Crosslinked acrylate adhesives for use on skin

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ABSTRACT *Human skin is a relatively poor substrate for adhesives, but some medical devices and bandages are held in place by taping them to the body. The effective use of pressure-sensitive adhesives on skin requires control of both the initial adhesion and the buildup of adhesion with time. Consequently, both the long-term and short-term flow properties of the polymer have to be determined and controlled. Two new approaches are (a) the use of macromolecular monomers and (b) the use of copolymerized photocrosslinkers, in which crosslinking is induced by radiation. These approaches offer some control of compliance, flow, and adhesion.*

KEYWORDS
Adhesives
Copolymerization
Monomers
Polymers

Adhering tapes are often used to hold medical devices and bandages onto the body, but skin is not an ideal surface for pressure-sensitive adhesives. On the other hand, the extended use of such a tape can be harmful to human skin. In manufacturing these adhesives, we need to understand how the bulk properties of adhesive polymers influence their effectiveness when skin is the substrate.

Skin as a substrate

As a substrate, skin poses many problems. It is rough and structurally weak, it exudes moisture and lipids, it varies from one part of the body to another and from one person to another, and it is systematically shed by the body, making any long-term adhesion impossible.

Figure 1 is an illustration of a cross-section of skin, showing the various structures, including the layered stratum corneum. **Figure 2** shows a cross-section of actual tissue in which the topography is clearly visible. To contact and wet the skin surface and form a bond, a polymer must flow relatively rapidly. If it continues to do so after an adequate bond is formed, the strength of the bond increases. This strength is good for securing anchorage for a device or dressing. Beyond a certain degree of adhesion, however, trauma to skin results when the adhesive is removed, or adhesive residue is left behind if the peel strength is greater than the cohesive strength. Therefore, we need (a) rapid initial flow for adequate bond formation, (b) limited long-term flow for the control of ultimate bond strength, and (c) good cohesion.

Technologies for skin adhesion

Conventional technology

The challenge of achieving the balance of properties needed in adhesives for skin is not a new one. Because this balance of properties may be different for different products and intended uses, several technologies have been used in the past. Among them are the use of reinforcing monomers such as acrylic acid, the incorporation of small amounts of difunctional crosslinking monomers, chemical crosslinking during processing, and radiation-induced crosslinking using an added photoinitiator.

Each method has its limitations. Reliance on molecular weight and reinforcement often leads to compromises in the balance of properties and to low concentrations in solution. Using difunctional crosslinking monomers requires careful control of the monomer ratios and concentrations, and it can lead to gelling. Chemical crosslinking relies on careful formulation and on attaining specified conditions during the manufacturing steps: any unreacted crosslinker poses the threat of leaching from the adhesive to the skin or wound surface. Finally, radiation-induced crosslinking also depends on accurate formulation and on controlling the curing conditions, rates, and possibly the atmosphere.

New technologies

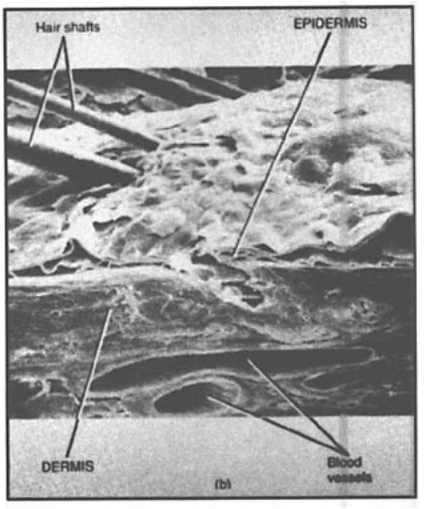
Two new technologies are available to achieve the correct balance of properties. One new alternative is to incorporate a "macromer" (or macromolecular monomer) into the backbone of the polymer (*1*). Each macromer unit acts like a polymeric side-

chain grafted onto the backbone. A macromer chosen for suitable T_g (glass transition temperature) and solubility contributes phase-separated domains that reinforce the polymer and act as reversible crosslinks. Two commonly used macromers are (meth)acrylate-terminated polystyrene and polymethylmethacrylate. By adjusting the macromer content and the inherent viscosity of the adhesive polymer, the rates of short-term and long-term flow can be controlled to a useful degree, leading directly to control of initial and long-term adhesion properties.

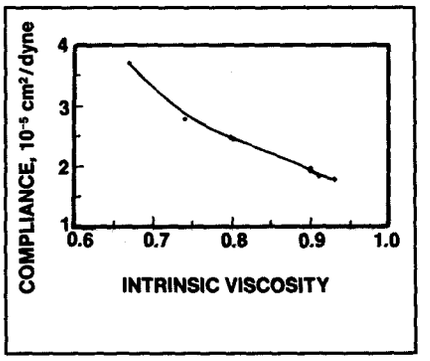
The second alternative is to use copolymerized photocrosslinkers in radiation-cured polymers (*2*). Though copolymerized aromatic ketones have been used in the past to increase shear strength of acrylate adhesives (*3*), their use in the control of flow of an adhesive offers two important advantages. The first is the improved efficiency of crosslinking and therefore the reduced amounts of photocrosslinker and radiant energy that are required. The efficiency of curing permits high processing rates with good control of the amount of crosslinking. The second advantage is the reduction in the amount of potentially leachable low-molecular-weight components in the formulation because the photocrosslinker is covalently bound to the backbone of the polymer.

1. Diagram of a cross-section of skin

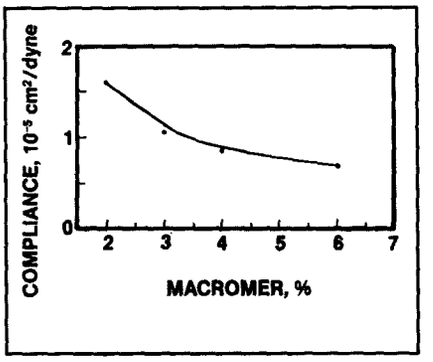
2. A cross-section of skin tissue



3. The effect of inherent viscosity (acrylic acid copolymers)



4. The effect of macromer concentration (N-vinyl-pyrrolidone)



Experimental procedures

The polymers used were made by mixing the monomers (iso-octyl acrylate, acrylic acid, or N-vinyl-pyrrolidone) in various proportions in a suitable solvent (usually ethyl acetate). A free-radical initiator such as azo-*bis*-isobutyronitrile was added, and the solution was flushed with nitrogen. Mixing in a water bath took place at 55°C for 24 h, at which time polymerization is essentially complete.

These polymers were coated on a substrate appropriate to the test, such as woven cellulose acetate fabric or polytetrafluoroethylene (PTFE). The polymer-coated substrate was dried in a circulating-air oven. The radiation source was a medium-pressure, mercury vapor, ultraviolet lamp. Units are in mJ/cm².

The creep test was performed according to a method described in the relevant literature (*4–6*). The adhesive was coated, oven-dried, and placed between plates of a creep compliance rheometer. The arrangement of plates was compressed and coupled to a strip chart recorder, and a stress of 500 g was applied. From the time displacement curve, the creep compliance is calculated according to the following equation:

$$J_t = 2A\,x/h\,f \qquad (1)$$

where

J_t = the compliance value, cm²/newton, or

A = the area of one face of the adhesive sample, cm²

x = the displacement at time t, cm

h = the thickness of the sample (greater than x), cm

f = the force from the applied stress, newton.

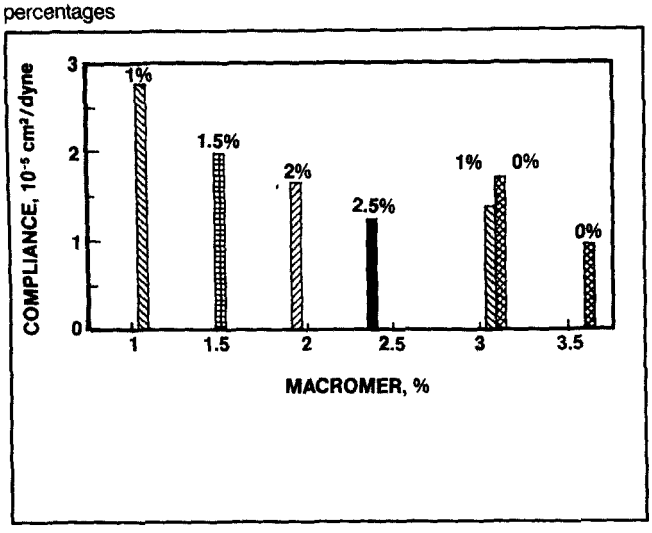
When A is expressed in cm², h in cm, x in cm, and f in newton, the compliance value J_t is given in cm²/newton.

The skin adhesion test is Pressure Sensitive Tape Council PSTC-1 peel test measured at a 180° angle. Tapes are applied to the backs of human volunteers, rolled down with a standard 1-kg roller, and peeled off after a set time. The peel force is recorded by a strain gauge mounted on a motor-driven carriage and is reported in grams per inch of width, or g/2.54 cm.

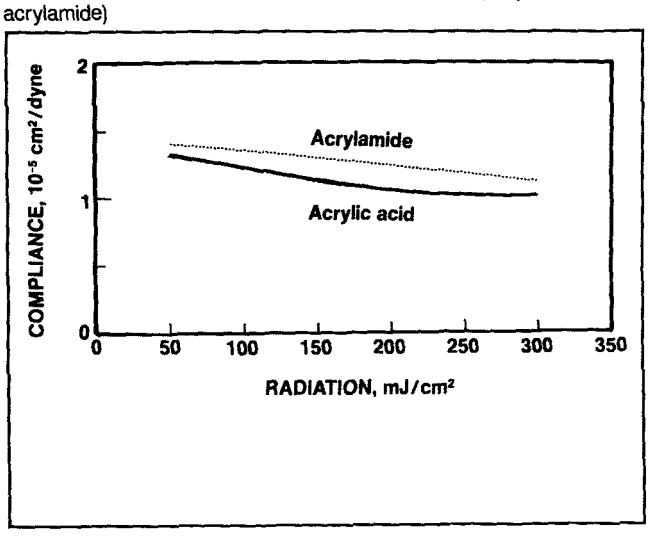
Results

Compliance (here, shear creep compliance) is the reciprocal of modulus (here, shear modulus). It is a measure of polymer flow and relates to the ability to conform to a surface. High compliance suggests rapid flow and wetting — and therefore high adhesion.

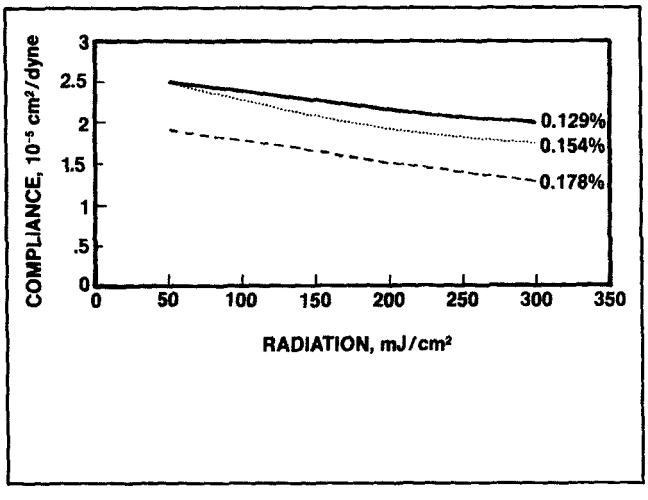
5. The effects of combining macromer and monomer at various percentages



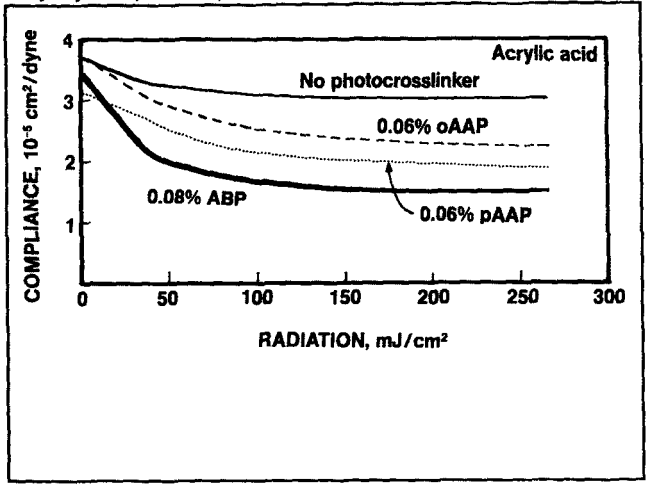
6. The effects of the amount of monomer used (acrylic acid and acrylamide)



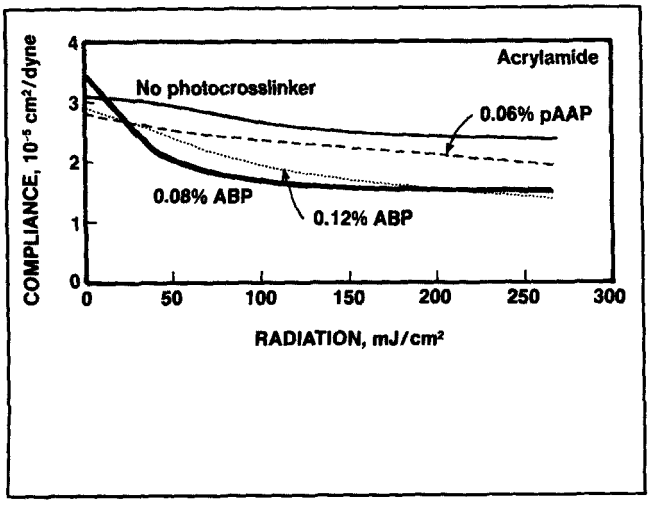
7. The effects of radiation on compliance for various percentages of photocrosslinker



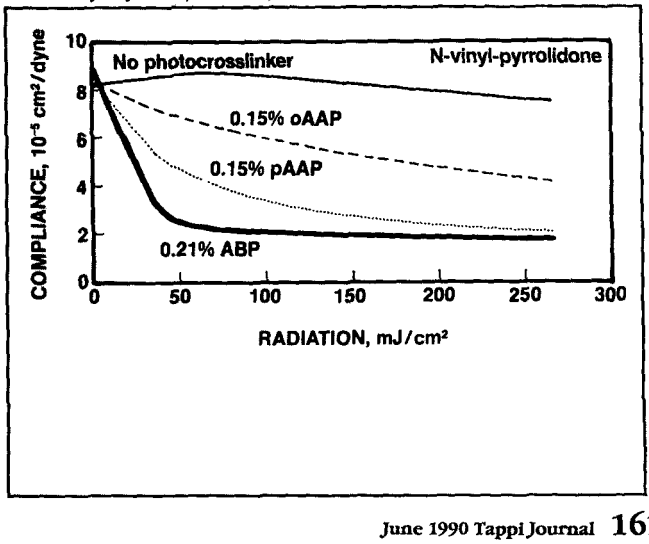
8. Photocrosslinkers in acrylic acid copolymers (ABP = Acryloxybenzophenone. pAAP = para-Acryloxyacetophenone. oAAP = ortho-Acryloxyacetophenone.)



9. Photocrosslinkers in acrylamide copolymers (ABP = Acryloxybenzophenone. pAAP = para-Acryloxyacetophenone.)



10. Photocrosslinkers in N-vinyl-pyrrolidone copolymers (ABP = Acryloxybenzophenone. pAAP = para-Acryloxyacetophenone. oAAP = ortho-Acryloxyacetophenone.)



I. Properties of acrylamide copolymers

Macromer, %	Acrylamide, %	Intrinsic viscosity	Compliance, cm^2/N
1	2	0.86	3.25
3	2	0.82	2.20
1	2	0.53	8.57
3	2	0.53	3.48
1	4	0.92	1.15
3	4	0.87	0.94
1	4	0.58	1.62
3	4	0.60	1.20

II. Adhesion performance of selected polymers

Macromer, %	Monomer, %	Intrinsic viscosity	Compliance, cm^2/N	T-0, g/25 mm	T-48, g/25 mm
		Acrylic acid			
2	2	0.84	1.65	85	190
2	2	0.93	1.80	79	127
2	2	0.94	1.46	76	157
		Acrylamide			
1	2	0.83	2.15	225	471
1	2	1.10	1.39	106	499
		N-Vinyl-pyrrolidone			
2	14	0.91	1.74	291	388
3	10	0.93	1.61	102	268
3	10	1.33	1.09	91	366

The compliance of macromer-containing adhesives depends on the nature of the acrylate ester, the macromer content, the amount and type of reinforcing monomers, and inherent viscosity. **Figure 3** shows the effect of inherent viscosity on the compliance of some macromer polymers of iso-octyl acrylate, acrylic acid, and polystyrene macromer with a ratio of 96:2:2 for the three components respectively. A systematic decrease in compliance is seen as inherent viscosity increases.

Figure 4 shows the effect of macromer concentration on the compliance of polymers made of iso-octyl acrylate, N-vinyl-pyrrolidone, and macromer with an N-vinyl-pyrrolidone content of 5% and inherent viscosity around 1.05. Because N-vinyl-pyrrolidone is only mildly reinforcing, the compliance depends to a large extent on the effect of the macromer.

The combined effects of both macromer and comonomer can be seen in **Fig. 5**, in which macromer and acrylic acid content vary at constant inherent viscosity. Because the mechanism of reinforcement is different for each of the monomers, each contributes differently to the performance.

In **Table I**, the contributions of acrylamide and macromer are compared. Though acrylamide is the more strongly reinforcing component, its hydrogen bonds are labile and can be disrupted by moisture or other hydrogen-bonding components or additives.

How these factors combine to affect adhesion is illustrated by the data in

III. Adhesion of acrylic acid polymers

Photocrosslinker, %	Radiation, mJ/cm^2	Compliance, cm^2/N	T-0, g/25 mm	T-24, g/25 mm
0.050	66	2.18	49	153
0.050	265	1.78	29	95
0.075	33	1.80	55	167
0.075	66	1.64	43	121
0.075	265	1.23	28	87
0.000*	...	...	46	199

*Control.

IV. Adhesion of *N*-vinyl-pyrrolidone polymers

Photocrosslinker, %	Radiation, mJ/cm^2	Compliance, cm^2/N	T-0, g/25 mm	T-24, g/25 mm
0.02	22	2.40	84	...
0.02	43	1.73	74	...
0.02	86	1.20	45	...
0.02	129	1.20	45	...
0.03	22	...	76	84
0.03	43	...	64	75
0.03	86	...	48	61
0.03	129	...	44	54
0.00*	...	...	51	205

*Control.

Table II. Polymers which incorporate each of the three comonomers were tested for initial adhesion (T-0) and long-term, 48-h adhesion (T-48). Some of the less strongly reinforced adhesives build to excessive T-48 values and could leave a residue after removal.

The use of a copolymerized photocrosslinker provides another method for controlling compliance and adhesion performance. The important factors are the nature and amount of comonomers, the level of photocrosslinker, and the amount of radiant energy. The effects of acrylic acid and acrylamide are compared in **Fig. 6**. In **Fig. 7**, the concentration of photocrosslinker is varied. **Figures 8-10** are plots showing the effect of radiation level on compliance for acrylic acid, acrylamide, and N-vinyl-pyrrolidone copolymers.

The choices of monomer, photocrosslinker, and radiation levels permit considerable control over rheology. These differences in rheology translate into differences in adhesion performance on skin, as shown in the two tables. In **Table III** are shown the results for performance tests for two compositions containing acrylic acid at 2% made into tape and cured at several levels of radiation. The sharp drop in long-term adhesion shows how effectively a small amount of photocrosslinker used with low doses of radiation can control the flow of the polymer. In **Table IV**, similar data are shown for polymers containing N-vinyl-pyrrolidone.

Summary

Considerable control can be exercised over the flow properties of the polymers for both macromer-containing and photocrosslinked adhesives. Performance testing gives us information on skin adhesion that leads to some control over performance in actual use.□

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Received for review May 31, 1989.

Accepted Nov. 6, 1989.

Presented at the TAPPI 1989 Polymers, Laminations and Coatings Conference.

dynes × 10^{-5} = N
cm^2/dyne × 10 = m^2/N = 1/Pa