Ionic Binding in Pressure-Sensitive Adhesive Polymers

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Synopsis

Ionic binding is affected in pressure-sensitive acrylate-based copolymers containing carboxylic groups by introduction of Na ions. The tack and peel force of pressure-sensitive polymers decreased and the resistance to creep increased with increasing degree of ionic binding. An infrared spectroscopic method for the assay of sodium content has been developed based on the ratio of absorbances at 5.75 and 6.28 μ due to ester carboxyl and ionized carboxyl, respectively.

Introduction

Ionic binding affected by introduction of metal ions into polymers containing carboxylic groups is an interesting technique available for varying polymer properties. Useful ionically bound polyolefin copolymers have been prepared and the effect of such binding on polymer properties has been reported by Bonatto and Purcell[1] and more recently in butadiene copolymers by Otocka and Eirich.[2] Such modified polymers exhibit some characteristics similar to the ones obtained by crosslinking. A significant difference between ionically bound and crosslinked polymers is that ionic binding, while effective at room temperature, is weakened at elevated temperatures. This property, obviously, makes such polymers more easily processable.

The purpose of this paper is to discuss the effect of ionic binding on pressure sensitive adhesives. Pressure-sensitive tapes, a household item for a long time, consist of an elastomer base compounded with plasticizers, tackifying resins, and other ingredients needed to make the compound pressure sensitive. It also has been known that many synthetic polymers possess pressure-sensitive properties without compounding, and some of these are used commercially for tapes. In the preparation of such polymers it is relatively simple to introduce various pendant functional groups, including carboxyl, into the polymer chain. Carboxylic acid groups are thus available for ionic binding with a variety of metal ions, the introduction of which has a considerable effect on the polymer properties. This is of interest not only in the pressure-sensitive adhesives but, also, in tailoring of polymers for other applications. In this paper, the effect of ionic binding on pressure-sensitive acrylate-based copolymers is discussed.

Determination of Ionic Binding

It is possible to show the presence of ionic binding by infrared spectroscopy. Metallic salts of carboxylic acids show strong absorption between 6.0 and 6.5 μ. In the case of the polymers used in these studies, this strong absorption (using sodium as the metallic ion) was observed at 6.28 μ. This is readily apparent in Figure 1, which shows the spectrum of the base polymer (A) before and (B) after reaction with sodium hydroxide. Another absorption band is apparent at 7.1 μ. This band at 7.1 μ has been observed in metallic salts of other materials. Nonpurified polymer samples were used after ascertaining that impurities did not affect the results obtained by infrared measurements. That the 6.28 μ band is indeed due to the ionized carboxyl group was shown by work with zinc abietate and zinc stearate. These were made by reaction of pure zinc oxide with the free acids. The spectra of these salts showed the typical absorption. The spectrum of an acrylate-based copolymer treated with zinc oxide (Fig. 2) shows this absorption at approximately 6.28 μ. Neither zinc oxide nor the ion-free polymer has absorption in this range.

On the basis of the work involving the zinc compounds as well as from the results obtained from purified and nonpurified polymers, it is considered safe to assume that the absorption bands subsequently utilized were analytically valid.
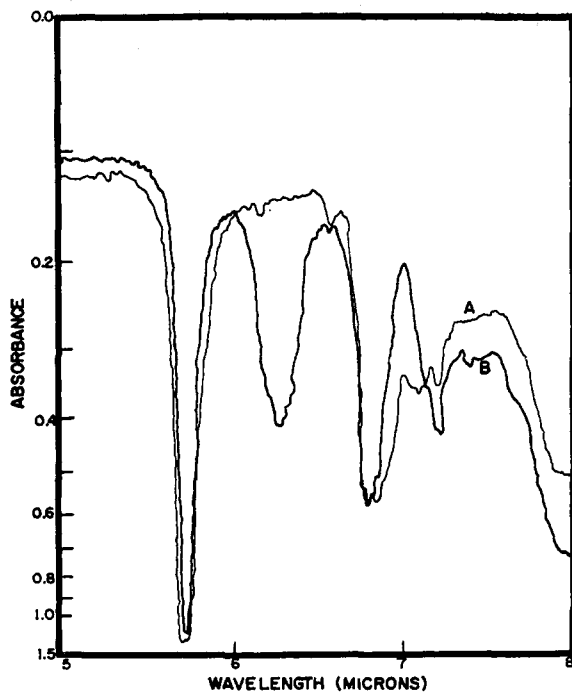

Fig. 1. Change of infrared absorption spectrum on treatment of the polymer with NaOH: (A) untreated; (B) treated polymer.
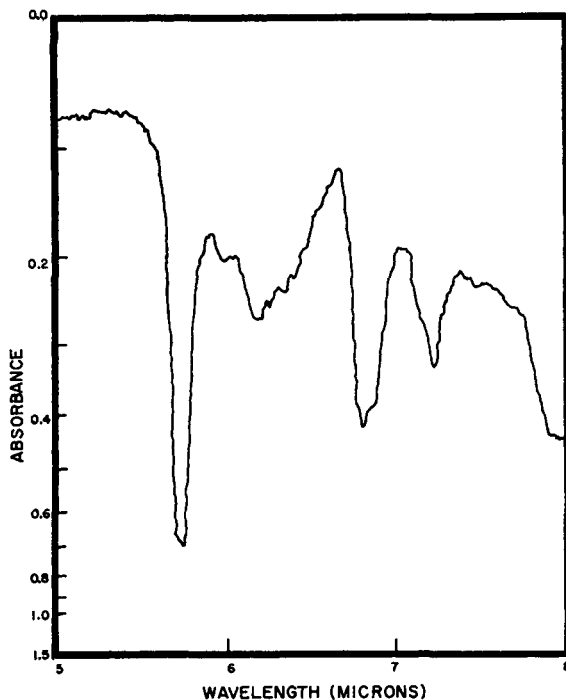
Fig. 2. Infrared absorption spectrum of polymer treated with ZnO.

In order to prepare a calibration curve which could be used to determine the quantity of sodium in the polymer samples, the sodium content was determined on purified polymers by a classic gravimetric method. The absorbance at 6.28 μ, due to the ionized carboxyl, can be correlated with the sodium content. However, the absorbance is also a function of sample thickness. The need for maintaining a constant sample thickness can be eliminated by using a ratio of absorbance—in our case the ratio between the ester carbonyl absorbance at 5.75 μ and ionized carboxyl absorbance at 6.28 μ. The ester absorbance acts as an internal standard of thickness.

The plot of the ratio of the two absorbance bands, i.e., 5.75 and 6.28 μ, versus the sodium concentration gave the empirical curve shown in Figure 3. This curve was then used as a means for the quantitative determination of sodium in subsequent work.

Incorporation of Metal Ions

Ionic binding has been imparted by soaking the polymer in a solution of an appropriate base. Reasonably uniform properties can be obtained if the polymer is in a form of porous crumbs. In case of a polymer prepared by emulsion polymerization, the emulsion can be introduced into the alkaline solution, thus providing a good penetration of metal ions into the polymer. Milling of solid hydroxide into the polymer mass on a hot two-
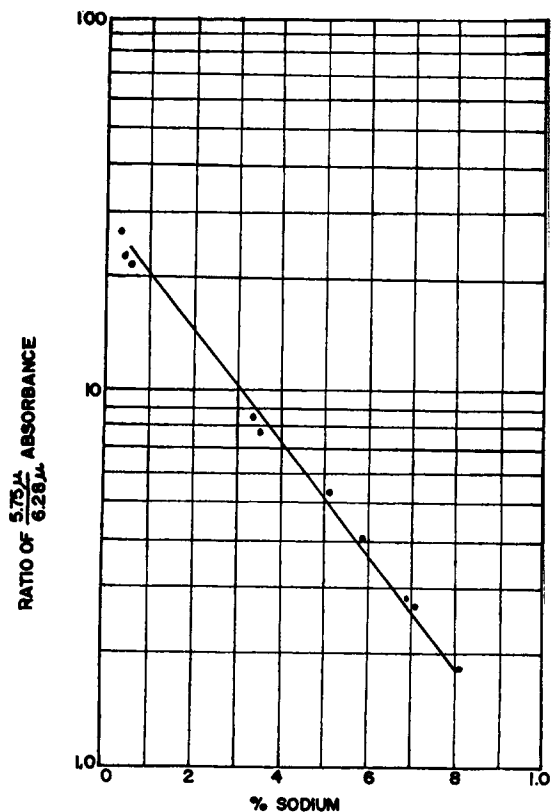
Fig. 3. Correlation of sodium assay by gravimetric and infrared absorption methods.

roll mill is also an available method, especially if the metal oxides or hydrox-
ides are difficultly soluble in water, e.g., ZnO.

Metal ions can also be introduced by neutralizing the monomers prior to
polymerization.   The effect of ionic binding in these samples was less than
expected from the amount of NaOH used in neutralization and the correla-
tion shown in Figure 3 was not valid.   Polymers that should have con-
tained 0.52 and 0.32% Na as determined from Figure 3 actually contained
1.87 and 0.85% Na, respectively, as determined gravimetrically.

It is believed that counterion binding can be of one of two types: the
ions may be bound to a specific site on a polyion or they may be merely
held in the vicinity of the polyion by the electrostatic field of the polyion.[3]
It has been shown that the electrostatic field is primarily responsible for
binding of sodium to carboxylic polymers.[4]   Various models of ionic
binding have also been discussed by Michaels.[5]

Adhesive Properties

The pressure-sensitive polymers investigated are easily soluble in un-
ionized form in ketones and aromatic solvents.   Introduction of ionic

binding changes the solubility behavior considerably.   The polymers with the higher densities of ionic binding did not go into the solution but only swelled in these solvents.   Addition of isopropyl alcohol was usually sufficient to remove this effect of the ionic binding, with the result that the polymers were soluble in solvent blends containing alcohol.

Pressure-sensitive adhesives are generally characterized by determination of tack, peel force, and creep.   The tack is indicative of the ability of the polymer to form a bond quickly under light pressure.   In our work the tack was determined by the Polyken Probe Tack Tester.[6]   This instrument provides a means of bringing the tip of a probe into contact with pressure-sensitive surface at a controlled rate and contact pressure and measuring the force required to separate the probe from the adhesive.   The peel force is determined by measuring the force required to remove the tape from a steel panel (ASTM D-1000).   The resistance to creep was measured by applying a weight of 1000 g to a vertical tape surface 1 in. wide, 2 in. long, bonded to steel and recording the time taken for complete failure.

The effect of sodium binding on the adhesive properties is shown in Table I.   The modulus of these adhesives increases with increasing ionic character.   It is also expected that the tack should decrease with increasing modulus and rigidity of the adhesive.   This is supported by the data in Table I showing that the tack decreases rapidly with increasing binding. Peel force depends on a number of factors.   In general, peel force decreases with increasing modulus of elasticity of the adhesive mass[7] which is also in agreement with the data in Table I.   The failure in the creep tests can occur either in the adhesive mass or at the bond interface, the former being the case in our tests.   The time required for the tape to fail increases with increasing cohesive strength of the polymer.   It is obvious from the data in Table I that ionic binding increase the cohesive strength.

The resistance to creep is temperature-dependent.   The ionic binding, although quite effective at room temperature, loses its effectiveness at

TABLE I
Effect of Bound Sodium on Pressure-Sensitive Adhesive Properties of the Polymer

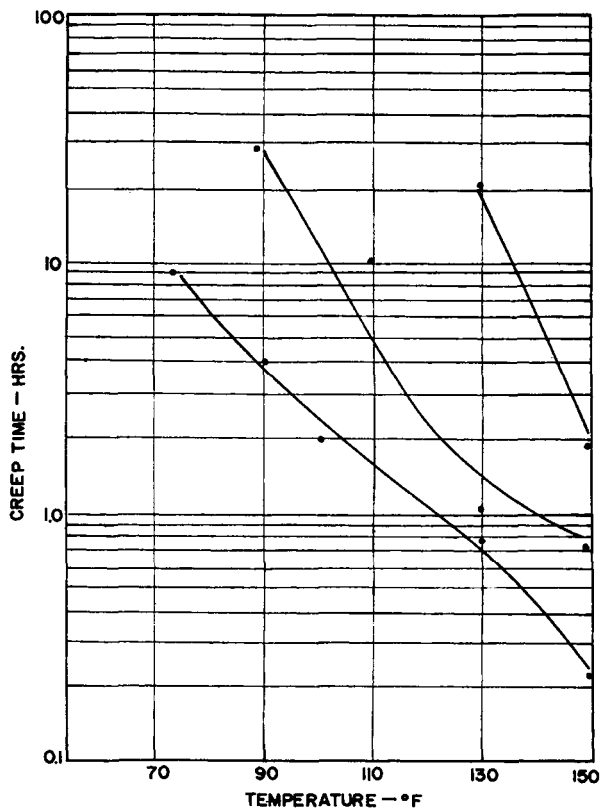| Sample	Bound Na, wt-%	Tack, g/cm² at 10 g contact pressure	Peel force to steel, oz/in. width	Resistance to creep, hr
1	0	163	47	0.6
	0.06	123	38	4.5
	0.08	77	43	1.7
	0.32	40	33	>100
	0	607	87	0.2
2	0.34	247	46	4.2
	0.50	142	45	7.5
	0.52	133	50	2.9
	0.59	92	25	68
	0.69	0	25	64

Fig. 4. Effect of temperature on creep resistance. Sodium content: (top curve) 0; (middle) 0.08%; (bottom,) 0.8%.

elevated temperatures. This indicates that ionically bound polymers could be processed at elevated temperatures on equipment designed for thermoplastic materials. The data shown in Figure 4 indicates that resistance to creep falls off rapidly with increasing temperature and that at elevated temperatures the effect of ionic binding is minor. In its temperature sensitivity, the heat-labile ionic binding is basically different from covalent crosslinking. The decrease of creep time with increasing temperature is accompanied by a change in infrared absorption spectra as shown in Figure 5, where the absorbance at 6.28 μ decreases with increasing temperature. The process is reversible, and the resistance to creep increases again on cooling.

Despite the heat sensitivity of the ionic binding, its effect is still noticeable even at much higher temperatures than conditions used to obtain the data shown in Figure 4. This is evident from Figure 6 showing the effect of temperature on 180° peel force from steel surface. Bright[3] distinguishes three different branches in such curves corresponding to adhesive, mixed and cohesive failures. At lower temperatures, the adhesive peels off cleanly
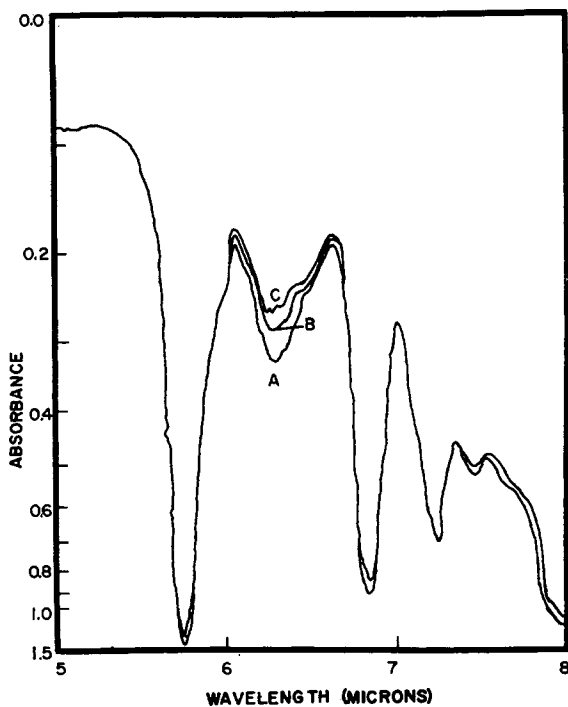
Fig. 5. Change of infrared absorption spectrum with temperature at 0.18% Na content:
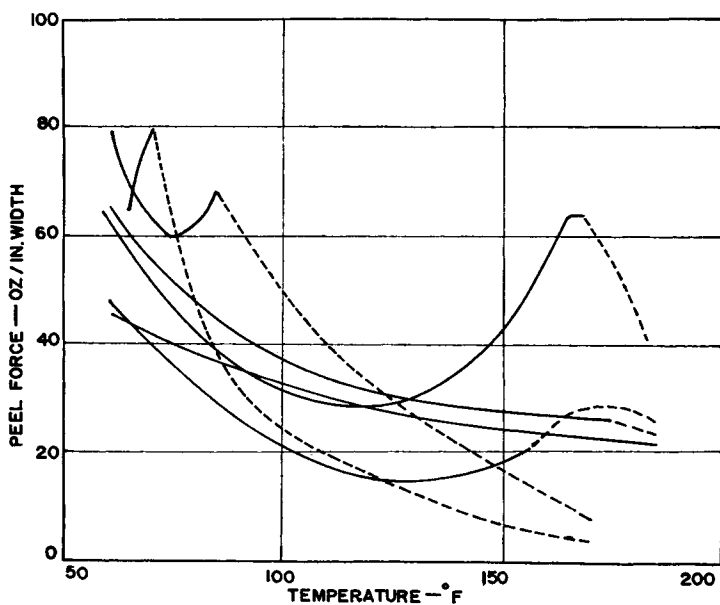(A) 70°F; (B) 140°F; (C) 200°F.

Fig. 6. Effect of temperature on 180° peel adhesion to steel at various sodium content:
curve top right, 0.50%; 0.34%; 0.59%; 0.69%; 0.18%; curve bottom right, 0%.

from the steel surface (solid lines in Fig. 6). As the temperature rises, the curve rises sharply to a maximum and then decreases smoothly. The latter branch of the curve corresponds to a different mode of failure; the adhesive tape does not peel off cleanly but fails cohesively (dotted lines in Fig. 6) leaving a deposition of adhesive on the steel plate. The test was run at a peel rate of 6 in./min. For practical purposes it is necessary and meaningful to make a distinction between these two types of failures, despite the recently advanced theories that an adhesive failure is impossible if a proper bond is formed.[9] The term "adhesive failure" as used here might not be semantically correct, but it is not necessarily implied that the failure is a truly interfacial one on a micro scale.

The effect of ionic binding is evident from inspection of Figure 6. The parent polymer (A) is a very soft material of low cohesive strength and shows a cohesive failure at a comparatively low temperature. Even a low density of ionic binding delays cohesive failure until higher temperature is reached (C,D). The polymer with a higher amount of sodium (F) did not fail cohesively within the temperature range employed but peeled off cleanly from the steel plate at temperatures tested.

Table II shows perhaps even more clearly than Figure 6 the effect of ionic binding on splitting temperature. Splitting temperature is defined as the temperature at which the mode of failure changes from adhesive to cohesive. As noted previously, instead of a clean peel as obtained in the case of the adhesive failure, the polymer splits at or above this temperature leaving a residue on the steel plate. The data shown are obtained from tests of samples from the same polymer batch differing only in the amount of bound sodium.

TABLE II
Effect of Bound Sodium on Splitting Temperature

Bound sodium, wt-%	Splitting temperature, °F
0	70
0.18	90
0.34	155
0.50	170
0.52	170
0.59	180
0.69	190

Ionic binding can be used quite effectively in pressure sensitive polymers to increase their cohesive strength. Such polymers are soluble and can be processed by regular methods used for thermoplastic materials. Decrease in tack and peel force is observed as a result of ionic binding. The infrared method of analysis presented is a fast and simple method to evaluate the amount of bound ions. The results of infrared analysis correlated well with the data obtained by a gravimetric method.

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