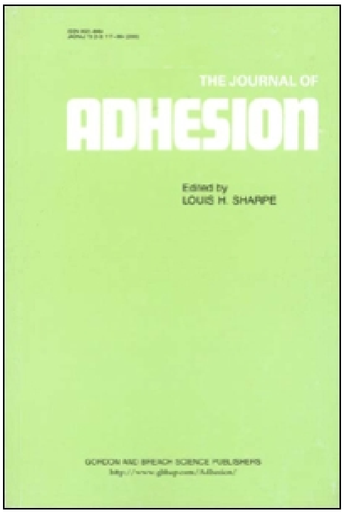

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Structure-Property Relationships in Acrylic Adhesives

Hung-Kong Chan[a,b]; G. J. Howard[a]
[a] Department of Polymer and Fiber Science, University of Manchester Institute of Science and Technology, Manchester, England [b] Cyanamid (UK), Bradford, England

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Structure-Property Relationships in Acrylic Adhesives

HUNG-KONG CHAN† and G. J. HOWARD

Department of Polymer and Fiber Science, University of Manchester Institute of Science and Technology, Manchester, England

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Three series of non-polar acrylic copolymers based on 2-ethyl hexyl acrylate and four series of polar copolymers based on ethyl acrylate were synthesised. Their adhesion performance was assessed by measurement of the force required to detach a probe (tack strength), that required to peel a strip (peel strength) and the resistance to a shear force (cold-flow time). The effect of test conditions on these measurements was also surveyed.

With non-polar copolymers the adhesion test values, which are strongly composition-dependent, may be placed on a common basis by relation to the glass transition temperature of the adhesive, provided samples of approximately equal molecular weight are compared. This is not possible with polar copolymers which thereby show the influence of specific interfacial interactions.

INTRODUCTION

A basic preoccupation of polymer science is to establish correlations between chemical structure and material properties. In the present paper we restrict our attention to pressure-sensitive adhesives composed solely of an acrylic copolymer. Despite the considerable number of studies of structure-property effects in adhesives, little progress towards an overall, formalised, relationship between polymer composition and adhesive performance has been achieved. That this is so is not surprising since the relative contributions of viscoelastic response, degree of interfacial contact and specific surface interactions to pressure-sensitive adhesion are not firmly established so that the compositional role in these factors is not readily elucidated. Furthermore, several studies have used multi-component adhesives; even where an individual

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† Present address: Cyanamid (UK), Bradford, England.

TABLE I

Homopolymers

Sample code	Composition	% conversion	$[\eta]^a$	$T_g{}^b$	$\gamma_l{}^c$
P-1	ethyl acrylate (EA)	17	1.08	−10	42.4
P-6	ethyl methacrylate (EMA)	14	0.63	74	41.5
P-11	methyl acrylate (MA)	25	0.72	23	45.2
P-34	*n*-butyl acrylate (nBA)	30	0.98	−33	39.2
P-35	*n*-butyl methacrylate (nBMA)	13	0.68	43	40.3
P-32	ethyl acrylate	54	0.46	−11	42.4
P-33	ethyl acrylate	59	0.29	−17	42.4

[a] dl/g. toluene 25°C. [b] °C DSC data. [c] mN m^{-1}.

TABLE II

Non-polar acrylic copolymers of 2-ethyl hexyl acrylate (2EHA)

Sample code	Mole % comonomer	% conversion	$[\eta]$	T_g	γ_l
	ethyl acrylate (EA) copolymers				
P-2	79	18	1.12	−23	40.2
P-3	65	16	1.08	−26	39.1
P-4	40	17	0.78	−38	37.9
P-5	24	17	0.70	−46	37.2
P-36	80	14	0.68	−19	
P-37	86	27	0.39	−20	
	ethyl methacrylate (EMA) copolymers				
P-7	75	18	0.80	14	39.6
P-8	58	27	0.76	−11	38.6
P-9	52	23	0.70	−28	38.3
P-10	35	26	0.68	−39	37.6
	methyl acrylate (MA) copolymers				
P-12	92	17	1.02	6	43.4
P-13	83	21	1.00	−28	42.0
P-14	72	25	0.94	−39	40.7
P-15	41	19	0.75	−52	38.2
P-16	3	6	0.72	−54	36.6

copolymer has been employed it had been formed at high conversion with the corresponding hazard of a broad compositional distribution. In the present work we have studied series of non-polar acrylic copolymers and also have investigated the effects of copolymerised polar groups; all the polymers were made to low conversion to minimise compositional drift during copolymerisation.

EXPERIMENTAL

Materials

With the exception of methacrylic acid, all the monomers as supplied showed only a single peak on gas chromatographic examination; non-polar acrylates were checked for acidity which was found to be negligible (<60 ppm). Methacrylic acid was passed through a column of silica gel and then distilled under reduced pressure; other monomers were used as supplied. Polymerisa-

TABLE III

Polar acrylic copolymers of ethyl acrylate (EA)

Sample code	Mole % comonomer	% conversion	$[\eta]$	T_g	γ_l
	acrylic acid (AA) copolymers				
P-17	1.1	21	0.98	−6	42.5
P-18	5.1	15	0.57	−1	42.9
P-19	7.6	32	0.30	5	43.5
P-20	24.1	38	n.d.	8	46.3
	methacrylic acid (MAA) copolymers				
P-21	2.6	15	1.04	8	42.5
P-22	6.5	16	0.66	12	42.8
P-23	8.3	13	0.42	16	43.0
	hydroxyethyl acrylate (HEA) copolymers				
P-24	1.9	17	1.15	−1	42.8
P-25	7.2	27	1.03	0	43.7
P-26	8.0	15	1.03	1	43.9
P-27	13.7	28	0.65	7	44.9
	acrylonitrile (AN) copolymers				
P-28	4.9	16	1.02	0	42.9
P-29	7.6	17	1.02	2	43.0
P-30	13.4	7	0.86	5	43.6
P-31	18.9	17	0.60	13	44.1

tion was radically-initiated with recrystallised azoisobutyronitrile and was carried out in toluene solution at 60°C (75°C in four preparations) under a blanket of nitrogen. The principal copolymer series were made with a fixed monomer/solvent/initiator/temperature formulation so as to minimise variations in molecular weight. Polymerisations were stopped at a time judged to give less than about 20% conversion. The reaction mixture was poured into a large excess of non-solvent (methanol or petroleum ether, depending on polymer composition) and the precipitate was thoroughly washed with non-solvent before being dried to constant weight *in vacuo* at 50–60°C.

Compositions of the non-polar copolymers were found by elemental analysis for carbon. Copolymers containing acrylonitrile were analysed by their nitrogen content; copolymers of acrylic and methacrylic acids were titrated against 0.1 M sodium hydroxide; the hydroxyl contents of copolymers containing 2-hydroxy ethyl acrylate were found by back-titration after refluxing with acetic anhydride. Characterisation data of the principal series of copolymers are presented in Tables I, II and III.

Methods

Intrinsic viscosities were measured in toluene at 25°C with a Fica "Viscomatic" automatic dilution viscometer. Glass transition temperatures were determined on a Perkin Elmer DSC2 differential scanning calorimeter at 80°C/min. The calorimeter sample pans were filled with concentrated polymer solutions which were then dried under vacuum for 24 hours before the pans were closed. The high rate of temperature scanning helped to pin-point the transition temperature and greatly reduced complications arising from moisture condensation in successive runs at sub-ambient temperatures.

The adhesive performance of the copolymers has been rated by three tests; tack adhesion, peel strength and cold flow. A polymer solution (30–40%) in toluene was initially laid down as a uniform layer on a sheet (200 × 254 mm) of silicone-coated release paper. This was achieved as follows. Two parallel, highly-polished, stainless-steel, rods mounted horizontally in the coating frame, were adjusted to the required gap by placing a feeler gauge at either end of the nip before clamping tightly; to obtain a dry polymer film of a particular thickness necessitated the use of a feeler gauge some ten-times thicker. A sheet of release paper was fed into the gap so that its lower edge protruded slightly. A small quantity of the viscous polymer solution was poured across the siliconised face of the paper held in the nip and then the paper was drawn steady through from underneath. When a second adhesive sheet was required the first was left with 20–30 mm above the bars; the second sheet was inserted behind this projection and was then drawn through as the first sheet was pulled clear.

The coated sheet was allowed to air-dry for 20 minutes and was then heated for exactly 3 minutes in an oven, fitted with air circulation, at 120°C after which it was removed and allowed to cool to room temperature. Both the air-drying and cooling stages were conducted under cover to minimise contamination with air-borne dust. A sheet of backing paper (white litho) was carefully placed over the polymer layer, taking care to avoid trapping air. The sandwich was then pressed by passing twice through a rubber-rolled mangle, guillotined into strips (200 × 25.4 mm) and placed in a conditioning vessel prior to testing. These vessels (glass desiccators) were kept at 23 ± 1°C and a relative humidity of $50 \pm 2\%$ was maintained inside them with a saturated solution of calcium nitrate. A minimum conditioning period of two days was allowed prior to testing.

The thickness of the adhesive layer was found by pressing a pre-weighed sheet of backing paper (100 × 100 mm) on to the adhesive-coated release paper, trimming off excess of the latter. After two passes through the mangle the release paper was carefully peeled off so transferring the adhesive to the backing paper which was folded and re-weighed. The thickness was calculated assuming all the polymers to have a density of 1000 kg m^{-3}.

Samples for the peel strength test were prepared as follows. A clean glass plate (152 × 38 × 5 mm) was used as substrate. One of the adhesive sample strips was taken and the release paper peeled back for half its length. The exposed portion was carefully pressed onto the glass plate, leaving release paper covering the rest of the specimen. The assembly was pressed by four traverses of the rubber-rolled mangle and allowed to stand for 20–30 minutes before testing. The specimen was mounted in an Instron tensile tester by clamping the further end of the glass plate in the fixed grip, turning back the free end of the flexible test piece and clamping it in the moveable grip. Extraneous release paper was removed and the assembly adjusted to be symmetrical so that the tension would be uniformly distributed. The sample was peeled at an angle of 180° with a cross-head separation rate of 200 mm min^{-1}; peeling was continued for at least half the bonded length to establish a steady peel force. For standard test purposes the adhesive layer was restricted to a thickness of 25–38 μm; four determinations were made and the mean and standard deviation are quoted. The visually-assessed mode of failure is also recorded: "cohesive" failure indicated an apparently even residue of polymer on the substrate; "interfacial" failure when the substrate appears free of residue; "mixed" failure when scattered islands of adhesive remain on the substrate after separation. In a few cases the failure was in the backing paper and this is so recorded.

Tack adhesion is the "force required to separate an adherend and an adhesive shortly after they have been brought rapidly into contact under a light load of short duration".[1] A tack meter was constructed as follows. The sample holder was in two parts; a collar with a circular hole 15 mm diameter screws onto the base so as to locate a test specimen with the adhesive facing upwards. The holder was clamped in the fixed lower grip of an Instron tensile tester. The probe was a flat disc 12.7 mm diameter made of stainless steel and polished to 0.4 μm surface roughness, as measured by a Talysurf tester. Some tests were performed with a similarly-sized probe with a PTFE surface. The probe holder is constructed as a free-sliding piston and may be loaded by selected weights. This part was attached to the moving cross-head of the Instron tester. The probe was lowered vertically onto the sample and for instrumental reasons the contact was made at the same rate as that selected for separation. As soon as contact was made the load was that of the free-sliding portion of the probe and its holder together with the selected additional weights. After the pre-selected contact time the probe is pulled off the specimen and the height of the sharp peak on the recorder chart was taken as the tack strength. The mean of four determinations, all on a fresh sample with a clean probe, was taken and the mode of failure recorded. The following conditions were adopted for standard testing; contact pressure 10.9 kN m^{-2}; contact time 1 second; separation rate 500 mm min^{-1}.

The cold flow test is a useful method for assessing the cohesive strength of the polymer and is defined by Dahlquist[2] as the resistance to a dead-load shearing force. We follow the common practice of finding the time required to pull a standard area of an adhesive-coated sample from a test substrate under a fixed load. In our work two layers of adhesive are bonded to each other. A test strip (200 × 25.4 mm) was cut into two halves across its length, the release paper peeled back and the adhesive faces pressed together to give 12.7 mm overlap across the 25.4 mm width of the sample. Excess release paper was trimmed off and the specimen pressed by four passes through the mangle. A mass of 200 g was placed over the bonded area for one hour. Hooked grips were tightly clamped to each end of the specimen, one was fixed to the upper bar of the test frame and a mass of 200 g carefully placed on the lower hook; the total force on the adhesive overlap is 2.16 N. As soon as the joint was loaded an automatic timer was started; the push switch was located directly below the hanging weight so that when the joint failed the timer was stopped and this was recorded as the cold-flow time. Times in excess of two weeks are recorded as infinity. Measurements were made in triplicate. Occasionally, samples failed prematurely by a catastrophic separation before one end of the tape had slipped appreciably along the bonded length. Unlike normal failure, in which the surfaces of the separated adhesive layers appeared smooth and uniform, "pop-off" failures exhibit patches where the adhesive has pulled away from the backing paper. These atypical failures occur at random and must be attributed to surface contamination or to non-uniformity of the adhesive layers; they were discounted and further tests made. Standard test conditions for cold-flow are overlapped length 12.7 mm with strips 25.4 mm wide; load 2.16 N, dwell time 1 hour, adhesive layer (per strip) 25–30 μm.

RESULTS

Standardisation of test conditions

Before finalising the conditions for standard testing, the effect of pertinent parameters was investigated. After the trials which are summarised in Table IV had been completed, the solvent removal conditions were fixed at 3 minutes at 120°C.

TABLE IV

Drying conditions for specimen preparation: polymer P-2

Time air-dried (min)	Time at 120°C (min)	Tack [a] (kN m^{-2})	Peel [a] (N m^{-1})
60	0	9.8±0.2 (i.f.) [b]	569±37 (i.f.)
20	1	9.4±0.9 (i.f.)	574±10 (i.f.)
20	3	9.3±0.9 (i.f.)	647±37 (i.f.)
20	5	9.4±0.5 (i.f.)	579±32 (i.f.)
20	10	9.9±0.4 (i.f.)	608±37 (i.f.)

[a] Four determinations; standard conditions. [b] Interfacial failure.

It was further shown that these drying conditions gave the same tack and peel strengths when a polymer (MA/2EHA : 89/11, 60% conversion) was deposited from acetone as from the standard solvent (toluene). It might be noted, however, that Engel and Fitzwater[5] find significant variation of the peel strength from a tin surface of a lauryl methacrylate/methyl methacrylate copolymer when deposited from a range of solvents. Having established the conditions for sample preparation it is now necessary to consider the various testing procedures.

Several factors may influence the measured peel strength. Hardy[3] has shown a linear relation between the force required to peel a specimen from a substrate and its width, irrespective of its mode of failure; this parameter was not, therefore, further investigated and we express the peel strength as the peeling force per unit width. Hardy also demonstrated that the peel strength does not vary so markedly with angles between 90° and 180° as it does at smaller angles. Kaelble's[4] analysis shows that, at angles greater than 90°, shear stress effects are small and that, close to 180°, cleavage stress predominates and the peel force should then become essentially independent of the direction of peel. In the present work, care was taken in mounting the peel test specimens so that the peeling was at 180°. This author[4] further predicts the 180° peel force to vary with adhesive thickness whereas Hardy[3] reports that experiments show this to be true only up to some critical thickness above which there is no further dependence. Other workers[5,6] report similar observations with soft linear polymers whilst Reegen and Ilkka[7] show that with cross-linked polyurethanes peel strengths are virtually independent of film thickness with extensible gels but show a stronger dependence when the polymers are more tightly cross-linked.

TABLE V

Variation of peel strength with adhesive thickness (other conditions as standard)

Layer thickness (μm)	Peel strength (N m^{-1})
7.6	201±15 (i.f.)
10.2	323±91 (i.f.)
15.2	511±11 (i.f.)
22.9	565±18 (i.f.)
30.5	560±52 (i.f.)

The effect of layer thickness was found for an acrylic copolymer selected to have a glass transition temperature around the mid-point of the range from the copolymers synthesised in the present study. As a consequence of these results, given as Table V, peel tests made under standardised conditions were restricted to adhesive polymers 25–38 μm thick. No significant difference in peel strength is found between specimens which have been pressed by 2, 4 or 6 passes through the rolls.

An important variable in peel testing is the rate of separation. Aubrey *et al.*[8] analysed the process as follows. At low rates, the peel behaviour is determined by viscoelastic flow and the peel force is strongly rate dependent. At high rates, little viscous deformation occurs and the peel strength becomes independent of rate and failure is usually interfacial, whereas at intermediate rates a "slip-stick" failure mode is predicted. In the present study the recorder traces show an irregular peel force indicative of continuous failure initiation[9] at all rates of testing and whatever the visually-assessed mode of separation. The extent of the dependence of peel strength on separation rate varies with the nature of the polymer and with its failure mode. Figure 1 shows some examples and the standard rate of 200 mm min^{-1} was selected rather arbitrarily.

Several variables of the tack test by probe separation were studied. The thickness of the adhesive layer is significant only when very thin (Table VI) and this observation is in accord with the results of Hammond.[10]

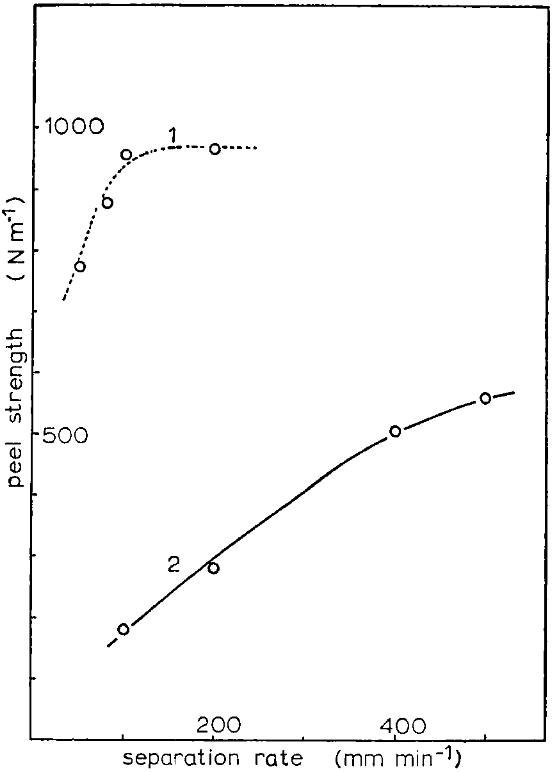

FIGURE 1 Variation of peel strength with peeling rate. Curve 1, sample P-32; curve 2, commercial, rubber-based, adhesive (E). —— interfacial failure; . . . cohesive failure.

Contact pressure was varied by placing different weights on the probe and the result for several polymers are given in Table VII. Higher tack strengths are found as the contact pressure is increased from small values: the selected contact pressure for standard testing is that which gives maximum separation between the samples, two of which undergo a changed mode of failure at higher contact pressures.

The period of contact between the polymer and the probe prior to its detachment is an important variable in this test and the results obtained

TABLE VI

Variation of tack strength with adhesive thickness polymer P-3 (other conditions as standard)

Layer thickness (μm)	Tack strength (kN m^{-2})
15.2	9.0±0.5 (i.f.)
17.8	11.2±0.5 (i.f.)
20.3	11.7±0.5 (i.f.)
27.9	11.1±0.6 (i.f.)
30.5	12.1±0.2 (i.f.)
33.0	12.1±0.2 (i.f.)

TABLE VII

Variation of tack strength with contact pressure (other conditions as standard)

Sample code	Contact pressure (kN m^{-2})					
	3.1	7.1	10.9	18.6	26.5	31.4
	tack strength (kN m^{-2})					
P-1	6.4±0.5 (i.f.)	8.5±0.6 (i.f.)	8.7±0.2 (i.f.)	10.8±0.8 (i.f.)	—	—
P-2	8.4±0.1 (i.f.)	9.0±0.6 (i.f.)	10.3±0.5 (i.f.)	10.9±0.9 (i.f.)	—	—
P-3	7.7±0.2 (i.f.)	9.0±0.6 (i.f.)	11.6±0.1 (i.f.)	11.2±0.9 (i.f.)	—	—
P-4	7.8±0.8 (i.f.)	9.3±0.5 (i.f.)	13.6±1.0 (i.f.)	11.5±0.6 (c.f.)[a]	—	—
C-24[c]	11.2 (i.f.)	11.3 (i.f.)	12.2 (i.f.)	15.1 (b.f.)[b]	15.1 (b.f.)	—
A[d]	9.8±0.2 (i.f.)	11.4±0.2 (i.f.)	11.8±0.5 (i.f.)	11.8±0.5 (i.f.)	—	11.5±0.5 (i.f.)

[a] Cohesive failure. [b] Backing failure. [c] EA/2EHA high conversion copolymer. [d] Commercial rubber-based adhesive.

TABLE VIII

Variation of tack strength with contact time (other conditions as standard)

Sample code	Contact time (sec)				
	0.1	1.0	5.0	10.0	15.0
	tack strength (kN m^{-2})				
P-1	5.5±0.8 (i.f.)	8.7±0.1 (i.f.)	10.7±0.4 (i.f.)	11.9±1.2 (c.f.)	14.6±1.0 (c.f.)
P-2	6.4±0.7 (i.f.)	10.3±0.5 (i.f.)	11.5±0.8 (c.f.)	13.4±0.5 (c.f.)	13.5±0.5 (c.f.)
P-3	6.5±0.5 (i.f.)	11.6±0.1 (i.f.)	11.7±1.0 (c.f.)	12.4±1.2 (c.f.)	13.9±0.7 (c.f.)
P-4	7.7±0.3 (c.f.)	13.6±1.0 (c.f.)	14.7±2.9 (c.f.)	13.4±0.7 (c.f.)	13.6±1.3 (c.f.)
A	10.2±0.2 (i.f.)	11.8±0.5 (i.f.)	12.8±0.2 (i.f.)	13.2±0.3 (i.f.)	—

with five samples are given as Table VIII. The tack strengths increase markedly as the contact period is increased from very short times but the softer polymers have tack strengths which remain fairly constant beyond one second contact although harder polymers are more dependent. The tack strengths are not noticeably influenced by the mode of failure, which changes to cohesive after longer contacts.

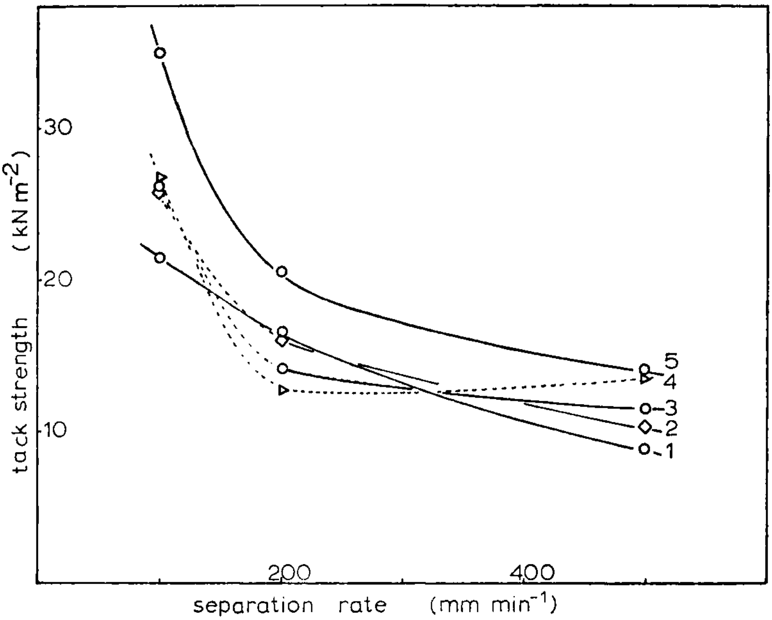

FIGURE 2 Variation of tack strength with probe separation rate. Curve 1, sample P-1; curve 2, sample P-2; curve 3, sample P-3; curve 4, sample P-4; curve 5, commercial, rubber-based, adhesive (A).

The effect of separation rate on tack strength is shown as Figure 2 from which it may be seen that large changes occur below 200 mm min^{-1} but that thereafter the tack stays more constant. However, it is the direction of the rate dependence that is surprising as it is opposite to that found by Hammond,[10] Dahlquist,[11] Bates[12] and Kambe and Kamagata[13]; of course the test conditions used by these various workers are not the same as in the present study and it should be noted that Bates employs a hemispherical probe whilst Kambe and Kamagata employ much slower rates of probe removal. This rate effect will be discussed later. We summarise in Table IX the standard conditions and those used by other workers who have employed this method of adhesive characterisation.

TABLE IX

Standard conditions for probe tack test

Author	Probe diameter (mm)	Probe material	Contact time (sec)	Contact pressure (kN m^{-2})	Separation rate (mm min^{-1})
Wetzel[1]	1.6	brass	1	52.3	500
Kambe & Kamagata[13]	unspecified	brass	80	39.2	1–20
Hammond[10]	5.1	stainless steel	1	9.8	140
ASTM[14]	5.1	stainless steel	1	9.8	600
Bates[12]	10 [a]	various plastics	10	various	various
Present work	12.7	stainless steel	1	10.9	500

[a] Hemispherical.

TABLE X

Variation of cold-flow time with specimen preparation: sample P-3 (other test conditions as standard)

Number passes through rolls	Cold-flow time (min)
2	278±10
4	265±47
6	311±21
8	340±49

TABLE XI

Variation of cold-flow time with thickness of individual adhesive layer: sample P-3 (other test conditions as standard)

Adhesive layer thickness (μm)	Cold-flow time (min)
10.2	220±17
12.7	230±26
33.0	123±15
48.3	78±3

Only two variables were investigated in connection with the cold-flow test. First the effect of the specimen preparation conditions were examined by altering the number of passes through the rolls (Table X). A low but adequate net contact was adopted to avoid the danger of softer adhesives being squeezed from the edges of the specimen under more severe pressures. The cold-flow times were also measured for specimens of different layer thickness; in Table XI the thickness is that of a single coated sheet prior to bonding to the second coated sheet. The data show a roughly linear relation to reciprocal layer thickness; for standard testing the original adhesive layers were made as close to 28 μm as possible.

Adhesion performance of non-polar copolymers

The parent homopolymers were examined by the standardised test procedures and gave results presented in Table XII. The zero entries in this table signify a complete absence of the adhesive property at the test temperature (23°C). The homopolymer of 2-ethyl hexyl acrylate could not be cast successfully to a uniform film onto the silicone-coated release paper from any of several solvent mixtures tried. The data in Table XII for sample P-16 are included as an indication of the likely magnitude of the homopolymer performance since this copolymer contains only a small quantity of methyl acrylate comonomer. As is already known,[6] acrylates are much superior to the corresponding methacrylates as would be expected from the large difference in glass transition temperatures between the two series. Amongst acrylates, as the alkyl group is lengthened, the glass transition temperature is reduced with a corresponding increase in tack strength and lowering of peel strength and resistance to shear.

TABLE XII

Adhesive performance of homopolymers

Sample code	Composition	T_g (°C)	Tack strength (kN m^{-2})	Peel strength (N m^{-1})	Cold-flow (min)
P-11	MA	23	0	0	0
P-1	EA	−10	8.5±0.2 (i.f.)	266±37 (i.f.)	22080±1660
P-34	nBA	−33	12.8+1.1 (c.f.)	125+5 (c.f.)	74±4
P-6	EMA	74	0	0	0
P-35	nBMA	43	0	0	0
P-16	2EHA/MA(97/3)	−54	15.5±0.1 (c.f.)	97±2 (c.f.)	3±0.7

Since 2-ethyl hexyl acrylate (2EHA) is an often-used component of acrylate

TABLE XIII

Tack strength against steel and PTFE probes; copolymers of 2-ethylhexyl acrylate

Comonomer	Ethyl methacrylate			Ethyl acrylate		
	%EMA	Tack strength (kN m^{-2}) Steel	PTFE	%EA	Tack strength (kN m^{-2}) Steel	PTFE
	100	0	0	100	8.51 ± 0.2 (i.f.)	0
	75	0	0	79	10.5 ± 0.5 (i.f.)	0.62 ± 0.08 (i.f.)
	58	6.97 ± 1.01 (i.f.)	0	65	11.6 ± 0.1 (i.f.)	0.70 ± 0.16 (i.f.)
	52	11.6 ± 0.4 (i.f.)	0.31 ± 0.08 (i.f.)	40	13.6 ± 1.0 (c.f.)	1.47 ± 0.16 (c.f.)
	35	13.2 ± 1.1 (c.f.)	0.46 ± 0.08 (i.f.)	24	12.8 ± 0.4 (c.f.)	1.63 + 0.24 (c.f.)

Comonomer	Methyl acrylate		
	%MA	Tack strength (kN m^{-2}) Steel	PTFE
	100	0	0
	92	4.26 ± 0.24 (i.f.)	0
	83	12.0 ± 0.4 (i.f.)	1.01 ± 0.08 (i.f.)
	72	11.2 ± 0.2 (i.f.)	0.77 ± 0.08 (i.f.)
	41	18.9 ± 0.4 (c.f.)	1.47 ± 0.16 (c.f.)
	3	15.5 ± 0.1 (c.f.)	1.39 ± 0.16 (c.f.)

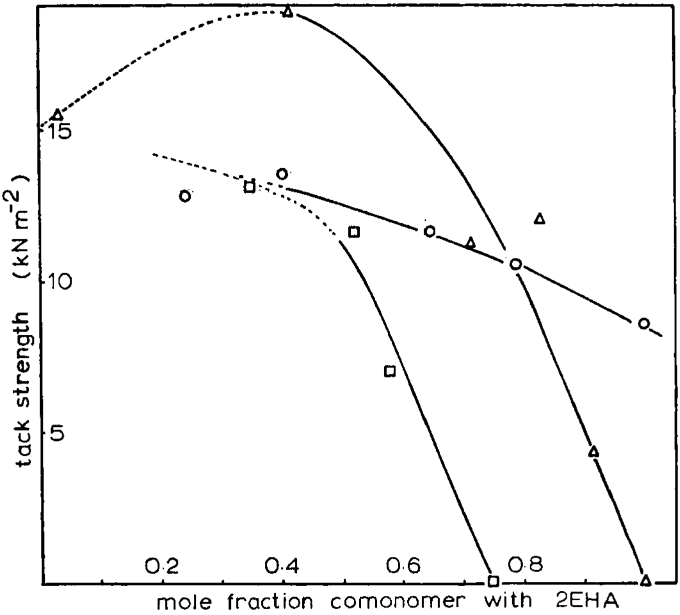

FIGURE 3 Variation of tack strength with composition of non-polar acrylic copolymers. ○ EA/2EHA; □ EMA/2EHA; △ MA/2EHA copolymers.

copolymers for pressure-sensitive adhesives we have chosen it as the comonomer common to three series of non-polar binary copolymers. The other monomers are ethyl acrylate (EA), ethyl methacrylate (EMA) and methyl acrylate (MA). Figures 3–5 show the tack, peel and cold-flow performance of these three series of copolymers and the mode of failure is indicated. Increase of the 2EHA content makes all these copolymers progressively softer and the tack strength increases and this trend is continued even when failure becomes cohesive. The MA/2EHA series has a maximum tack strength

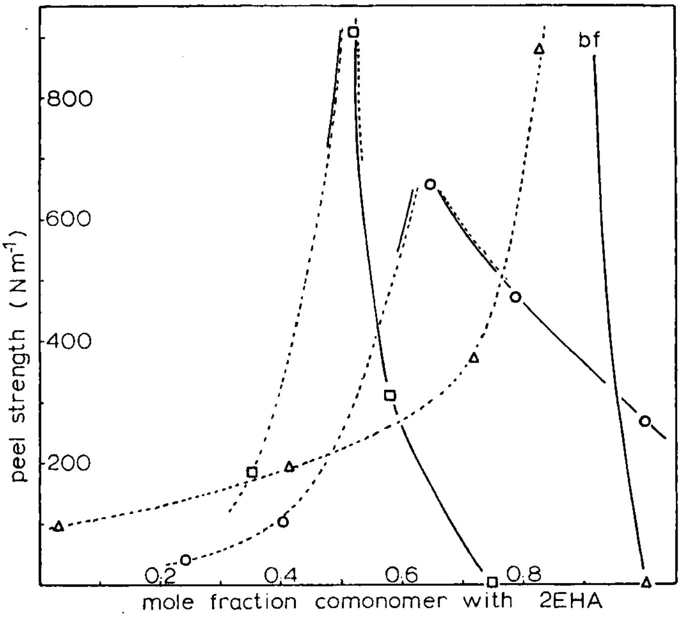

FIGURE 4 Variation of peel strength with composition of non-polar acrylic copolymers. (Key as in Figure 3.) ⁄⁄, mixed failure; BF, backing failure.

around 60% 2EHA but the other two series do not appear to peak. Copolymers of high 2EHA content give a small, but finite, tack strength with a PTFE probe and, in general, the mode of failure stays the same as with the stainless steel probe (Table XIII).

The peel strengths (Figure 4) depend on the mode of failure; as the 2EHA content is raised the peel strengths go to a maximum and then decline as failure becomes cohesive. Unlike polyethyl acrylate, MA and EMA homopolymers are not tacky and have no peel strength, but when suitable quantities of 2EHA are copolymerised, samples may be formulated to have an adhesive performance equal or better than that of the EA/2EHA series.

When the bulk mechanical properties of amorphous polymers are placed on a master curve by a time-temperature superposition it is found that the factor a_T by which relaxation times are shifted when the temperature is changed from the test temperature to a standard temperature may be expressed in terms of a universal equation with T_g as the reference temperature. Adhesion behaviour as assessed by the tests employed here may be partially a bulk property and partially interfacial. It is of interest, therefore, to see if the results of Figure 3–5 may be superposed by an iso-free volume approach. This may be accomplished by plotting the test values against T_s-T_g where T_s is the test temperature. A more elaborate method is to plot the WLF factor,[15] $\log(a_T)$, which is defined for T_g as the reference temperature by

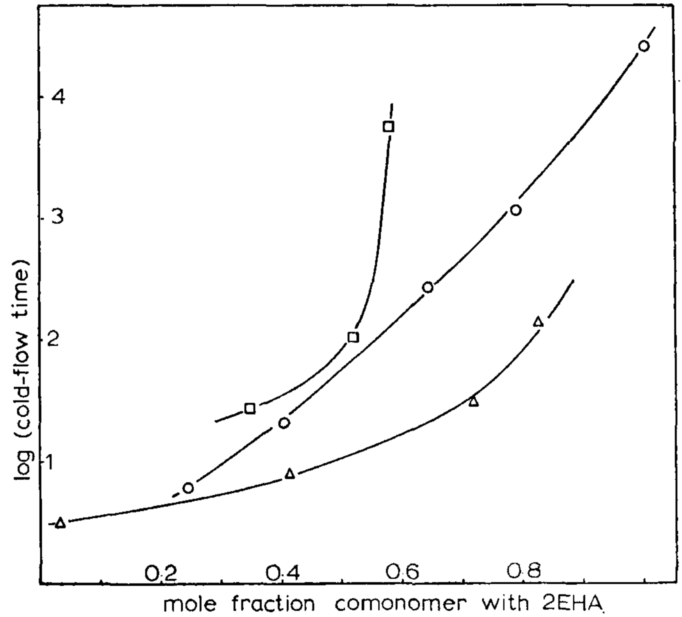

FIGURE 5 Variation of cold-flow time with composition of non-polar acrylic copolymers. (Key as in Figure 3.)

$$\log(a_T) = -\frac{17.44(T_s-T_g)}{51.6+(T_s-T_g)} \tag{1}$$

against the test value multiplied by the factor T_g/T_s.

However, before seeking to correlate the adhesion performance with copolymer glass transition temperatures some comments on these latter measurements are necessary. Because of the fast temperature scanning the values obtained for homopolymers are noticeably higher than those in the

TABLE XIV

Glass transition temperatures of homopolymers: differential scanning calorimetry at 80° min^{-1}

	T_g(°C)	
Polymer	Measured	Literature[16]
polymethyl acrylate	23	10
polyethyl acrylate	−10	−24
poly *n*-butyl acrylate	−33	−54
poly 2-ethyl hexyl acetate	−59[a]	−70
polyethyl methacrylate	74	65
poly *n*-butyl methacrylate	43	20

[a] Indirect estimate.

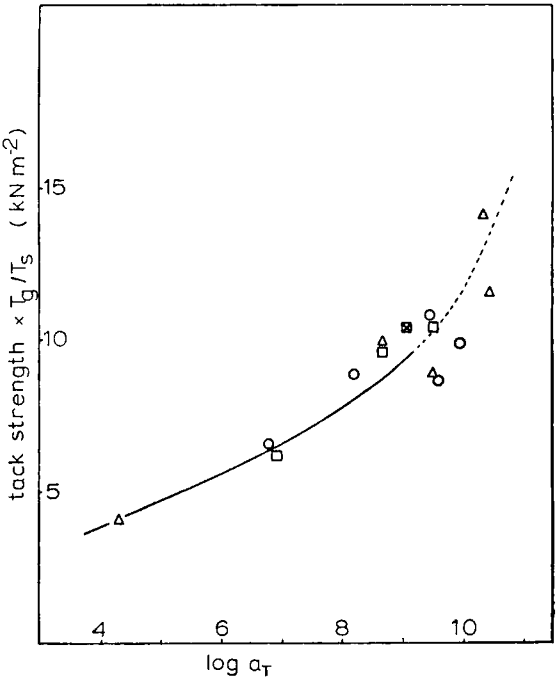

FIGURE 6 Variation of weighted tack strength with WLF function; non-polar acrylic copolymers (key as in Figure 3; (x) PnBA).

literature (Table XIV). The data for the three series of copolymers fit the equation

$$T_g = \Phi T_1 + (1-\Phi)T_2 \tag{2}$$

where T_1 and T_2 are the homopolymer transition temperatures and

$$\Phi = \frac{F_1}{F_1 + \alpha(1-F_1)} \tag{3}$$

with F_1 the mole fraction of monomer 1 and α is a constant. Such analysis of the data for the three series of copolymers gives a mean value of -59 ± 2°C for the T_g of poly2-ethyl hexyl acrylate.

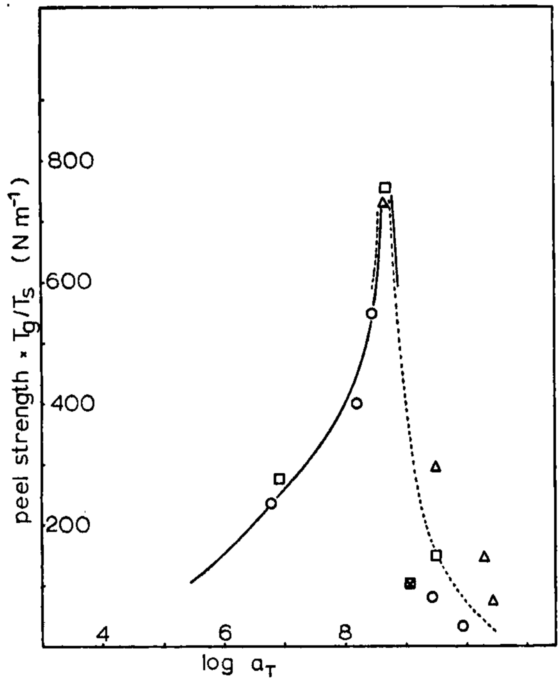

FIGURE 7 Variation of weighted peel strength with WLF function; non-polar acrylic copolymers (key as in Figure 3).

Figures 6–8 show the extent to which the adhesion test data are superposed by plotting against the expression given as the right-hand side of Eq. (1). The tack strength of these non-polar copolymers is related to $(T_s - T_g)$ with no specific influence from chemical composition (Figure 6). The scatter of peel strengths, especially in the region of cohesive failure, is greater than with tack strengths but comparison of Figures 4 and 7 shows the greater significance of T_g relative to that of chemical composition *per se*. The cold-flow times also give a unique plot against the WLF expression (Figure 8).

However, these master curves must not be taken to mean that adhesive performance at T_s is determined by the value of T_g alone. Figures 3–8 show data for polymers of generally similar molecular size which were all synthesised under similar conditions; the mean intrinsic viscosity of these polymer samples is 0.85 with a standard deviation of 0.16. To see if molecular weight has an effect on adhesion behaviour additional to its influence on the glass transition temperature some polymers were prepared at higher initiator contents. In Table XV the first entry in each set is for the sample made under normal polymerisation conditions. It is obvious that the slight shifts in T_g's are not the cause of the major changes in adhesion properties which thus depend on a molecular size factor additional to the glass transition parameter. The trend observed is as predicted by the general considerations of Satas.[17]

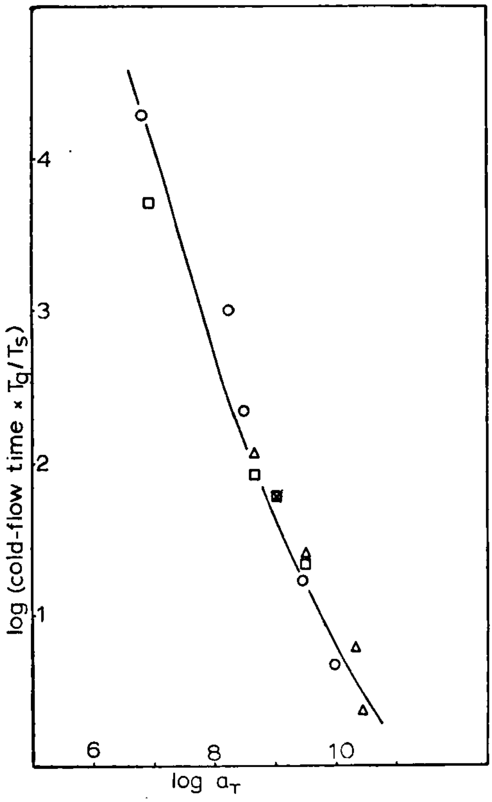

FIGURE 8 Variation of weighted cold-flow time with WLF function; non-polar acrylic copolymers (key as in Figure 3).

TABLE XV

Effect of molecular weight on adhesion performance

Sample code	Composition	$[\eta]$ [a]	T_g [b]	Tack strength (kN m^{-2})	Peel strength (N m^{-1})	Cold-flow time (min)
ethyl acrylate homopolymers						
P-1	PEA	1.08	−10	8.5+0.2 (i.f.)	266±37 (i.f.)	22080±1660
P-32	PEA	0.46	−11	12.0±0.2 (i.f.)	965± 1 (m.f.)	198±7
P-33	PEA	0.29	−17	15.1±0.6 (i.f.)	656± 1 (c.f.)	27±1
ethyl acrylate/2-ethyl hexyl acrylate copolymers						
P-2	EA/2EHA: (79/21)	1.12	−23	10.5±0.5 (i.f.)	473±11 (i.f.)	1180±9
P-36	EA/2EHA: (80/20)	0.68	−19	12.3±0.4 (i.f.)	627±28 (c.f.)	48±6
P-37	EA/2EHA: (86/14)	0.39	−20	17.0±0.9 (c.f.)	382±9 (c.f.)	5±1

[a] dl g^{-1}, toluene, 25°C. [b] °C; D.S.C. scanning rate 80° min^{-1}.

Adhesion performance of polar copolymers

Small amounts of polar comonomers are frequently incorporated into acrylic adhesive formulations as property modifiers. Because of the results obtained in the non-polar copolymers it seemed necessary to establish whether the influence of polar co-monomers was through bulk properties as summarised in the value of T_g or through specific interfacial interactions.

Ethyl acrylate was copolymerised with acrylic acid, methacrylic acid, hydroxyethyl acrylate and acrylonitrile; the quantities of these co-monomers was kept low and ethyl acrylate, rather than 2-ethyl hexyl acrylate, was chosen as reference monomer as homopolymer data were lacking for the latter. The data are restricted to tack strength measurements since many of the specimens did not peel cleanly, the joint being so strong that the backing paper failed. Further, all had a greater resistance to shear (cold-flow test) than the parent polyethyl acrylate, which itself has a high value. The variation of tack strength with composition is shown as Figure 9. In all cases incorporation of a small amount of polar co-monomer increases tack up to a maximum beyond which it drops, the failure mode being apparently interfacial in all cases. Acid groups have by far the greatest effect, reaching a peak at 3–4% incorporation of either acrylic or methacrylic acid. When the data are plotted against the WLF expression of Eq. (1), far from a common curve resulting, the series are further separated (Figure 10). Thus, at low levels of polar co-monomer the adhesion is much influenced by the improved interfacial interactions with the substrate and not by the bulk polymer properties; at

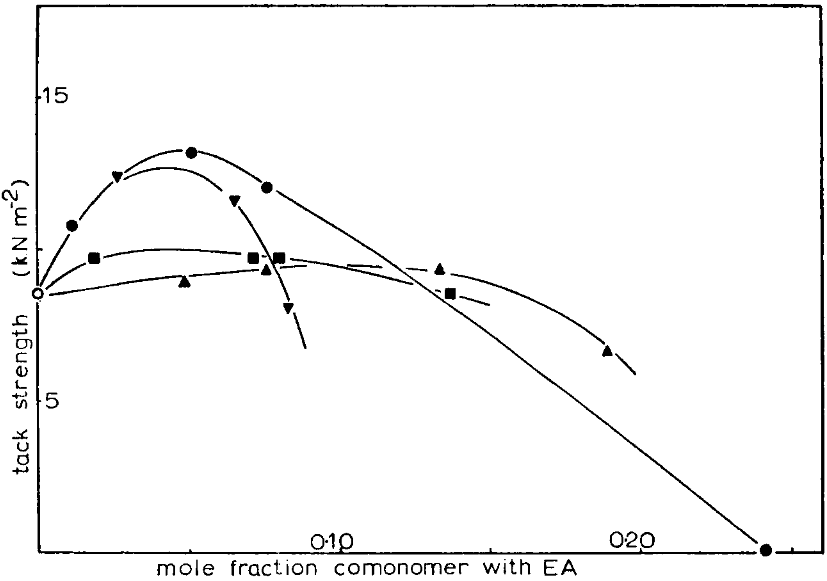

FIGURE 9 Variation of tack strength with composition of polar-acrylic copolymers. ● AA/EA; ▼ MA/EA; ■ OHEA/EA; ▲ AN/EA.

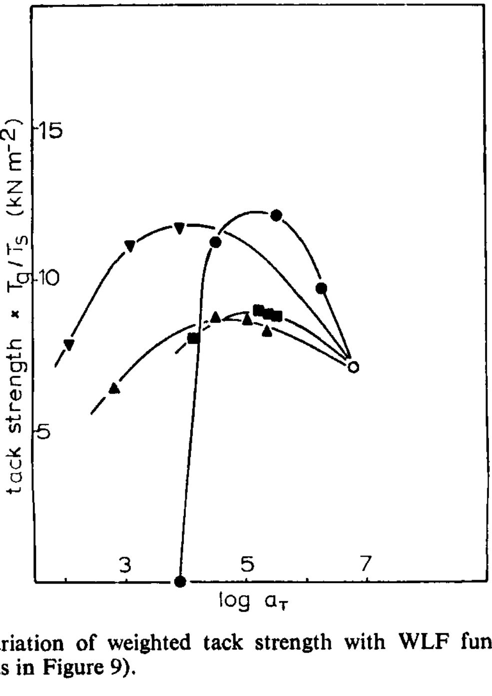

FIGURE 10 Variation of weighted tack strength with WLF function; polar acrylic copolymers (key as in Figure 9).

the higher polar contents the hardening of the polymer is sufficient to bring down the tack strength.

Surface free energies of copolymers

Satisfactory adhesion may be expected only when the polymer wets the substrate in the time interval allowed for bond formation. Although the test methods employed here do not necessarily allow equilibrium wetting a knowledge of the surface tensions of the copolymers is of interest. We have calculated approximate values by a method described by van Krevelen[18] in which the parachor and the molar volume are estimated by summing the contributions from the atomic groupings in the copolymer. It seems likely, both from the examples quoted by van Krevelen and these calculated here, that these estimates are somewhat high. In Table XVI are given our calculated values for surface tensions of homopolymers and experimentally obtained values [16] for their critical surface tensions as defined by Zisman.[19] Despite the revealed discrepancies the group contribution values for γ_l should be adequate to exemplify trends in surface energy with copolymer composition and to see if there is a correlation to the adhesion data; the calculated values are incorporated in Tables 1–3. It is reasonable only to compare calculated γ_l values with those test results in which failure was apparently interfacial. Few systems had an interfacial failure mode in peeling so that the comparison is restricted to tack strength. When non-polar copolymers are so examined it is evident that (i) the predicted changes in surface tension with composition are small and (ii) are not related to experimental tack values (Figure 11), and (iii) the molecular weight dependence is not explained. With polymers made with a polar comonomer, the calculated γ_l values are

TABLE XVI

Calculated surface tensions and experimental critical surface tensions (Ref. 16)

Polymer	γ_l (calc)[a]	γ_c (exp)[a]
polymethylacrylate	45	41
polyethylacrylate	42	35
poly *n* butylacrylate	39	28
polyethylmethacrylate	42	33
polyacrylonitrile	61	44

[a] mN m^{-1}.

again restricted to a narrow band, since the amount copolymerised is small. Further, the γ_l values increase monotically whereas the tack strength increases up to the point at which the increased hardness of the polymer reduces tack.

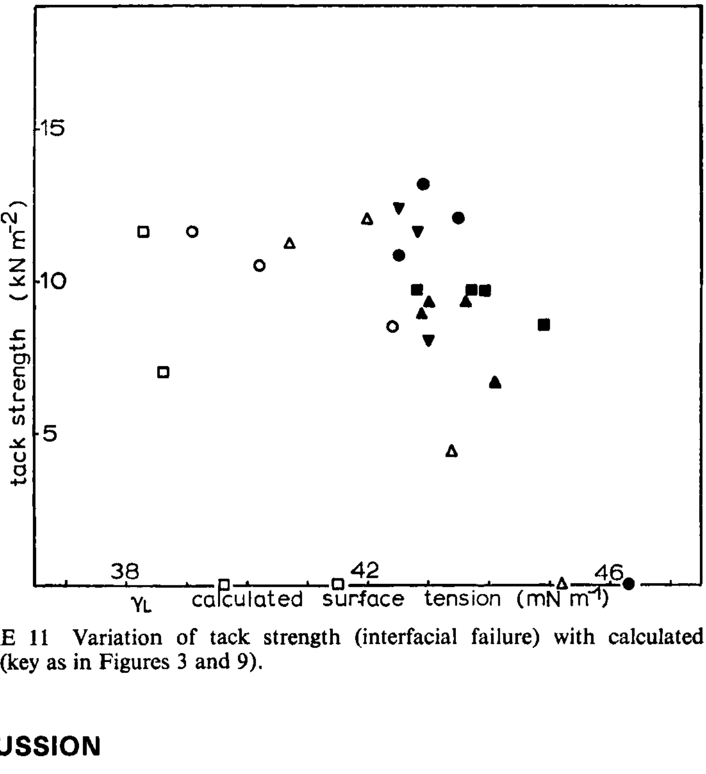

FIGURE 11 Variation of tack strength (interfacial failure) with calculated surface tension (key as in Figures 3 and 9).

DISCUSSION

The non-polar copolymers synthesised for this investigation may be expected to have a random chain sequence of monomer residues. The justification for this statement is in the magnitude of the product of the monomer reactivity ratios; these, when calculated from the Q,e values[16] for the monomers, are 0.98 for 2EHA/EA copolymers, 0.98 for 2EHA/EMA and 0.95 for 2EHA/MA. A strictly random arrangement of chain residues is formed in ideal copolymerisation when the reactivity ratio product is equal to one. The polar copolymers, since the second monomer is present in only small quantities, will tend to have isolated polar groups. In both cases, the main series, by virtue of the synthesis conditions and, judged by solution viscosity data, will consist of copolymers roughly similar in molecular size. Three of the homopolymers (ethyl methacrylate, *n*-butylmethacrylate and methylacrylate) were of too high T_g to exhibit adhesion properties at the test temperature although Mao and Reegen[6] report the contrary in respect of the latter two polymers. However these workers were using a different substrate and it is clear from their synthesis conditions that their polymers were of higher conversion and of lower molecular weight than ours.

Before consideration of the adhesion performance of the copolymers, one aspect of the test methodology must be discussed; this is the dependence of tack strength on the rate at which the probe is separated from the specimen. The results (Figure 2) show a declining tack strength at faster separation rates and, where a change in failure mode occurs, this is from cohesive to interfacial. The rate dependence is common to a range of copolymers and is also shown by a commercial, rubber-based, adhesive. Use of a smaller probe and consequent higher contact pressure gives the same rate effect. Previous workers[10-13] have reported the opposite dependence and, indeed, this is what would be expected on a simple analysis of the tack test as the deformation of a viscoelastic material. Thus, if the adhesive was relaxed and had reached equilibrium wetting of the probe surface, on separation at a slow rate a cohesive failure would be expected provided that the stress necessary for interfacial separation σ_a was greater than the failure stress of the polymer σ_p. At a higher separation rate the stress-strain curve will be shifted upwards as the instantaneous modulus becomes greater and, in general, the failure stress will get larger. This process would continue to give higher tack strengths as the separation rate was raised until the situation is reached in which the stress σ_a is attained before bulk failure, when a limiting tack value, with interfacial failure, should be observed.

A practical probe tack test involves three stages; deformation of the adhesive on probe contact, relaxation during the dwell period followed by the separation process. The experimental requirements of the present test are such that the initial contact of the probe with the specimen is made at the same rate as that of the subsequent separation; this is, however, true of the procedure of some other workers.[1,10,11] The hardening affect at higher rates, described above, must also be evident during the initial contact. Thus, at high rates, the effective wetting of the probe surface will be less and, furthermore, stress concentrations will be set up where the polymer is near to asperities on the probe surface. If, as is likely,[20] a dwell time of one second is insufficient to ensure stress relaxation of the polymer or adequate wetting of the probe surface then on probe withdrawal, failure will occur at, or close to, the interface; the tack strengths will be lower for the specimens subjected to the higher rates of deformation on contact. This explanation of the results summarised in Figure 2 concentrates on the bonding conditions rather than the ultimate separation and predicts that samples which fail cohesively at low rates may change to interfacial failure at high rates. Dahlquist[11] shows that tack increases with temperature so long as the test is sensing the bonding stage but that, at higher temperatures, a decrease sets in as the unbonding process takes over. This author also shows that the increasing tack strength with rate of probe separation has the same slope as that of the modulus; but these data refer to higher test temperatures where the tack test is a measure of the unbonding process of a well-wetted probe from a relaxed adhesive. Dahlquist[11] further shows that with specimens formulated with high resin contents the effect of separation rate on tack strength is reversed; that is, as the compositions become harder the direction of the rate effect becomes as observed in the present study.

The tack test is so designed that the deformation of the polymer in an annulus surrounding the probe is restricted by the collar which holds down the specimen. It may be[23] that this factor plays a role in the rate effect described here. Further work is planned to establish more clearly those parameters which determine this "anomalous" rate effect.

The glass transition temperatures were measured at a high scanning rate and should so be appropriate for discussion in connection with adhesion tests made at relatively high rates of deformation. Some authors[21,22] have used the WLF[15] transform to place adhesion test data obtained for a single polymer at various rates and temperatures on to a common master curve. Our data for non-polar copolymers were obtained at a fixed rate of testing at a standard temperature but the use of the WLF expression places the different chemical species on to common curves (Figures 6–8), providing that molecular weights are kept roughly constant. The fit is not restricted to cohesional failure of the adhesive joint. Molecular weight has an influence on the test data additional to its effect on T_g; it is well-known that the glass transition temperature is much less affected by variation in chain length than are bulk properties such as viscosity. The usefulness of the WLF expression in correlating the adhesion performance of three sets of non-polar copolymers illustrates the importance of bulk viscoelastic properties even when failure is apparently interfacial. Thus, in tack testing, copolymers with low values of (T_s-T_g) fail interfacially because wetting and stress relaxation are poorer with these harder polymers; at higher (T_s-T_g) values, where the probe surface is in better contact with the adhesive, the polymers are intrinsically weaker so that cohesive failure occurs on separation.

It is also significant that the WLF transform does not suffice to place the adhesion behaviour of the polar copolymers on to a common basis. Thus the specific interfacial interactions consequent on the incorporation of polar comonomers is well illustrated. Certainly, on the steel surface, acid groups are more effective than hydroxyls, these being in turn better than nitriles; speculation on the exact form of the adsorption interactions with an ill-defined metallic surface seems, however, inappropriate.

Equilibrium wetting, as assessed by calculated γ_l values does not seem to be important in determining the level of performance. Thus the tack strengths, albeit low, with a PTFE probe (Table 13) are shown by softer polymers only, some of which have higher γ_l's than samples which do not adhere to PTFE.

Acknowledgements

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References

1. F. H. Wetzel, *ASTM Bulletin* **221,** 64 (1957).
2. C. A. Dahlquist, in *Treatise on Adhesion and Adhesives,* Vol. 1, R. L. Patrick, Ed. **2** (Dekker, New York, 1969), p. 219.
3. A. Hardy, in *Aspects of Adhesion* D. J. Alner, Ed. **1** 47 (Univ. London Press, London 1963).
4. D. H. Kaelble, *Trans. Soc. Rheol.* **9,** 135 (1965).
5. J. H. Engel and R. N. Fitzwater, in *Adhesion and Cohesion,* P. Weiss, Ed. (Elsevier, Amsterdam 1962), p. 89.
6. T. J. Mao and S. L. Reegen, in *Adhesion and Cohesion,* P. Weiss, Ed. (Elsevier, Amsterdam 1962), p. 209.
7. S. L. Reegen and G. A. Ilkka, in *Adhesion and Cohesion,* P. Weiss, Ed. (Elsevier, Amsterdam 1962), p. 159.
8. D. W. Aubrey, G. N. Welding and T. Wang, *J. Appl. Poly. Sci.* **13,** 2193 (1969).
9. J. L. Gordon, in *Treatise on Adhesion and Adhesives,* Vol. 1, R. L. Patrick, Ed. (Dekker, New York, 1967), p. 269.
10. F. H. Hammond, *ASTM Special Bulletin No.* **360** (1964).
11. C. A. Dahlquist in *Adhesion Fundamentals and Practice,* Edit, UK Ministry of Technology (Maclaren, London, 1969), p. 143.
12. R. Bates, *J. Appl. Poly. Sci.* **20,** 2941 (1976).
13. H. Kambe and K. Kamagata, *J. Appl. Poly. Sci.* **13,** 493 (1969).
14. ASTM D903-49 (1975).
15. M. L. Williams, R. F. Landel and J. D. Ferry, *J. Amer. Chem. Soc.* **77,** 3701 (1955).
16. *Polymer Handbook,* 2nd Edition. J. Brandup and E. H. Immergut, Eds. (Wiley, New York, 1975).
17. D. Satas, *Adhesives Age* **15,** (10) 19 (1972).
18. D. W. van Krevelen, *Properties of Polymers* (Elsevier, Amsterdam 1972).
19. H. W. Fox, E. Hare and W. A. Zisman, *J. Coll. Sci.* **8,** 194 (1953).
20. W. C. Wake, *Adhesion and the Formulation of Adhesives* (Appl. Sci. Publ., London 1976), p. 141.
21. C. A. Dahlquist, *ASTM 71-Vibra-47,* New York.
22. A. N. Gent and R. P. Petrich, *Proc. Roy. Soc.* **A310,** 433 (1969).
23. W. C. Wake, Private communication.