

## Polymer composite principles applied to hair styling gels

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### Synopsis

A novel approach is taken to understand the mechanical performance of fixative-treated hair tresses. Polymer composite principles are applied to explain the performance. Examples are given for polyacrylate-2 cross-polymer that show that the choice of neutralizer affects the film properties of anionic acrylic polymers by plasticization or by hardening through ionic (physical) crosslinking. The effect of these changes in the polymer film on the composite properties was determined by mechanical stiffness and high-humidity curl retention testing. It is shown that both adhesion to the hair and polymer cohesion are important in determining fixative polymer performance. The implications of the results for the formulation of fixative systems are discussed.

### INTRODUCTION

Hair fixative gels are widely used to create and maintain a variety of hairstyles. Two important properties desired in hair gel products are stiffness and hold, which are controlled by the fixative polymer in the formulation. To satisfy increasing consumer demands, performance with respect to these properties must be improved relative to the current fixative polymers. Understanding the science behind fixative gel-treated hair is essential to achieving these improvements.

A hair fixative gel is a cosmetic product; however, it will be argued here that its performance is governed by polymer composite mechanisms. When a gel is applied to the hair, a polymer–fiber composite is created that is morphologically similar to high-performance fiber composites (1) used in load-bearing applications. The differences between fixative-treated hair and industrial fiber composites are primarily in the mode of fabrication and the performance specifications. Industrial composites start with the polymer and add fibers for reinforcement; there is a critical amount of fibers that must be achieved for strengthening. In contrast, fixative composites start with fibers (hair), and a minimum amount of polymer gel must be used to achieve composite strength

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properties. As is the case for the industrial composites, the hair fibers provide the primary strength to the fixative composite. (With respect to fixative gel products, this sometimes goes against popular belief.) In both cases, it is important that the polymer adheres to the fibers. (2) The fixative gel glues multiple hair fibers together, creating a composite fiber with a larger effective diameter, and thus, higher stiffness. Good adhesion between the polymer and the fibers allows stress transfer between the polymer and fiber and is necessary to achieve composite properties. Polymer cohesion, which is affected by molecular weight, architecture, crystallinity, polar interactions, hydrogen-bonding, environmental conditions, and additives, contributes to the composite strength when there is sufficient polymer–hair adhesion.

To demonstrate the connection of composite science and cosmetic formulation, the effect of the neutralizing base on the polymer film and hair fiber composite mechanical properties will be shown for polyacrylate-2 crosspolymer (Fixate™ Superhold polymer, Lubrizol Advanced Materials, Inc., Noveon® Consumer Specialties). Film testing will show how the neutralizer affects the cohesive properties of the polymer, and testing fixative–hair composites will measure the combined adhesive and cohesive properties. The results will be considered with respect to polymer composite principles, and the implications for fixative gel performance will be discussed.

## EXPERIMENTAL

### MATERIALS

Gels were prepared using 3 wt% (solids) polyacrylate-2 crosspolymer (a (meth)acrylic acid-ester copolymer) and neutralizing to pH 7 with sodium hydroxide (NaOH), 2-amino-2-methyl-1-propanol (AMP), or triethanolamine (TEA).

### SAMPLE PREPARATION AND METHODS

Polymer films were prepared on Mylar; the dry film was approximately 0.25-mm thick. The films were allowed to dry for a minimum of 48 hours at 23°C, 50% relative humidity (RH).

Tensile testing of the films was done with an XT-Plus Texture Analyser (Texture Technologies). All testing was performed at 23°C, 50% RH using the sample geometry described in ASTM D 882-02 (3) and a rate of 5 cm/min. Young's modulus (4), calculated as the slope of the linear portion of the stress versus strain curve, and elongation at break were obtained for comparison.

Dynamic mechanical analysis (DMA) was performed on a TA RSA3 Dynamic Mechanical Analyzer (TA Instruments) using rectangular samples of polymer film. Samples were tested in extension from  $-100^{\circ}$  to  $200^{\circ}\text{C}$  at a frequency of 1 Hz and a strain of 0.05%. The glass transition temperature ( $T_g$ ) was chosen as the onset of the decrease in the elastic modulus ( $E'$ ).

The stiffness of the fixative–hair composite samples was performed using an XT-Plus Texture Analyser in a three-point bend configuration. Composite samples for this test were prepared by applying 0.8 g of fixative gel to virgin Chinese hair tresses weighing 2.5 g and measuring 16.5 cm in length. The prepared tresses were sandwiched between

perforated, Teflon-coated plates and clamped using spacers to maintain a flat, rectangular geometry while the samples were dried for 24 hours at 23°C, 50% RH. For high-humidity testing, the dried samples were conditioned for an additional 24 hours at 25°C, 90% RH. Testing was done using a support span of 2.54 cm and a flexure rate of 40 mm/s. The data were plotted as force versus time. Peak force was used as a measure of stiffness instead of Young's modulus (5), which is in the linear deformation region of the curve, because it is a better probe of adhesion (6). Five samples were prepared per gel, and the averages were reported.

High-humidity spiral curl retention (HHSCR) testing was performed on fixative-composite samples. Gel (0.1 g) was applied to a European brown hair tress weighing 0.5 g and measuring 16.5 cm in length. Application and distribution of the gel was done with the tress on a balance to ensure accurate loading. The treated tresses were wrapped onto curlers with a machined spiral groove, secured, and dried for 24 hours at 23°C, 50% RH. The dried tresses were carefully unwrapped and hung on a ruled peg board. The initial length of the curls was recorded, and the peg board assembly was placed into a humidity cabinet at 25°C, 90% RH. Readings were taken every 15 minutes for the first hour, then every half hour for hours two through four, and every hour for hours five through eight. The curl retention is calculated as:

$$\% \text{ Curl retention} = (L - L_t) / (L - L_o) \times 100 \quad (1)$$

where  $L$  is the length of the uncurled tress,  $L_t$  is the length of the curl at the time of the reading, and  $L_o$  is the length of the curl at the start of the experiment. The length of the tress is denoted as the lowest line number (on the peg board) that is below the entire tress. Ten tresses were prepared per gel, and the averages were reported.

## RESULTS AND DISCUSSION

Traditionally, rigid polymers have been used in fixative applications to create stiff-hold hairstyles. It is generally believed that the fixative polymer stiffens the hair since the stiffness of treated hair is more rigid than that of the untreated hair fibers. However, it will be demonstrated that fixative-treated hair is a polymer-fiber composite. Thus, the hair fibers are the primary source of strength of the composite, and adhesion is of prime importance in achieving polymer composite properties. Nonetheless, this does not mean that the cohesive properties are unimportant. With adequate adhesion, the cohesive strength of the polymer affects the stiffness of the composite. Therefore, the cohesive properties of potential fixative polymers must also be considered. Cohesion of fixative polymers is probed by mechanical tests on thin films.

### FILM PROPERTIES

Dynamic mechanical analysis (DMA) and tensile testing are conducted to give complementary information on polymer cohesion. DMA is used to measure the glass transition temperature ( $T_g$ ), melting temperature(s), and crosslinking, all of which affect the stiffness of the polymer. Since most fixative polymers are amorphous,  $T_g$  is the most important parameter for describing rigidity.  $T_g$  is a measure of the cohesive energy of the polymer. It represents the thermal energy needed to overcome attractive forces and

morphological factors to allow the polymer chains to move past each other with long-range coordination.

In the example shown in Figure 1, the effect of the neutralizing base on an amorphous (meth)acrylic acid-ester copolymer (polyacrylate-2 crosspolymer) is shown relative to the unneutralized (acid form) of the polymer. The elastic modulus,  $E'$ , is plotted versus temperature, and the onset of  $T_g$  is indicated by the temperature at which  $E'$  begins to decrease. The neutralizing bases have very different effects on the polymer.

Relative to the acid form of the polymer, AMP causes very little change, while TEA causes a significant decrease and NaOH causes a major increase in  $T_g$ . In fact,  $T_g$  for the sample neutralized with NaOH is indiscernible. The effects of the neutralizers on polymer cohesion were confirmed with tensile testing (Figure 2). The sample neutralized with TEA was softened, as evidenced by a significantly lower Young's modulus and a significantly higher elongation to break. TEA plasticizes the polymer, lowering  $T_g$  and allowing the polymer to relax instead of breaking under the applied stress (increased elongation to break) (7). On the other hand, tensile testing of the polymer film neutralized with NaOH revealed that the polymer was hardened, as demonstrated by a higher Young's modulus and a lower elongation to break. This phenomenon is explained by ionic crosslinking (8). In polymers with ionizable groups, such as the carboxylic acid groups in polyacrylate-2 crosspolymer, electrostatic attraction between ionic species can create physical crosslinks in the polymer. The potential effects on polymer properties

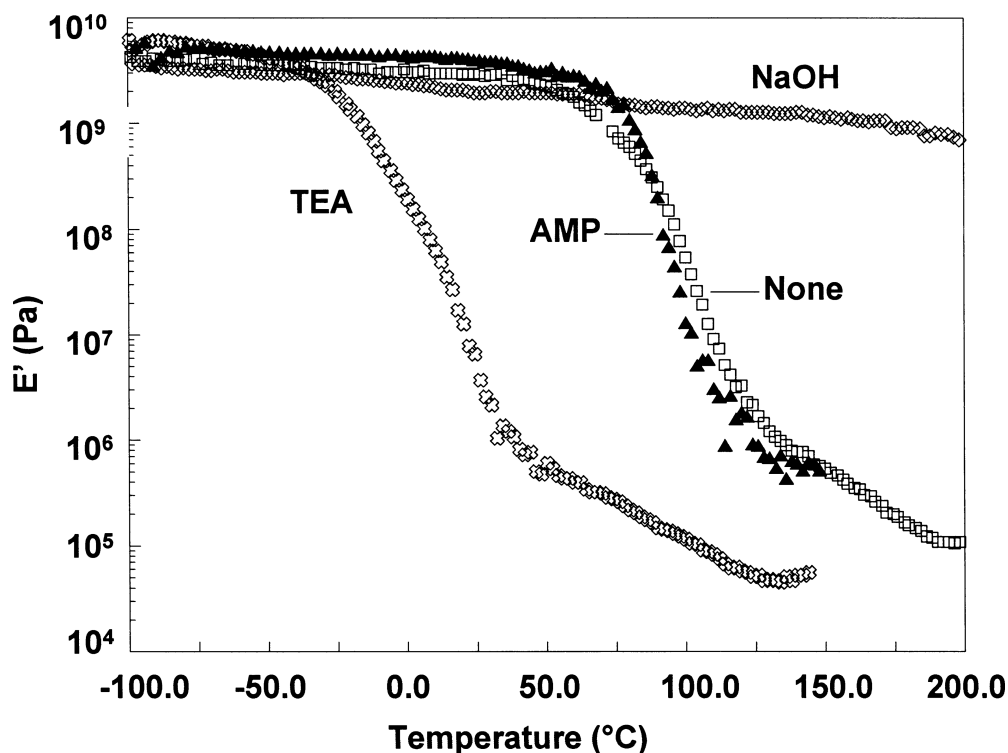


Figure 1. DMA temperature sweep data for thin films of polyacrylate-2 crosspolymer, neutralized to pH 7 with NaOH, AMP, or TEA. The unneutralized polymer (none) is also shown for comparison.

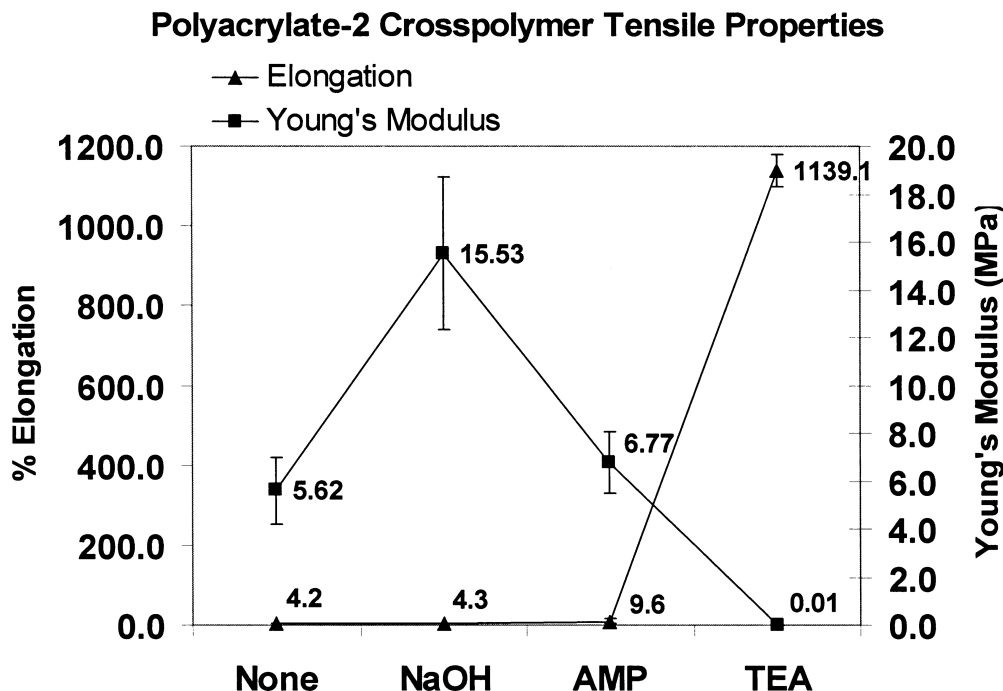
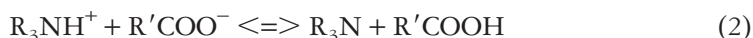


Figure 2. Average tensile data for thin films of polyacrylate-2 crosspolymer, neutralized to pH 7 with NaOH, AMP, or TEA. The unneutralized polymer (none) is also shown for comparison. The error bars represent  $\pm 1$  standard deviation for the test.

are the same as for chemical crosslinks: the rubbery plateau modulus increases and the glass transition temperature increases at higher crosslink densities (9,10). It has been shown that  $T_g$  is proportional to  $cq/a$ , where  $c$  is the amount of ionic groups,  $q$  is the charge, and  $a$  is the distance between ionic centers, which is related to the size of the counterion of the base (11). Because of the different chemical natures of the bases used in this study, it is expected that  $c$ ,  $q$ , and  $a$  will vary for each of them. This is true even though the pH was adjusted to be the same for all polymers prior to film formation. A series of simple arguments can be used to establish a reasonable ordering for the  $cq/a$  parameter.

The case for NaOH is relatively clear. It is expected that Na will exist as the +1 ionic species. Thus  $q = +1$ , and  $c$  depends simply on the equivalents of COOH and Na. The relative size of  $a$  for Na vs TEA and AMP is easily seen to be:  $a_{\text{Na}} < a_{\text{AMP}} < a_{\text{TEA}}$ .

Assigning  $c$  and  $q$  values for TEA and AMP is more problematic. In the case of these amines, it is clear that  $c$  and  $q$  will both depend on the value of the equilibrium constant for the following reaction scheme:



where R represents H or an alkyl group. Estimation of this quantity is not trivial (12–14). This is mainly due to the possibility of encountering steric effects with non-primary amines. The situation will be further complicated in the present case since the carboxyl group has additional constraints due to the fact that it is part of a polymer.

Related work allows us to make reasonable estimates of the relative sizes of the equilibrium constants for TEA and AMP (15,16). To see how this can be done, first note that AMP is a primary amine whereas TEA is a tertiary amine. Thus, there would be little or no steric effects for AMP but large effects for TEA. Smith and Goulet (15), working with primary amines, make a good case for these molecules having close to 100% neutralization of the acid species. Thus it is to be expected that  $q \sim 1$  for AMP and  $c$  is close to the equivalence ratio of AMP and carboxyl. Likewise, Weiss and Agarwal (16) show that tertiary amines have a significantly lower level of ionic species. Thus  $q < 1$  for TEA, and there will be a significant amount of neutral TEA as well as COOH.

These data allow reasonable comparisons to be made for the  $c$ ,  $q$ , and  $a$  variables for the molecules being investigated here. First consider  $a$ . As noted above, it is readily apparent that the size of the ion will be in the order TEA>AMP>Na. Next consider  $c$ . It is apparent that  $c$  will be the greatest for Na since its bond with a carboxylate group is purely ionic. However, again as already discussed, TEA and AMP can both exist either as the cation or as the neutral species. Consequently, they will each exhibit a somewhat lower effective charge than the Na species. Even so, the considerations in the previous paragraph indicate that  $c_{\text{AMP}} \sim 1$  and  $c_{\text{TEA}} < 1$ . Thus, the relative order for  $c$  is Na  $\sim$  AMP > TEA. Finally consider  $q$ . This quantity can be estimated in a similar manner to  $c$ . Again, Na will be expected to have a value of about 1, but TEA and AMP will be expected to be lower. The expected order will be AMP > TEA since AMP has greater access to the H atom of the COOH moiety, which gives it a higher effective charge. Therefore, the relative order for  $q$  is Na > AMP > TEA.

The results of these arguments can be summarized as shown in Table I. It can be seen that they are sufficient to order the  $cq/a$  parameter and hence the  $T_g$  results for the molecules of interest.

In addition to ionomeric crosslinking, AMP and TEA are low-molecular-weight organic molecules, which can plasticize the polymer and lower  $T_g$ . The same type of arguments used above can be used to establish the relative ordering for plasticization effects. First, note that both size and charge effects are expected to be of importance in determining plasticization. It is expected that a larger size and a smaller charge (i.e., a greater effective amount of neutral species) will produce a greater degree of plasticization. As shown in the table, TEA will have both the greatest amount of neutral species available and also the largest size compared with AMP. Likewise, AMP is larger and less charged than Na. This means that the plasticizing ability is predicted to be in the order TEA > AMP > Na, as is actually seen in Figures 1 and 2 and discussed above. It will be shown below that these same arguments can also be used to understand relative humidity effects.

The overall outcome on polymer cohesion thus depends on the relative levels of ionomer and plasticizer effects caused by the neutralizer. At the two extremes, the sodium

Table I  
Relative Estimates for the Variables of Importance for Determining  $T_g$

Base	$c$	$q$	$a$	$cq/a$
NaOH	High	High	Low	High
AMP	Medium-high	Medium	Medium	Medium
TEA	Low	Low	High	Low

Definitions for each variable are given in the body of the text.

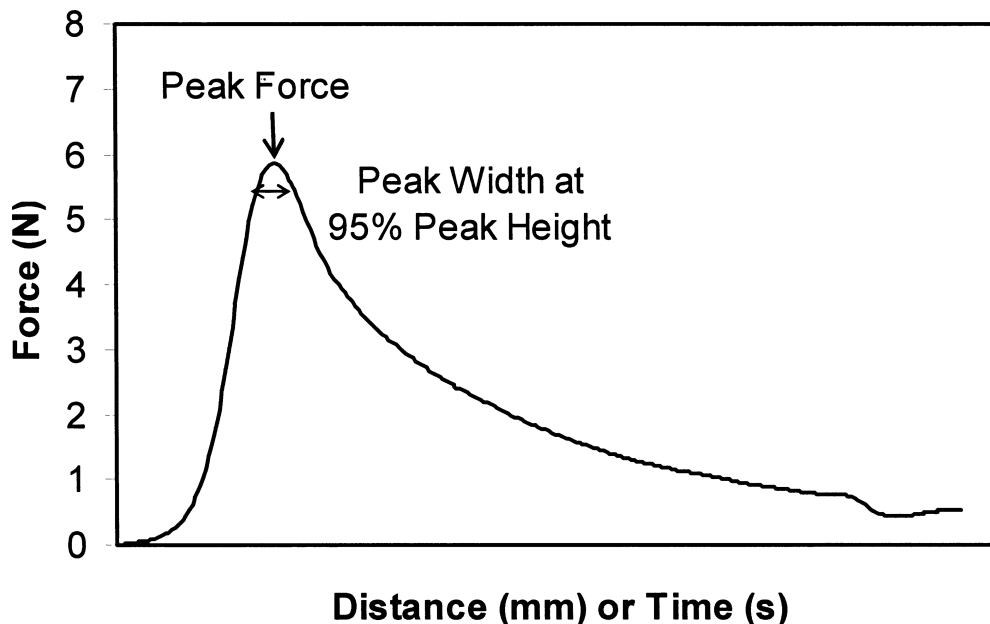


Figure 3. Sample data for the three-point bend stiffness test. Force versus time is measured; stiffness is calculated as the peak force, and crispness is calculated as the width of the peak at 95% of the height.

counterion has the strongest ionomer effect without plasticization, and the TEA counterion has the weakest ionomer effect and causes considerable plasticization. The ionic crosslinking and plasticization effects appear to cancel each other out for AMP, and the  $T_g$  is nearly unchanged from that of the acid form. Therefore, with respect to fixative applications involving acrylic copolymers with acid functional groups, NaOH may be used to make the polymer harder, AMP may be used to maintain the hardness of the acid form of the polymer,<sup>1</sup> and TEA may be used to soften a polymer that has a tendency to crack and flake but may cause an increase in tack (if the  $T_g$  is lowered to below room temperature).

#### PERFORMANCE PROPERTIES

If the composite theory presented here holds, then fixative performance tests should be able to probe the adhesive as well as the cohesive properties of the polymer. Two of the most important fixative performance tests are stiffness and crispness. A three-point bend method developed from a standard test for composite materials (17) was used to measure the stiffness and crispness of fixative composite samples. The data from this test can be plotted as force versus time, as shown in Figure 3. The stiffness of the fixative composite is defined as the force needed to bend or break the hair composite; for this method, stiffness is measured as the peak force of flexure instead of Young's modulus or work. As

<sup>1</sup> The AMP polymer has the same  $T_g$  as the acid form of the polymer under dry nitrogen conditions. At higher humidity conditions, the  $T_g$  may be lower since neutralization of the acid groups increases the hydrophilicity of the polymer.



discussed in the Experimental section, peak force is a good probe of interfacial bond strength (adhesion), while Young's modulus is not. Crispness is how the fixative composite sample breaks; it is related to the sharpness of the peak and it can be measured as the peak width at 95% of the height. The shape of the peak provides information about the break of the hair composite. A relatively sharp peak represents a composite having a crisp break, or snap. On the other hand, a sample that is not crisp will break more gradually, resulting in a broader peak. The work to break (area under the curve) couples stiffness with crispness. Thus, the use of peak force as a measure of stiffness and peak width as a measure of crispness allows these parameters to be evaluated separately. Measurement of crispness is important for correlation with sensory data, as will be discussed below. In this test, the sample is flexed to failure. The mode of failure depends on several factors, including test rate and film thickness, and it can be altered by fixative formulation additives and environmental conditions. The test rate and amount of fixative applied per gram of hair (film thickness) are held constant in this study, but the environmental conditions (relative humidity) are varied.

The stiffness values for polyacrylate-2 crosspolymer versus neutralizer and environmental conditions (50% and 90% relative humidity) are shown in Figure 4. Contrary to the cohesive properties, which show significant differences with neutralizer type (presented in Figures 1 and 2), the stiffness of the fixative-hair composite measured under the conditions of this test are relatively insensitive to neutralizer type. The fact that the low  $T_g$  polymer (neutralized with TEA) yields a stiff hair tress is taken here as strong evidence for the composite nature of fixative gel-treated hair. The basic physical model that is used to explain the phenomena is as follows: the polymer acts primarily to glue the hair fibers together, creating a composite fiber with an effectively larger diameter that is accordingly stiffer. Thus, it is primarily the adhesive properties of the polymer to

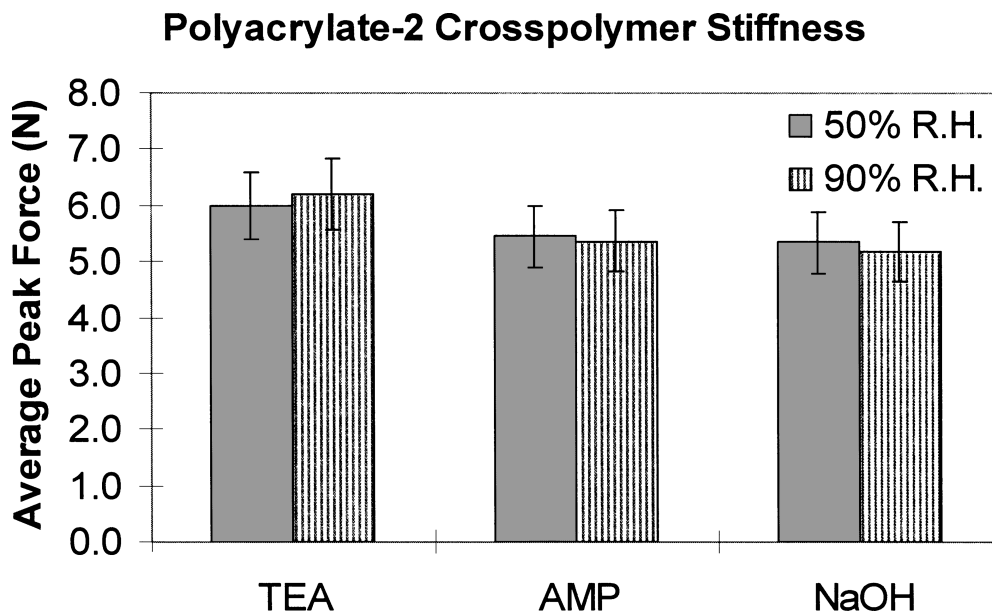


Figure 4. Average stiffness data for polyacrylate-2 crosspolymer versus neutralizing base at 50% RH and 90% RH. The error bars represent  $\pm 1$  standard deviation for the test.



the hair that dominate in this stiffness test. The data also show that the measured stiffness of the composite samples is insensitive to relative humidity. For all three neutralizers, the measured stiffness values at 50% and 90% relative humidity are about the same. However, polymer response can be rate-dependent. The rate used for this test is quite fast, chosen for the purpose of determining crispness, which is a short-time event.

Figure 5 shows that the measured composite crispness is independent of neutralizer type at 50% relative humidity, but at 90% relative humidity the crispness of the samples neutralized with TEA and AMP decreases (as measured by an increase in peak width). As discussed above, the TEA and AMP molecules are in equilibrium with their respective cations in the polymer film. In the presence of moisture, the amines can also enter into a competition with the water molecules for the  $H^+$  ion. This additional equilibrium will tend to produce a greater amount of free molecules available to plasticize the polymer. The order should be  $TEA > AMP > Na$ . It can be seen that this is the approximate order of plasticization shown in Figure 5 at 90% RH. Evaluation of these results with respect to composite theory shows that with the reinforcing properties of the hair fibers and adequate adhesion, relatively stiff hair styles can be achieved even in plasticized systems. However, the decrease in crispness at high humidity suggests that the sensory properties may differ with plasticization. Low  $T_g$  polymers may impart a tacky feel on the hair, especially at high humidity.

Another performance test that is done to evaluate fixative polymers is high-humidity curl retention. In this study, a spiral curl configuration was used instead of the traditional rolled configuration (Figure 6), and so this test will be referred to as high-humidity spiral curl retention (HHSCR). The spiral curl is more challenging and

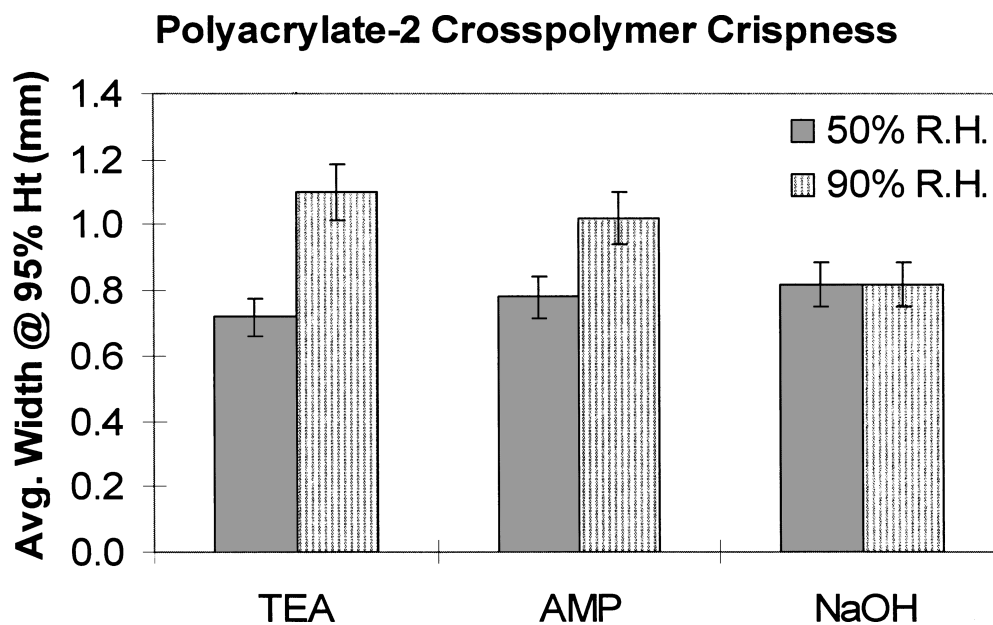
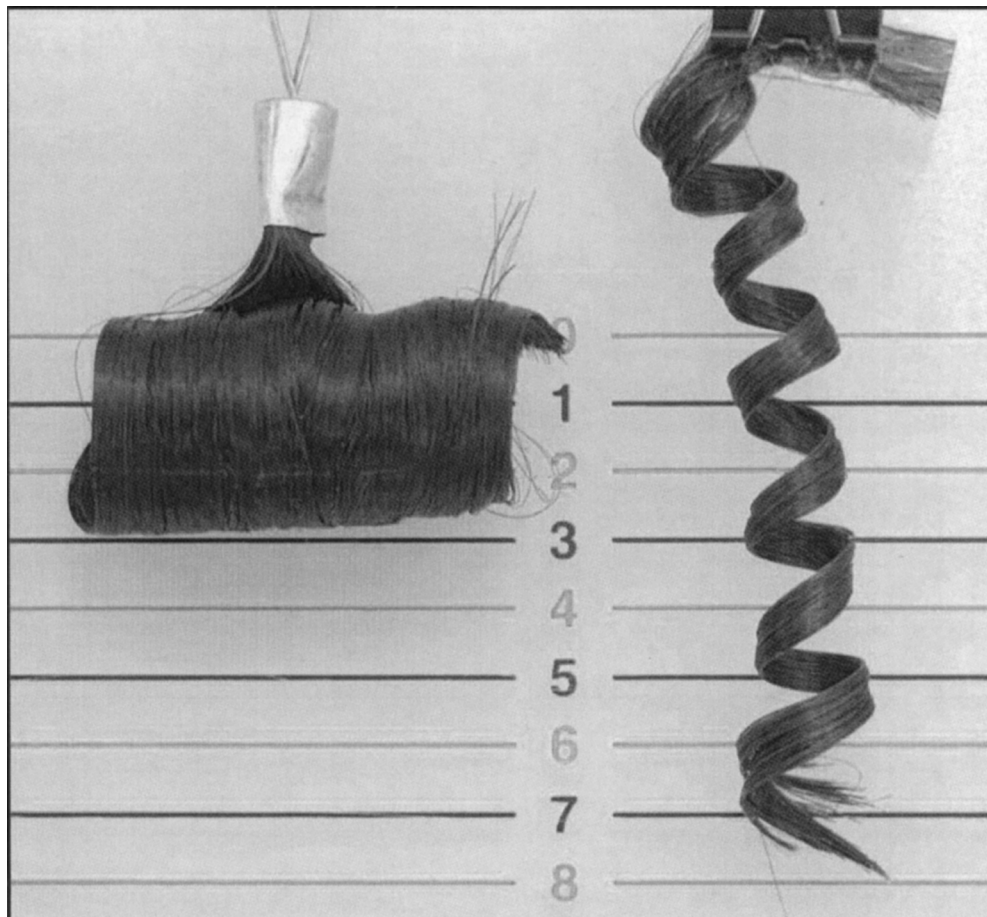


Figure 5. Average crispness data for polyacrylate-2 crosspolymer versus neutralizing base at 50% RH and 90% RH. The error bars represent  $\pm 1$  standard deviation for the test.



**Figure 6.** Curl configuration comparison: traditional curl (left) versus spiral curl (right). The spiral curl was used in this study.

sensitive than a rolled curl because the curl must support its weight without assistance from hair-to-hair adhesion that is present in a rolled curl. As such, the HHSCR test is essentially a polymer composite creep test. The curl is formed with a wet set, where the hydrogen bonds in the hair are broken upon wetting and reformed upon drying while wrapped on the curler (18). Gravity creates a stress on the curled hair tress, which is maintained over a long time frame. The increased moisture level in the high-humidity chamber drives the hair to return to its natural configuration, creating an additional stress on the fixative polymer. Thus, the ability of the fixative to resist these stresses, or resist creep, is measured.

The averaged HHSCR results for composite samples neutralized with AMP, TEA, and NaOH are shown in Figure 7. The retention of the sample neutralized with TEA is the lowest, while the retention of the samples neutralized with AMP and NaOH are not statistically different. The lower retention of the sample neutralized with TEA is attributed to its low  $T_g$  caused by plasticization and humectancy. The low  $T_g$  of this polymer allows long-chain coordinated polymer chain movement at room temperature;

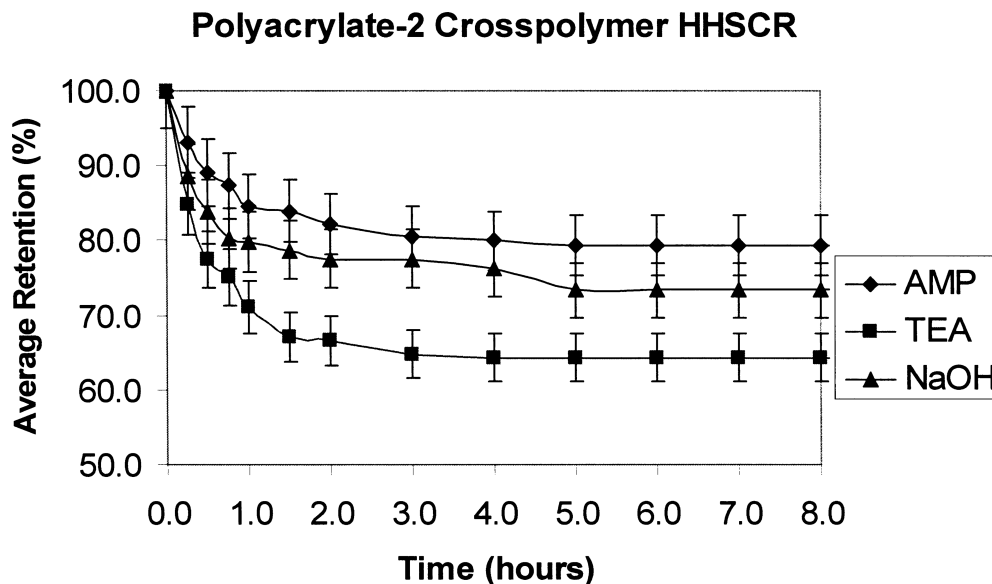


Figure 7. Average high-humidity spiral curl retention (HHSCR) values for polyacrylate-2 crosspolymer versus neutralizing base.

creep is enabled. At high humidity, absorbed moisture further plasticizes the polymer. The improvement in retention for AMP relative to TEA may be explained by recalling the DMA data: the TEA sample is dominated by plasticization, while plasticization for the AMP sample is mitigated by ionic crosslinking. The samples neutralized with NaOH are highly strengthened by ionic crosslinks, which add moisture sensitivity to the polymer. Even so, the retention values are good, even when plasticized by moisture. From a formulation point of view, these results show that when curl retention is critical, AMP or NaOH are better choices for neutralization than TEA. However, the use of humectants with AMP and NaOH are expected to have a negative impact on curl retention.

## CONCLUSIONS

Polymer composite science applied to fixative-treated hair tresses allows better understanding of performance and provides guidance for product formulation. The choice of neutralizer causes significant changes in the cohesive properties of the polymer, but these changes do not necessarily translate to the composite. In the example used in this work, it is shown that NaOH hardens the polymer through ionic crosslinking, as indicated by the suppression of  $T_g$ . AMP and TEA, on the other hand, plasticize the polymer as well as harden it by ionic crosslinking. For AMP, the two effects cancel each other out and have no overall effect on  $T_g$  with respect to the unneutralized polymer. Plasticization is dominant with TEA, with a large decrease in  $T_g$ . The importance of adhesion relative to the cohesive properties of composites is demonstrated by the insensitivity of the measured stiffness to polymer  $T_g$ . However, the difference in crispness for the neutralizers at high humidity suggests that polymer  $T_g$  and neutralizer acid strength have an impact on the sensory properties of the fixative polymer. Furthermore,

significant plasticization of the polymer is shown to affect high-humidity curl retention. This suggests that neutralizers that are good plasticizers and humectants, as well as ingredients typically used for humectant properties, should be avoided in a fixative formulation where good curl retention and low tack are essential.

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