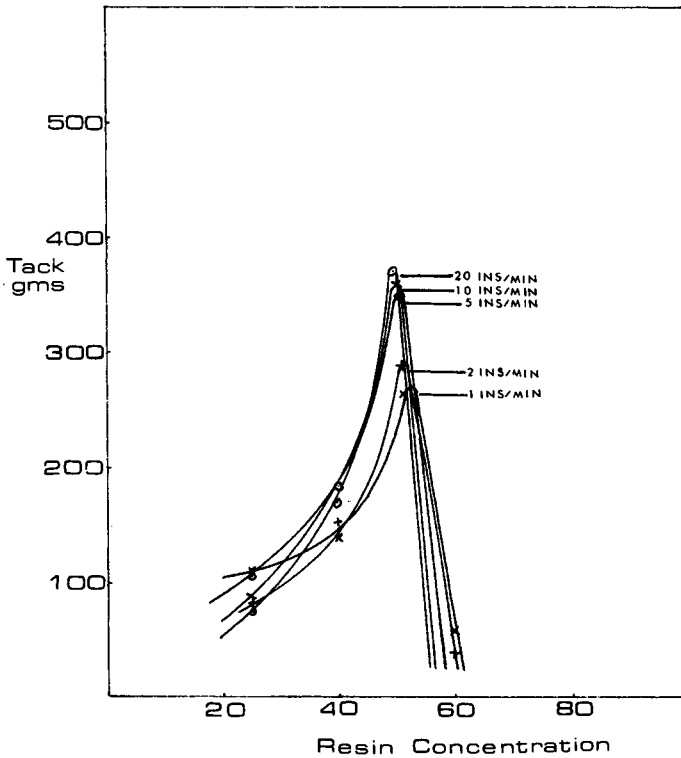


Fig. 15. Effect of varying withdrawal speed on the tack of Arkon P.125/natural rubber mixtures (contact time = 0.5 sec).

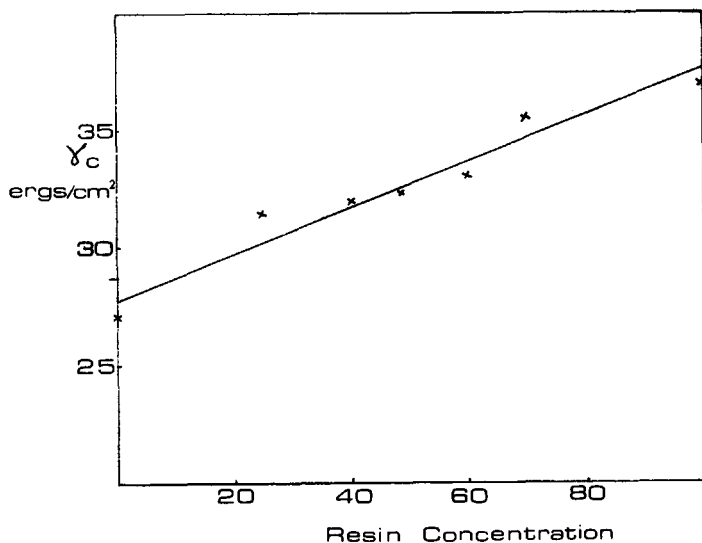


Fig. 16. Variation of the critical surface energy (γ_c) with resin concentration for Pentalyne H/natural rubber mixtures.

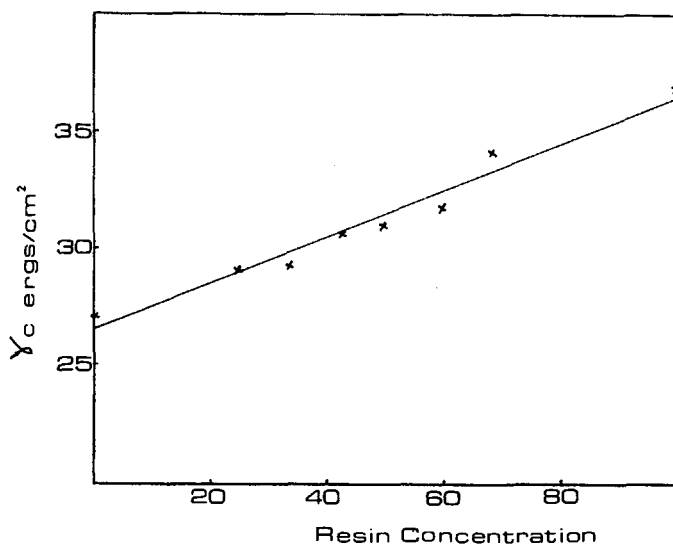


Fig. 17. Variation of the critical surface energy (γ_c) with resin concentration for Arkon P.125/natural rubber mixtures.

decreases. It can be seen that this increases the measured G' of the adhesives, and so the value of tack at the maximum increases.

The surface energies of the probe and adhesives were then considered. The critical surface energy of the mixtures increases linearly with the resin concentration from the value of pure rubber to that of pure resin (Figs. 16 and 17). Figure 18 shows the effect of measuring probe tack using probes

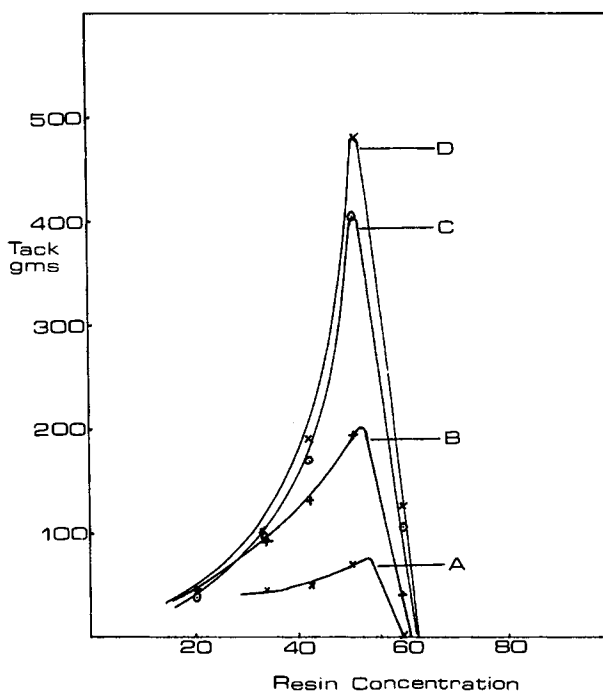


Fig. 18. Effect of probe surface energy on the tack against resin concentration curve for Arkon P. 125/natural rubber mixtures (contact time = 0.5 sec, withdrawal speed = 20 in./min). Probe materials: (A) polytetrafluoroethylene, $\gamma_c = 18.5$ ergs/sq cm; (B) polypropylene, $\gamma_c = 34.1$ ergs/sq cm; (C) poly(methyl methacrylate), $\gamma_c = 41.2$ ergs/sq cm; (D) phenolic resin, $\gamma_c = 42.1$ ergs/sq cm.

prepared from materials of different surface energy. It can be seen that the change of surface energy of adherend alters the value of the maximum tack, but does not alter the resin concentration at which maximum tack occurs. It appears that surface energy, while altering the strength of the bond, does not affect the resin concentration of maximum tack.

CONCLUSIONS

From these results we consider Wetzel's theory of tackification to be inadequate, since it has been shown that poly- β -pinene tackifiers are fully compatible with natural rubber, and also the theory does not explain the observed rate dependence of tack tests.

We consider that the tackifier acts by bringing the viscoelastic state of the adhesive to one more suitable to bonding and unbonding. This action occurs independent of the compatibility of the tackifier with the rubber, as long as it is not fully incompatible. Solvents and plasticizer oils are inefficient as tackifiers as they reduce the viscoelastic spectrum over the entire frequency range and do not raise the T_g . The softening point of the resin, related to the resin T_g , determines the resin content for maximum tack by its effect on the adhesive T_g .

Thus, the action of a tackifying resin can be explained by the balance of its effect upon the viscoelastic properties of the adhesive and the effect upon the T_g of the adhesive.

The authors would like to thank Dr. D. W. Aubrey of the National College of Rubber Technology and Mr. M. E. Hodgson of Smith and Nephew Research, Ltd., for their helpful advice and discussion during the course of this work.

One of us (M. Sherriff) wishes to thank the Science Research Council for the award of a research studentship during which this work was carried out.

References

1. F. H. Wetzel, ASTM Bulletin No. 221, 1957, pp. 64-68.
2. F. H. Wetzel, *Rubber Age*, **82**, 291 (1957).
3. F. H. Wetzel and B. B. Alexander, *Adhesives Age*, 28 (1964).
4. C. W. Hock and A. N. Abbott, *Rubber Age*, **82**, 471 (1957).
5. C. W. Hock, *J. Polym. Sci.*, **C3**, 139 (1963).
6. C. A. Dahlquist, *Adhesives Age*, **2**, 25 (1959).
7. C. A. Dahlquist, *Adhesion Fundamentals and Practice*, The Ministry of Technology, Maclaren, London, 1969.
8. A. N. Gent and R. P. Petrich, *Proc. Roy. Soc.*, **A310**, 433 (1969).
9. T. K. M. Wong, Ph.D. Thesis, C.N.A.A., 1969.
10. N. Bekkedahl, *J. Res. Nat. Bur. Stand.*, **13**, 410 (1934).
11. K. Walters and R. A. Kemp, *Rheol. Acta*, **7** (Pt. 1), 1 (1968).
12. J. D. Ferry, *Viscoelastic Properties of Polymers*, 2nd ed., Wiley, New York, 1970.
13. K. Fukuzawa and T. Kosaka, Preprints of 7th Symposium on Adhesion and Adhesives, Tokyo, Japan, June 3-4, 1969, p. 79.
14. D. W. Aubrey and M. Sherriff, to be published.

Received March 2, 1973

Revised April 26, 1973