A Method of Measuring Tackiness

HIROTARO KAMBE and KAZUO KAMAGATA,* *Polymer Research Division, Institute of Space and Aeronautical Science, University of Tokyo, Meguro-ku, Tokyo, Japan*

Synopsis

For measuring the tackiness of viscous materials to the solid surface, we designed an attachment to the tensile tester driven with constant speeds. Blends at high molecular weight polyisobutylene with low molecular weight polyisobutylene or with a hydrogenated rosin were used as samples. The maximum force f_b at the time t_b of the force-time relation recorded on a chart was determined as a measure of the tackiness. The relation between f_b and t_b satisfies the equation $f_b \propto t_b^{-1/2}$ derived by Eley. The f_b depends on the time t_c and the pressure p_c at contact, the temperature and the rate of separation r, and the rosin content of the sample. The activation energy, obtained from the slope of plots of f_b against the reciprocal of the absolute temperature shows a value of 2–6 kcal/mole, which is similar to the activation energy of the viscous flow. To decide whether the failure occurs at the interface or within the adhesive itself, f_b was measured with cylinders made of various materials such as polytetrafluoroethylene, polyethylene, poly(methyl methacrylate), and brass.

INTRODUCTION

Tackiness is a very important property for many industrial materials. It has been studied by various methods by many investigators,[3-3] but because of its very complex nature it has not been clarified sufficiently. The phenomena comprising tackiness may be roughly divided into three cases with respect to the material concerned.

First mentioned is the tackiness of rubbers or elastomers. In this case, tackiness means that the material does not adhere to the other materials, but adheres to itself on application of a light pressure. Such a tackiness between similar materials is called the autohesion. This has been fully discussed by Voyutskii.[2]

Secondly, there is tackiness connected with a viscous liquid like a printing ink. On printing, the tackiness shows up as the resistance to separating the printing surface from the paper surface, when the ink remains on both surfaces as thin layers. The partition of the ink layer is caused by an abrupt fracture of the ink membrane. The ink flows along the line of the weakest resistance, becomes a thin thread, and comes to fracture with a weak force.

Thirdly, tackiness is involved in pressure-sensitive adhesive tape on which is applied a resin layer having a moderate viscosity. Several detailed studies have also been carried out regarding this type of tackiness.

This report deals with a method for measuring the tackiness of tacky adhesives. We designed and constructed an assemblage attached to a tensile tester driven with a constant speed and measured the tackiness of polyisobutylene–rosin blends.

EXPERIMENTAL

Materials

Polyisobutylenes used were Vistanex L 120 ($\bar{M}_v = 1.32 \times 10^6$), LMMH ($\bar{M}_v = 4.88 \times 10^4$), and Oronite 32 ($\bar{M}_n = 1.0 \times 10^3$). Staybelite Resin (Hercules Powder Co., Inc.; softing point, 76°C; acid value, 162) was used as sample of hydrogenated rosin. The viscosity-average molecular weight $\bar{M}_v$ of the high molecular weight polyisobutylene was determined from the limiting viscosity number measured with an Ubbelohde capillary viscometer. The molecular weight of Oronite 32 was referred to a literature value.[9] The compositions of the samples are shown in Table I. Solutions in toluene of 10–15 wt-% of these samples were coated on a cellophane film or a copper plate as a layer 0.2 mm thick and dried to remove the solvent. The thickness of the sample films was 0.035 mm.

TABLE I

Compositions of Samples

	Components, parts by weight				Rosin content (based on total solid), vol-%	Viscosity of sample $\times 10^{-7}$, poise
Sample No.	Poly-isobutylene (Vistanex-L 120)	Poly-isobutylene (Vistanex-LMMS)	Poly-isobutylene (Oronite-32)	Hydro-genated rosin		
1	1	—	1	—	0	4.71
2	2	1	1	—	0	—
3	4	—	3	1	10.9	6.15
4	2	—	1	1	22.2	4.76
5	1	—	—	1	46.0	6.13
6	1	—	—	3	71.9	0.276

The viscosity of the samples shown in Table I was measured by the shear creep method at 30°C and calculated by the equation:[8]

$$\eta = \frac{FL}{A}\left(\frac{1}{dx/dt}\right) \tag{1}$$

where F is load, L the thickness of the sample, and A the contact area. The deformation rate dx/dt was obtained from the slope of the plots of displacement x against time t, as shown in Figure 1.
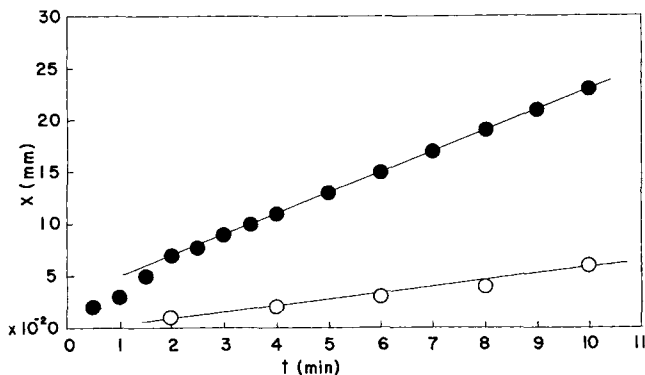
Fig. 1. Displacement-time relations for shear creep measurements.

Apparatus and Procedure

The measuring assemblage was attached to a Tensilon UTM II tensile tester (made by Toyo Measuring Instruments Co., Ltd., Tokyo, Japan) driven at a constant speed. A schematic diagram of the assembly is shown in Figure 2a. We fixed an unbonded strain gauge of 300-g or 1000-g capacity by an L-shaped plate to a movable crossbar of the testing machine. A cylindrical rod of brass or polytetrafluoroethylene, polyethylene, and poly(methyl methacrylate) was connected upwards to the sensitive part of the strain gauge. The surface of the rod was polished with No. 1000 emery paper. A sample adhesive was spread on the surface of a cellophane or copper sample plate, which is, in turn, put face-downwards on the upper face of the hollow sample ring placed on a holder fixed to the upper bar of the tester. Then the tacky sample surface appears through the hole of the sample ring. A weight was loaded on top of the sample plate from the back.

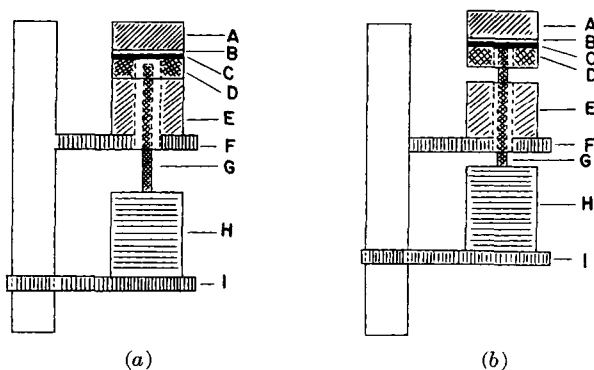(a)   (b)

Fig. 2. Schematic diagram measuring assembly attached to the tensile tester (a) before contact or after failure of adhesive joint and (b) at contact: (A) weight; (B) sample plate; (C) sample; (D) sample ring; (E) holder; (F) fixed bar; (G) cylindrical bar; (H) strain gauge; (I) movable crossbar.
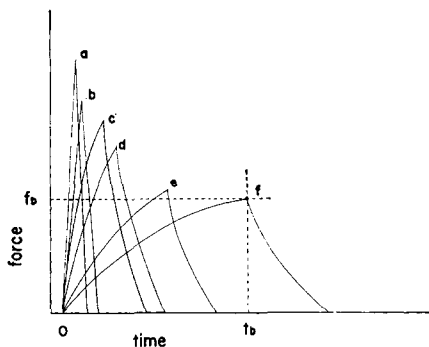
Fig. 3. Force–time relation at various separation rates r: (a) 20 mm/min; (b) 10 mm/-min; (c) 5 mm/min; (d) 4 mm/min; (e) 2 mm/min; (f) 1 mm/min.

To make measurements, the crossbar was driven upwards and the upper flat surface of the cylindrical rod was pushed upwards onto the tacky surface of the sample, and the sample plate was lifted for a given time with the load as shown in Figure 2b. Then the sample surface was in contact with the cylinder surface under constant pressure by the loaded weight.

Next, the crossbar was lowered at a definite speed. From the instant the sample plate made contact with the sample ring, a force necessary to separate the surface of the cylinder from sample surface was recorded on a chart. The rate of separation was between 1 and 20 mm/min, and the temperature was between 10 and 50°C. The force–time relations obtained for sample 4 at 30°C at various rates of separation r are shown in Figure 3. The maximum force f_b at time t_b of the force–time relation was determined as a measure of the tackiness.

RESULTS AND DISCUSSION

From five measurements, the middle three values were averaged to obtain a mean value of f_b. In any case, the difference of maximum and minimum values was less than 20% of the mean value.

The tackiness f_b depends on the time of contact t_c and the pressure at the contact p_c. The relation of f_b to t_c and p_c are shown in Figures 4 and 5. Figure 4 shows that f_b approaches an almost constant value at a contact
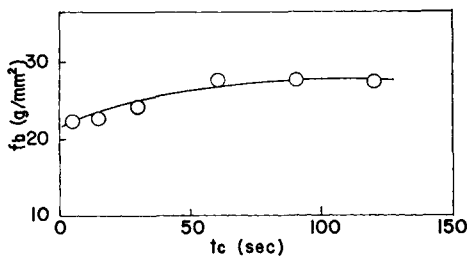

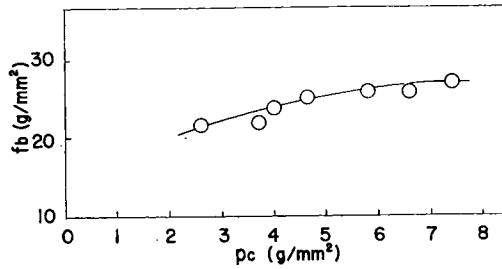Fig. 4. Dependence of the tackiness on the contact time.

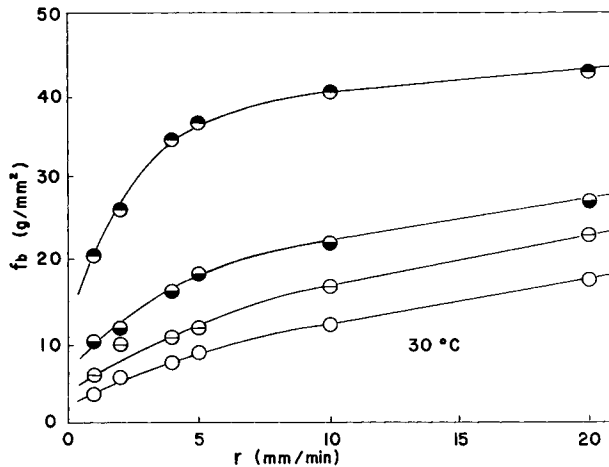Fig. 5. Dependence of the tackiness on the contact pressure.

Fig. 6. Dependence of the tackiness on the rate of separation.

time longer than 60 sec. In the relation between f_b and p_c in Figure 5, f_b shows a slight increase as p_c increases, due to the increase of contact area by the flow of the sample. In this report, unless otherwise noticed, the contact time and the contact pressure were held at 80 sec and 4 g/mm, respectively.

As is shown in Figure 3, f_b increases with the rate of separation. The curves showing the dependence of f_b on the rate of separation for the samples with various rosin contents are shown in Figure 6. The value of f_b increases with the rosin content up to 46.0%.

To eliminate the influence of the rate of separation, the values of f_b relative to the value for the sample containing no rosin (sample 1) f_b^0 were determined; these are shown in Figure 7. In sample 3, having a rosin content of 10.9%, the effect of the rate of separation almost disappeared. As the rosin content increases, however, f_b/f_b^0 decreases with the rate of separation.

In sample 6, having a rosin content of 71.9%, conversely, f_b/f_b^0 shows a slight increase with the rate of separation. This may be caused by the
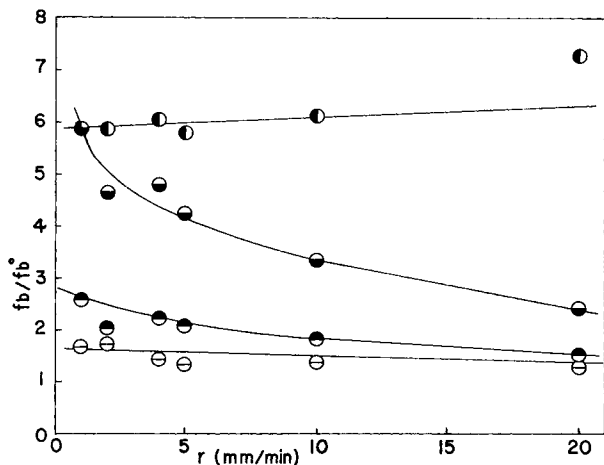
Fig. 7. Dependence of the relative values of the tackiness on the rate of separation.
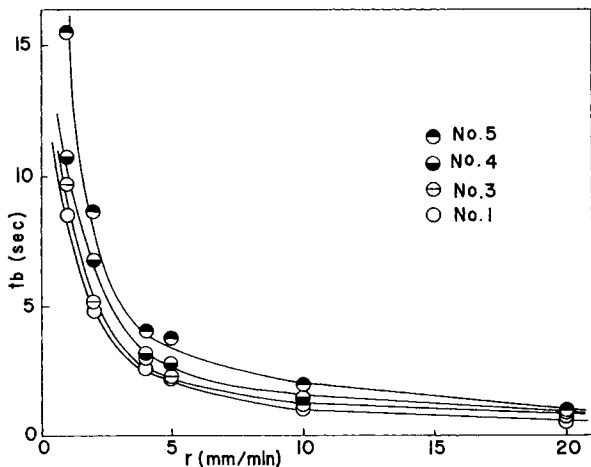

Fig. 8. Dependence of breaking time on the rate of separation.

phase reversal taking place at between 46.0% and 71.9% of the rosin content.

When a tacky thin layer of the sample was pulled away from the solid surface, f_b indicates the viscous resistance caused by the radial inward flow of the sample. At a rosin content lower than a certain critical value, $f_b/f_b{}^0$ decreases with the rate of separation. This means that the rosin aggregates in the solution at a lower rate of separation, and the solution shows a higher resistance to flow. At a higher rate of separation, the resistance becomes smaller on the disintegration of the rosin aggregates. As the rosin content exceeds a critical value, reversal of the phase occurs. The rosin phase changes to a continuous phase, and $f_b/f_b{}^0$ becomes almost constant, as shown in Figure 7.
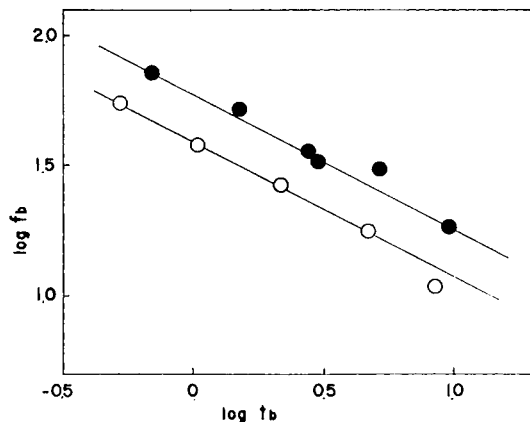
Fig. 9. Relationship between the tackiness and the breaking time.
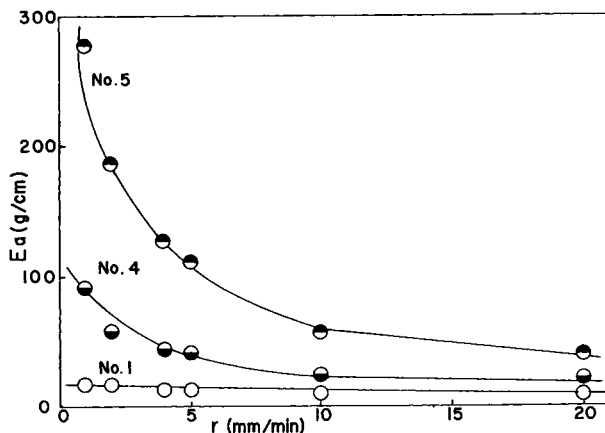

Fig. 10. Dependence of the adhesion energy on the rate of separation.

As shown in Figure 3, the breaking time t_b decreases with f_b as the increase of the rate of separation. The relations between t_b and r for samples of various rosin contents are shown in Figure 8. It seems t_b is the time when the type of the sample flow varies from contraction for the radial direction to elongation for the vertical direction. The relation between $\log f_b$ and $\log t_b$ is shown in Figure 9. It satisfies the equation $f_b \propto t_b^{-1/2}$ derived by Eley.[10] The value of f_b is characteristic of the sample. In other words, its relation to the rate of separation and the temperature is determined as above, and its value is considered to be a measure of the tackiness.

Moreover, t_b is also characteristic of the sample and may be used as another measure of the tackiness. The value decreases with increasing rate of separation and increasing temperature. The adhesive layer between the surface of the sample and the cylindrical bar is held continuous until the force shown in Figure 3 becomes zero.
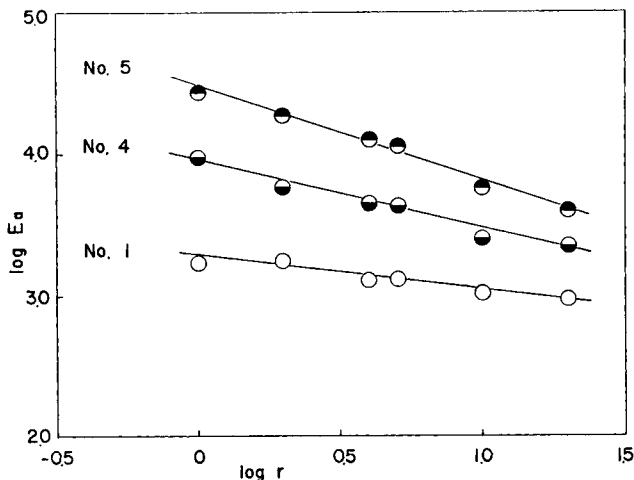
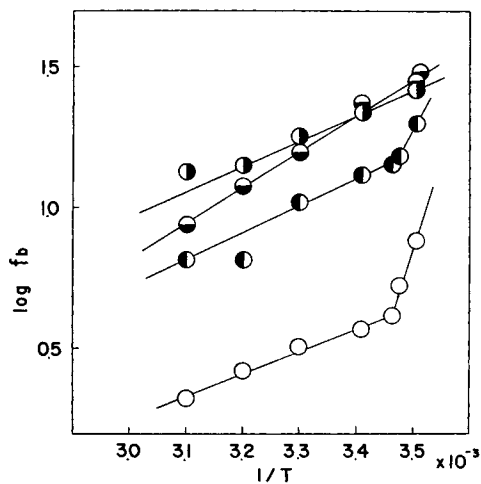Fig. 11. Double logarithmic plots of adhesion energy vs. the rate of separation.

Fig. 12. Arrhenius plots of temperature dependence of the tackiness for sample 1 at various
r: (◐) 20 mm/min; (◒) 10 mm/min; (◓) 5 mm/min; (○) 1 mm/min.

In this experiment, as the rate of separation is kept constant, the time axis is proportional to the strain.   Therefore, the adhesion energy E_a is obtained by eq. (2).

$$E_a = \int_0^t f\,dt \tag{2}$$

The relation of E_a to the rate of separation r is shown in Figure 10. E_a increases as the rosin content.   Double logarithmic plots of E_a against r are shown in Figure 11.   The curves are indicated by eq. (3):

$$E_a{}^n = kr \tag{3}$$

where n is 4.3 for sample 1, 2.0 for sample 4, and 1.5 for sample 5.

The value of f_b increases with temperature. Plots of f_b against the reciprocal of the absolute temperature are shown in Figures 12–14. In every case, there appear two straight lines with different slopes. The activation energy calculated in the range of higher temperature is shown in

TABLE II
Activation Energies for Tackiness at Elevated Temperatures

Rate of separation, mm/min	Activation energy, kcal/mole		
	Sample 1	Sample 4	Sample 5
20	4.2	2.1	5.1
10	6.0	4.2	5.1
5	4.4	4.0	5.8
1	3.7	6.1	6.1

Table II. These values are similar to the activation energy for the viscous flow of the polymer solutions and correspond to the activation energy for the viscous radial flow at the separation of surfaces. Therefore, the tackiness in this case is based upon the viscous flow of the sample solution. In the temperature range examined so far, the activation energy is almost equal in all cases. Voyutskii[2] reported an activation energy of 2.4 kcal/mole for the autohesion of polyisobutylene. Recently, Gul[5] reported an activation energy of 4.5 kcal/mole in a peeling test with cellophane and polyethylene, though the tackiness with these materials involves a process
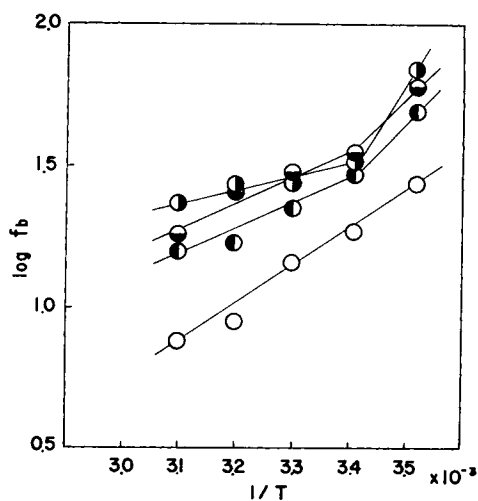

Fig. 13. Arrhenius plots of temperature dependence of the tackiness for sample 4 at various r: (◑) 20 mm/min; (◒) 10 mm/min; (◐) 5 mm/min; (○) 1 mm/min.

essentially different than in our tackiness study. The similarity of the activation energy indicates similarity of two mechanisms.

In Figures 12–14, the activation energy in the range of lower temperatures appears slightly larger than in the range of higher temperature.
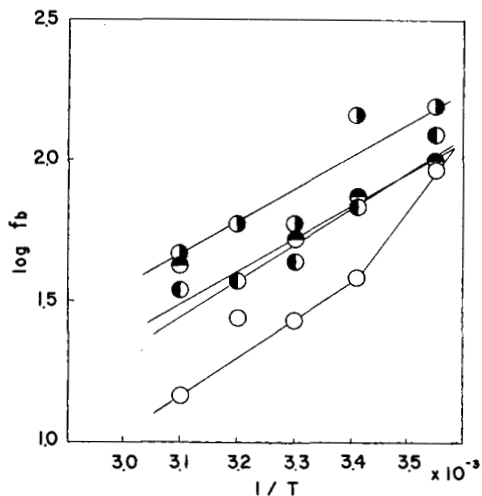

Fig. 14. Arrhenius plots of temperature dependence of the tackiness for sample 5 at various r: (◑) 20 mm/min; (◒) 10 mm/min; (◐) 5 mm/min; (○) 1 mm/min.
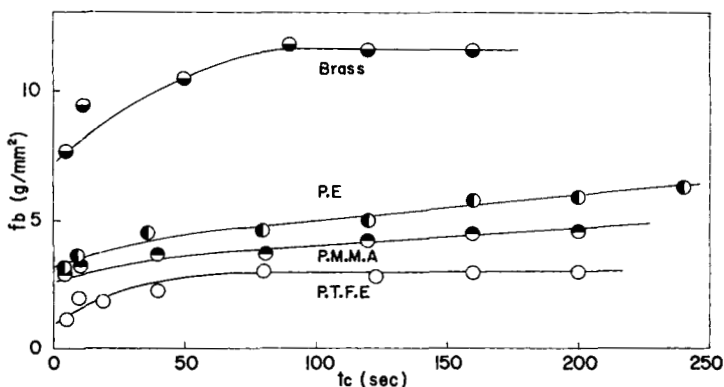

Fig. 15. Dependence of the tackiness on the contact time for $r = 20$ mm/min.

In this condition, a force other than viscous force may be involved in the mechanism of the separation. A clear interpretation of the mechanism has not yet been obtained.

To judge whether failure occurs adhesively at the interface or cohesively within the adhesive itself, we measured the tackiness with cylindrical rods made of brass, polyethylene, poly(methyl methacrylate), and polytetrafluoroethylene. The results are shown in Figures 15 and 16. The sample
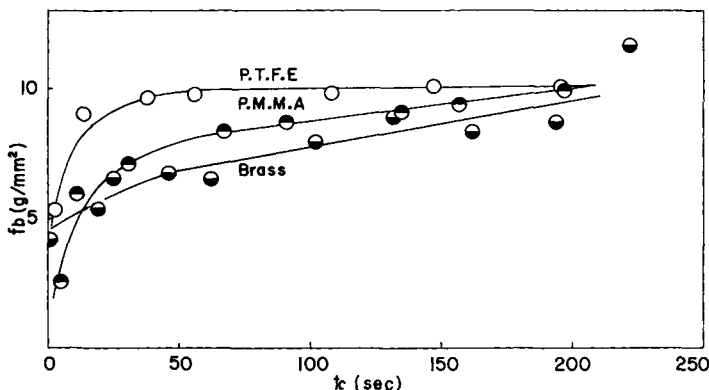
Fig. 16. Dependence of the tackiness on the contact time for $r = 1$ mm/min.

was coated on a copper plate of 0.2 mm thickness in order to remove the influence of the deformation of backing. From Figure 15 for $r = 20$ mm/min, it is clear that f_b depends on the quality of the cylindrical rod. In Figure 16 for $r = 1$ mm/min, f_b became almost constant with increasing t_c, irrespective of the type of cylindrical rod. From these results, it is concluded that the failure occurs adhesively at the interface for $r = 20$ mm/min and cohesively within the adhesive for $r = 1$ mm/min.

CONCLUSION

The tackiness of the sample blends of the high molecular weight polyisobutylene with a low molecular weight polyisobutylene or with a hydrogenated rosin was measured. The maximum force f_b at time t_b of the force–time relation was determined as a measure of the tackiness during the separation of the tacky surface of the sample and the solid surface of various materials. The adhesion energy E_a estimated by the area between the curve and time axis was considered as another measure of the tackiness. As a result, f_b, t_b, and E_a increase as the rosin content of the sample increases. Moreover, f_b increases and t_b and E_a decrease with increasing rate of separation of the surfaces. From the value of the activation energy obtained from the temperature dependence of f_b we conclude the tackiness defined in this way is based upon the viscous resistance of the sample flow. The failure occurs adhesively at the interface at a rate of separation r of 20 mm/min, and cohesively at $r = 1$ mm/min.

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