

Water Solubility Characteristics of Some Ion-Containing Acrylic Copolymers

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Synopsis

The water solubility characteristics of a series of ionic copolymers of acrylic acid with acrylic esters was determined. A relationship was developed between solubility and the ionic character of the copolymers. In addition to water solubility, the effects of the composition and degree of neutralization upon other copolymer properties were also examined. Moisture effects upon the physical properties can be minimized by limiting the ionic character of the copolymer to that required for water solubility. The effects of molecular weight on the solubility and speed of dissolution was also investigated and found to have no effect, within the range of composition of the copolymers investigated.

INTRODUCTION

Although there are a large number of water-soluble polymers available on the market, most of them have some significant deficiencies as packaging materials. Poly(vinyl alcohol) (PVOH), the most familiar of the synthetic polymers, shows generally excellent properties as a water-soluble packaging film and has a large share of this market. The only real problem with PVOH is the potential for thermally induced crystallization during processing.¹ This can result in less soluble films, especially if the degree of acetylation is allowed to vary slightly. One deficiency that is rarely considered is the sensitivity of PVOH to strong oxidizing agents. This too can lead to water insolubility through the conversion of hydroxyl groups to oxidized species. Packaging of oxidants in PVOH for extended periods therefore can result in a controlled release package that will not release its contents. Poly(ethylene oxide) (PEO) is another water-soluble polymer which has a large number of uses but has not found extensive utilization as a packaging film, due to both property and economic limitations. Although PEO is not as sensitive to oxidants as PVOH, it is affected by contact with various oxidants, resulting in loss of efficacy of the total product. Most of the other commercially available water-soluble polymers, such as cellulose derivatives, poly(vinyl pyrrolidone), polyacrylamide, and poly(acrylic acid), all show cost or property deficiencies that have thus far precluded their participation in the packaging market. All of these also are sensitive to oxidants, with the exception of poly(acrylic acid).

For a number of years we have been interested in the utilization of acrylic acid copolymers as temporary coatings for protection of hard surfaces such as floors, painted surfaces, etc. These polymers are usually relatively low molecular weight materials, which do not give self-supporting films with usable mechanical properties. It was believed that higher molecular weight copolymers of acrylic acid would possess sufficiently attractive mechanical properties to be candidates

for water-soluble packaging films. In addition the oxidative stability of the all acrylic copolymers should allow their use in applications where other water-soluble polymer systems would be ineffective.

In order to extend our knowledge base in this area, we were interested in the effects of polymer structure upon the water solubility and the physical and mechanical properties of higher molecular weight acrylic acid containing copolymers. In this paper we will attempt to show relationships among the structural features such as the level of acrylic acid in the copolymer, molecular weight, degree of neutralization of the acid moiety, and comonomer composition on the chemical and physical properties such as water solubility and moisture absorption. Thermal and mechanical properties of films prepared therefrom will be the subject of a subsequent paper.

EXPERIMENTAL

The monomers and solvents used in this study were commercially available materials and were used as received. The copolymers were prepared by solution polymerization in methanol at about 35% solids, using conventional laboratory glass reaction equipment. A typical polymerization procedure is as follows:

A solution consisting of 20% of the final monomer mixture, 15% of the total initiator [azo-bis-isobutyronitrile (AIBN)] and 62 wt % of the total solvent (methanol) was charged to the reaction vessel and heated to reflux (60–65°C). The remainder of the monomer mixture and 60% of the total initiator were dissolved in 27% of the total methanol and added slowly to the reaction flask over a 1.5 h period. After a 1 h agitated hold period, the remaining 11% methanol and 25% initiator was added over a 0.5 h period. The reaction mixture was maintained at reflux overnight. Total reaction time was 24 h.

Molecular weights were determined by gel permeation chromatography, using a Spectra Physics isocratic pump, four microStyragel columns (100, 10, 10, and 10 Å; Waters Associates, Inc.), and R401 differential refractometer detector, and an IBM 9000 computer to facilitate data storage and handling. The calibration curve was determined by fitting a third order polynomial to a plot of $\log(\text{molecular weight})$ vs. retention time. THF was used as the mobile phase at a flow rate of 0.7 mL/min.

Polymers were neutralized using sodium and potassium hydroxides. Neutralization was most commonly accomplished by addition of an aqueous or methanolic solution of the corresponding hydroxide to the agitated polymer solution. In certain cases the neutralized polymer showed considerably different solubility characteristics compared to the unneutralized polymer; the specific method of neutralization was chosen after consideration of these solubility differences. Polymers were isolated from the solvent by casting onto release paper or polyethylene film and allowing the copolymer to air dry.

Moisture content of the copolymers were measured both gravimetrically and by Karl Fischer titrations after storage at various conditions of temperature and humidity. Solubility characteristics of the compositions were determined by turbidimetry and by dissolution experiments. For the turbidity measurements, polymer compositions were neutralized to 100% of their acid contents with sodium hydroxide and isolated by air drying of a cast film. A measured amount of the neutralized polymer was then dissolved in deionized water to

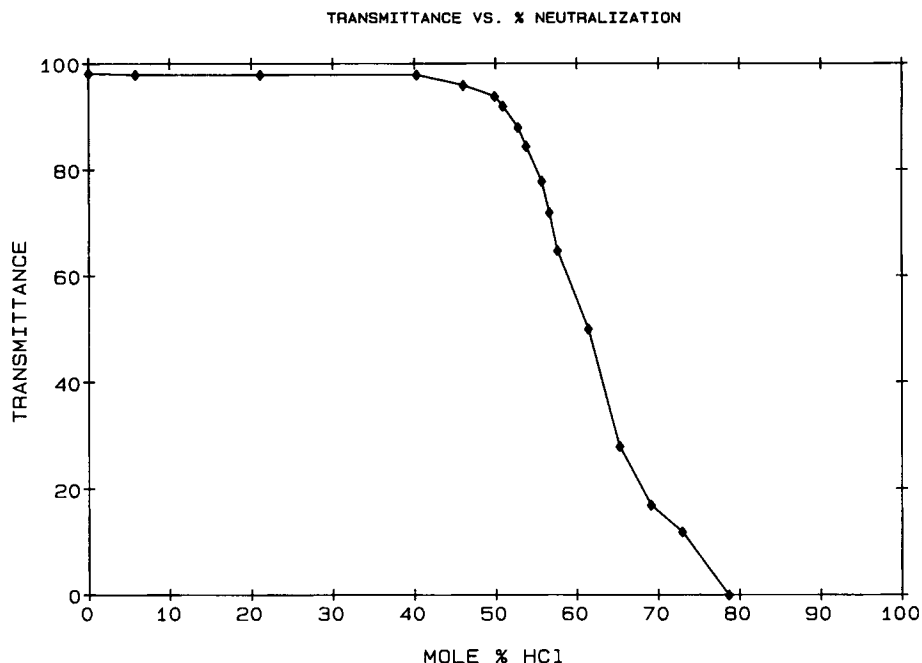


Fig. 1. Percent transmittance as a function of percent neutralization of an acrylic ester/acrylic acid copolymer.

give a dilute aqueous solution. The clear solution was then backtitrated with 0.5 *M* HCl, while monitoring the turbidity either visually or with a Bausch and Lomb visible spectrophotometer. The end point of the titration, indicating a degree of neutralization necessary for solubility, was taken as the point at which the solution became distinctly cloudy. Polymer solubility by dissolution was determined by addition of an approximately 1 g sample of dry polymer film to 150 mL of stirred deionized water at 23°C and observing the dissolution characteristics (time and clarity of the solution).

DISCUSSION

The polymerization and copolymerization of acrylate monomers have been the subjects of extensive research for many years and considerable literature has been generated on these polymer systems.²⁻⁴ In order to obtain useful information on some of the key polymer properties of interest, simple acrylate copolymer systems were evaluated. Polymers were prepared by a solution polymerization method to obtain linear, random copolymers. In selecting the polymerization system, consideration was given to a number of reaction parameters of the polymerization process. These parameters included monomer, initiator, and solvent selection, polymerization conditions, final polymer composition, and neutralization counterion (nature and degree of neutralization).

The simplest acrylic acid/acrylate ester system is one containing acrylic acid and a single acrylate ester. The ester preferably should have a reactivity ratio similar to that of acrylic acid in order to ensure a random copolymerization

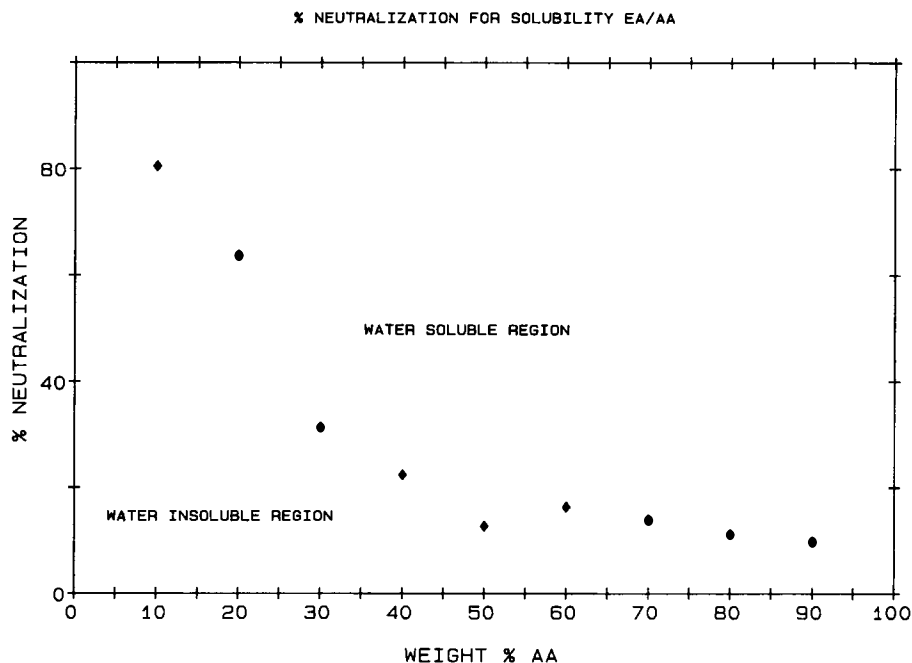


Fig. 2. Percent neutralization required for solubility of an ethyl acrylate/acrylic acid copolymer.

at high conversion. An acrylic acid/ethyl acrylate copolymer system was chosen as the first such system. An azo type free radical initiator was chosen based both on solubility in polymerization media and on the tendency of the initiator radical not to abstract hydrogen, thereby producing relatively linear copolymers.⁵ Methanol was selected as the polymerization solvent since as a solvent for the acrylic monomers, the initiator, and the copolymers it should offer the highest probability of producing a truly random copolymer. In addition, the low reaction temperature which results from the use of methanol at reflux reduced the probability of side reactions which could lead to branching. Methanol is also a poor chain transfer agent; therefore, its participation in the polymerization by transfer is minimal. The polymer compositions examined were initially chosen to give a series of copolymers which would allow the development of the solubility-composition relationships. In these systems we started with the acrylic acid/ethyl acrylate systems. As the relationships among structure, neutralization, and solubility became clearer, we were able to design compositions which possessed properties such as tenacity, elongation, flexibility, and antiblocking, necessary for a packaging film application.

Solubility

Polymer dissolution is the result of favorable polymer-solvent, solvent-solvent, and polymer-polymer interactions. The study of polymer solution thermodynamics is an active area of polymer science. Several theories and models attempt to explain deviations from ideal solution behavior,⁶ taking into account the polymeric nature of the solute. The situation is more complex in the case

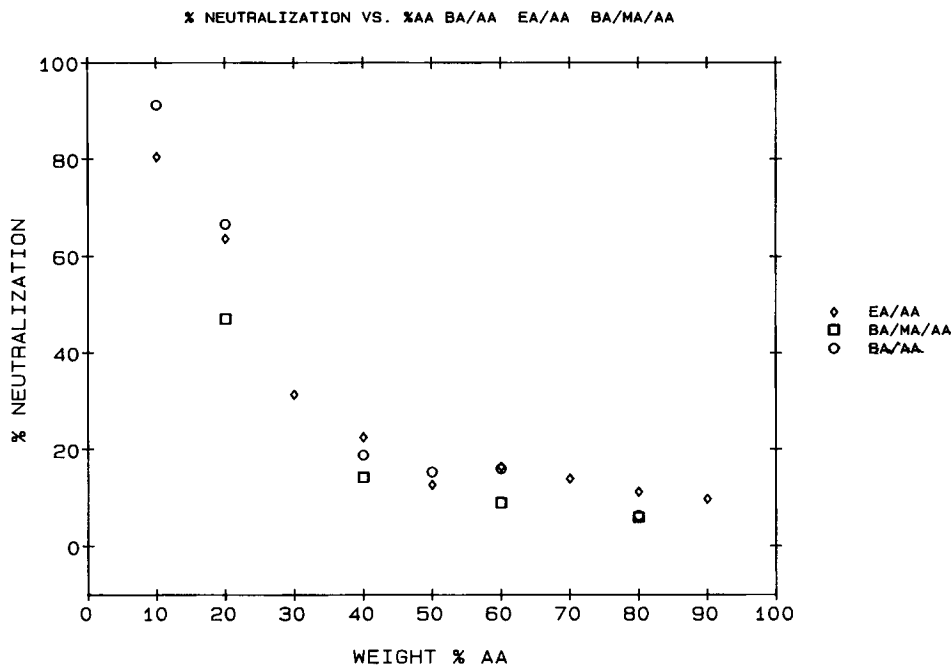


Fig. 3. Percent neutralization required for solubility of acrylic acid copolymers.

of ion-containing polymers. For the purposes of this study, we arbitrarily assigned certain conditions to our definition of solubility. We were interested in a relatively rapid dissolution rate such that a film of about 5–8 mil thickness would dissolve completely in water at room temperature (23°C) in about 5 min. The polymer should remain in solution in water under a variety of conditions of pH and temperatures (i.e., no upper or lower critical solution temperatures in the range of 0–95°C). These rather strict requirements for polymer dissolution and the low final polymer concentrations for the end use applications of interest (typically less than 0.1%) allowed us to forego an equilibrium/thermodynamic treatment of solubility. Among the factors which influence solubility are: polymer composition and conformation, branching, crystallinity, temperature, concentration, molecular weight, and choice of solvent.

Poly (acrylic acid) is water-soluble over a broad range of molecular weights. Upon introduction of relatively hydrophobic acrylate esters into the main chain, however, the polymer becomes water-insoluble. The incorporation of these acrylic esters is desirable from the standpoint of reducing the hygroscopic nature and modifying the mechanical properties of a polymer. Their incorporation, however, imposes the need for the introduction of ionic character into the copolymer to maintain water solubility. For ethyl acrylate/acrylic acid (EA/AA) copolymers containing 80, 60, 40, and 20% AA, the amount of ionic character (which results from partial neutralization) required for water solubility was determined by the turbidimetric technique and verified by dissolution described earlier. A typical turbidity curve for titration of a completely neutralized copolymer with a standardized dilute HCl solution is shown in Figure 1. A transmittance of about 80% was found to be about the point of readily discernible cloudiness of the solution. In later experiments no appreciable differ-

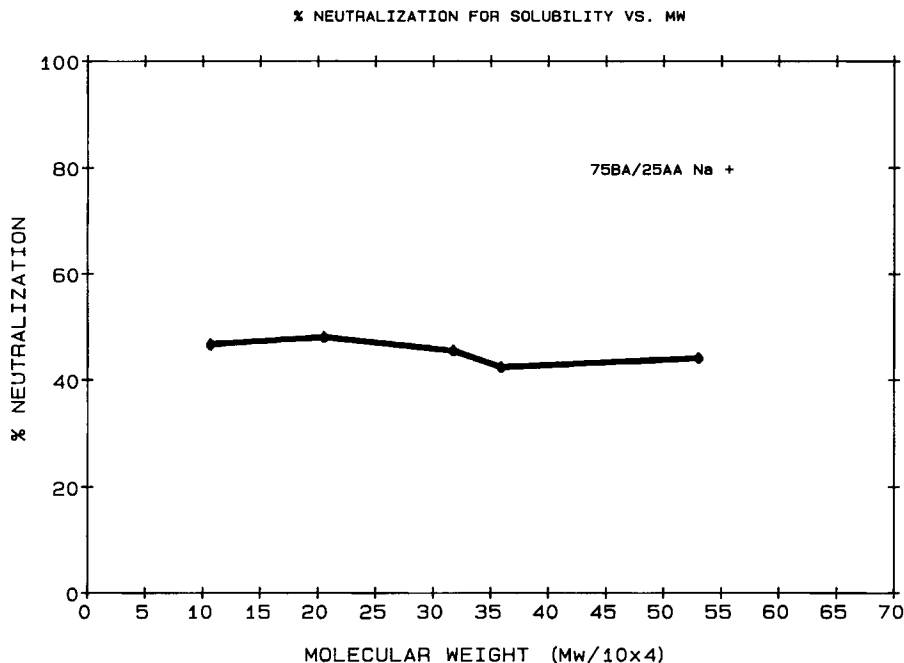


Fig. 4. Percent neutralization required for solubility as a function of molecular weight for butyl acrylate/sodium acrylate copolymers.

ences were found between determinations made with the use of the spectrophotometer and those performed using a visual end point determination. In the interest of simplicity and convenience, therefore, the visual end point method was adopted as the method of choice for determination of solubility.

Realistically the rather crude turbidimetric technique yielded some very specific solubility information. At a given concentration, temperature, and pH, the polymer conformation in solution was such that it resulted in the onset of a visibly turbid solution. The solubility data generated by this technique was found to correlate well with that found in the solubility by the dissolution test performed with polymer film samples.

Using the turbidimetric titration data, we were able to generate a phase diagram which indicates the degree of sodium hydroxide neutralization required for water solubility at a given level of acrylic acid in the copolymer system. Figure 2 illustrates the data generated from a series of acrylic acid/ethyl acrylate copolymers in which the compositions were varied in 10 wt % increments over the entire composition range of 0–100% acrylic acid. Acrylic acid/butyl acrylate/methyl acrylate and acrylic acid/butyl acrylate systems were also evaluated as the sodium and potassium salts and similar curves were obtained. When the phase diagrams are plotted as wt % acrylic acid against level of neutralization, the phase boundaries for all of these copolymer systems fall nearly on the same line (Fig. 3). The concurrence of the solubility boundaries for the various acrylic ester systems is the result of the manner in which the data were treated. Use of the wt % acrylic acid gives a constant ratio of carboxylic acid groups to carbon residue for the polymer. The indication from these curves is that the

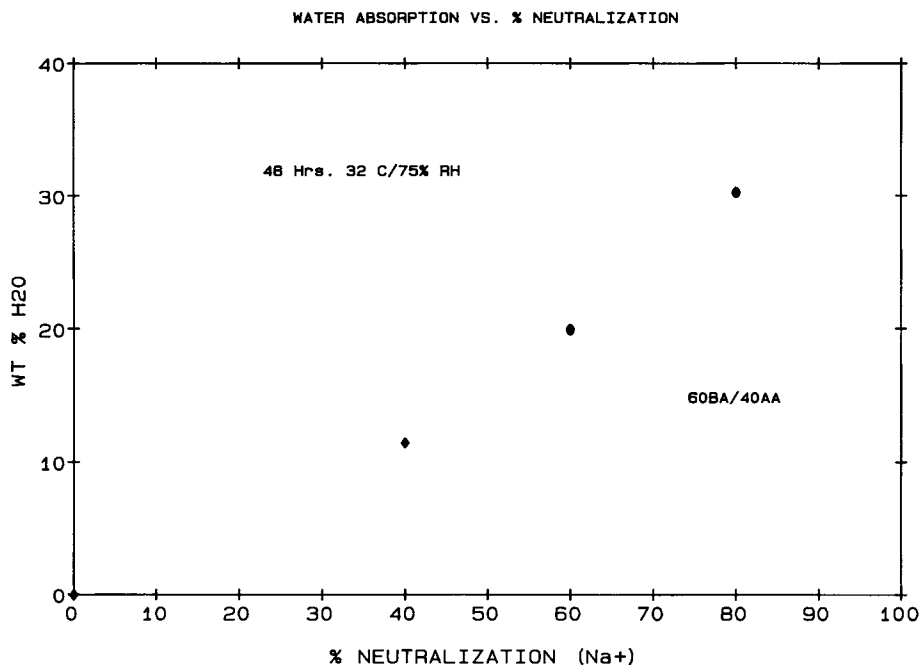


Fig. 5. Water absorption as a function of percent neutralization for a butyl acrylate/acrylic acid copolymer neutralized with sodium hydroxide.

important factor in the solubility of these copolymers is the polarity/ionic character ratio.

With this information we are able to estimate the degree of neutralization required for water solubility for any of our acrylic acid/acrylate ester copolymer systems. Since the phase boundaries are so similar, one need only evaluate two or three different compositions within a specific acrylate system to verify the boundaries. The general curve (Fig. 3) was the same, regardless of the nature of the cationic species utilized. These phase diagrams thus serve to give us guidance to a molecular design for water-soluble acrylate copolymers. Used in conjunction with other more traditional methods of designing acrylate polymers (T_g , etc.), we have been able to design compositions with varying properties needed for specific applications. The added control obtained by utilization of the solubility phase diagrams reduces the amount of time and experimental work previously needed to design an appropriate composition required for water-soluble polymers to fill our application needs.

The second solubility requirement that we have for the polymer films is that they dissolve rapidly. It had been assumed that the dissolution rate would be a function not only of the composition and geometry but also of the molecular weight. Examination of the solubility of copolymers with molecular weights from 100,000 to 550,000 (Fig. 4) indicates that there is no difference in the degree of neutralization required for solubility, for a typical copolymer. All of the copolymers utilized in this study were within this range. In less quantitative dissolution trials, little or no differences were seen in the time to cause complete disintegration of films of these same copolymers. Although extremely high molecular weight materials would undoubtedly show much slower dissolution rates,

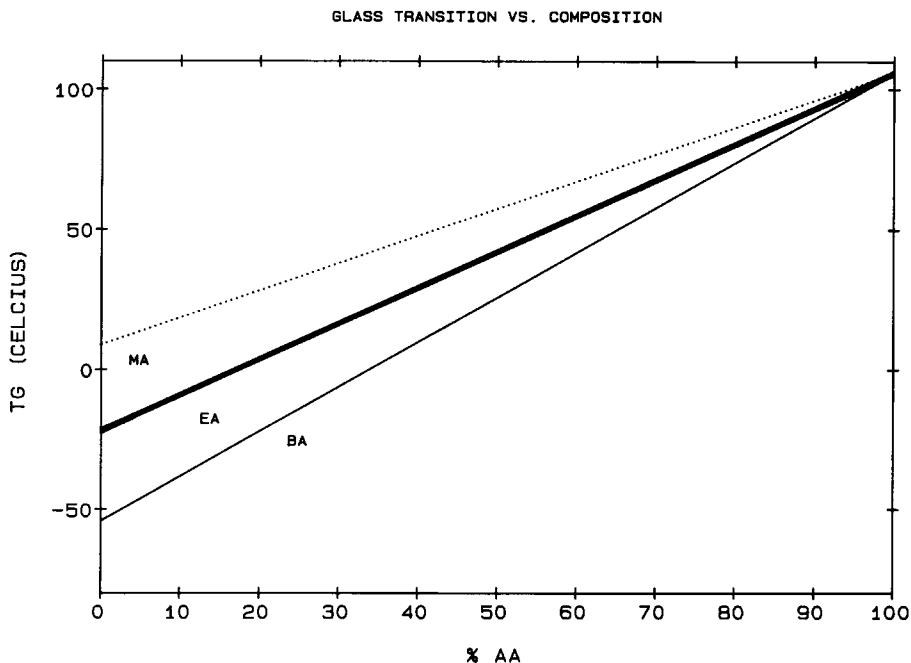


Fig. 6. Glass transition temperature as a function of composition for a series of acrylic ester/acrylic acid copolymers.

it appears that the polymers evaluated are of sufficient molecular weight to provide both rapid dissolution and mechanical strength.

Moisture Sorption

Due to the ionic nature of the polymers, films prepared from these polymers are hygroscopic. Depending on the temperature, relative humidity, and ionic content of the polymer, these films can absorb large amounts of moisture. Under ambient conditions typical films have been found to contain more than 5% of bound moisture, and about 25% under conditions of 32°C/75% relative humidity. Figure 5 shows the effect of partial neutralization on the water absorption of a 60 butyl acrylate/40 acrylic acid polymer. In these experiments the acid polymer was neutralized with sodium hydroxide to 40, 60, and 80 mol % of the acid content. The polymer films were found to absorb 11.5, 20.0, 30.3% (wt %), respectively, when equilibrated at 32°C/75% relative humidity. As expected, moisture sorption increased with increasing ionic character in the polymer (Fig. 5). From the phase diagram (Fig. 3) generated on degree of neutralization required for solubility, it can be seen that the 60 BA/40 AA copolymer requires about 20% neutralization for solubility. This corresponds to about a 5% moisture absorption level in this polymer. Moisture sorption can therefore be minimized by introducing only enough ionic character into the polymer to yield water solubility (recall our definition of solubility). While the moisture sorption was still high, neutralizing only to a point required for solubility minimized the sorption of water into the polymer. This is an important property of the polymer since many of the products that might be packaged or

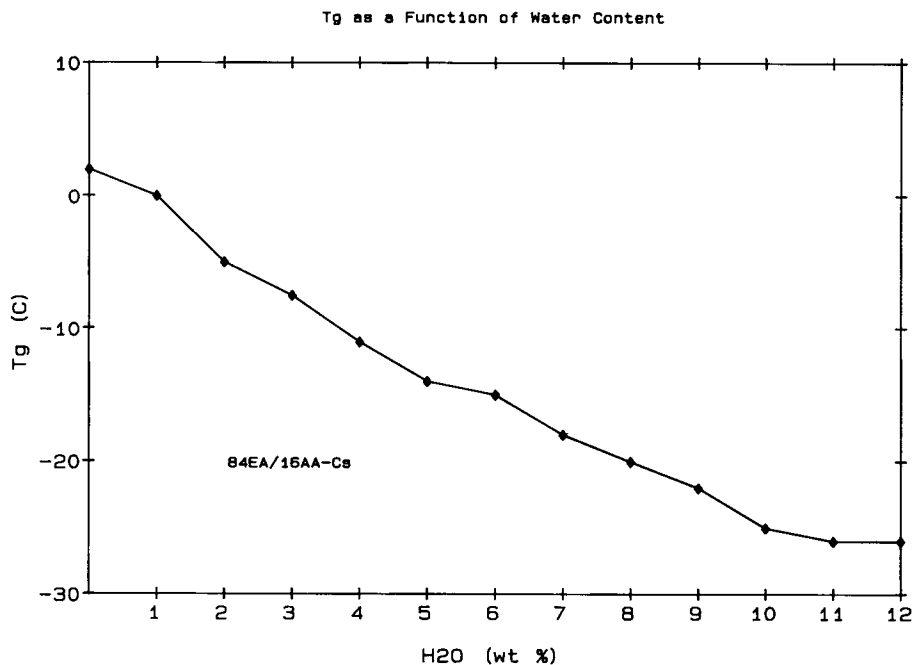


Fig. 7. Glass transition temperature as a function of water content for an ethyl acrylate/acrylic acid copolymer neutralized with cesium hydroxide.

contained in structures made from these films may be moisture sensitive or change appearance on contact with moisture. If the moisture absorbance of the film is too great, it could result in the contained product being unuseable. The ability to moderate the moisture absorption of these polymers is important therefore to their potential as packaging films.

Mechanical Properties

Films prepared from the polymers are expected to be flexible and maintain their mechanical integrity over a broad range of temperatures and humidities. In order to obtain copolymers that are sufficiently flexible, we limited the compositions to those which would be expected to give materials with a T_g of 0°C or less. As can be seen from Figure 6, which shows the T_g , as calculated from the Fox equation,⁷ as a function of composition, this results in compositions of 20–40% acrylic acid, depending upon the acrylic ester used. Matsuura and Eisenberg⁸ have shown that the glass transition temperatures of neutralized acrylic acid copolymers are strongly influenced by their water content. Considering the plasticizing effect of absorbed water, as illustrated in Figure 7, it is apparent that the physical properties of the film will be variable. Compositions formulated to accommodate this “range of properties” have a tendency to be brittle at completely dry conditions and become tacky and blocky, flowing at elevated temperatures and humidity (32°C/75% RH). Attempts to control the limits of this property range alter the solubility characteristics. It has been found, not surprisingly, that the copolymer physical properties are improved with polymers of higher molecular weight. A crude comparison of polymer

TABLE I
Polymer Properties

Property	Emulsion EA/AA	Solution EA/AA
M_w	68,000	320,000
M_n	17,000	43,500
M_z	152,000	665,000
Creep	Flowed under its own weight	Nonflowing except at high humidities
Block	Blocking	Nonblocking except at high humidities

properties between similar copolymers of differing molecular weights is shown in Table I.

Much of the preliminary evaluation of mechanical properties of these films has been done subjectively. We have carried out more quantitative evaluation of the effects of certain variables upon the physical properties. This work will be the subject of a subsequent paper.

CONCLUSIONS

The results reported in this paper demonstrate that control of acrylic acid levels and of the degree of neutralization in acrylate ester copolymers can exert a high degree of control over the physical and mechanical properties of the material. Among those properties which have been shown to be affected by variations in acid level and degree of neutralization are water solubility, moisture absorption, and sensitivity. Oxidative stability, while not being a function of these two structural variations, was also found to be excellent for all of the acrylic acid copolymer systems examined. The physical and mechanical properties are also strongly affected by the copolymer variations, and packaging films with useful properties have been prepared from certain compositions.

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