# Effects of Cholesteric Order on Mechanical Properties of (E-CE)C/PAA Composites

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## SYNOPSIS

The ethyl-cyanoethyl cellulose [(E-CE)C]/poly (acrylic acid) [PAA] composites were prepared via *in situ* photopolymerization of the (E-CE)C/acrylic acid (AA) solutions, in which the morphology and structure of (E-CE)C was retained as the same as that in the solution. The strength and the modulus of the composites depended on their morphology and structure. The strength of the composites with a completely amorphous state or with a completely cholesteric order did not significantly change with increasing (E-CE)C content, although the strength of the composites with completely cholesteric order is much higher than with the completely amorphous state. However, when the (E-CE)C content changed from 33.8% to 42.5%, in which the composites had both cholesteric order and amorphous phases, the strength of the composites greatly increased with increasing (E-CE)C. The elastic modulus of the composites with completely isotropic structure decreases with increasing (E-CE)C content but abruptly increases with increasing the fraction of cholesteric phase in the composites. The (E-CE)C with cholesteric order had a significant enhancing effect on the strength of the composites. The stress–strain curves indicated that the composites with completely amorphous or completely cholesteric order were breakable, while they were tough in the case when they had both cholesteric and amorphous phases. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

In the past decade, many studies focusing on the preparation of molecular composites, containing coiled polymers and rigid polymers via *in situ* polymerization have been reported.[1–6] The rod-like polymer/coiled polymer composites with mesomorphic structure can be prepared by polymerizing the vinyl monomer in the rigid polymer/vinyl monomer liquid crystalline solution. Although the preparation, morphology, structure, and optical characteristics of the composites with liquid crystalline structure have been reported, the mechanical properties and the relationship between the mechanical properties and the structure have rarely

been discussed. It is always an attractive subject to use liquid crystalline material to make materials with high strength, or to enhance other polymer materials.[7]

Since cholesteric liquid crystals were observed in the hydroxypropyl cellulose/water system by Werboyj and Gray,[8] it has been found that cellulose and many of its derivatives can form liquid crystals under appropriate conditions, and cellulose derivative/random-coiled polymer composites with cholesteric structure have been obtained by polymerization of vinyl monomer in the cellulose derivative/vinyl monomer solutions.[4–6,9] Because cellulose is an abundant reproducible natural polymer, it is of interest to prepare a cellulose derivative/synthetic polymer composite that has a mesomorphic structure with good mechanical properties.

The formation of the (E-CE)C/acrylic acid (AA) cholesteric liquid crystalline solutions and the free

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radical polymerization of AA in (E-CE)C/AA solutions have been reported.[6,10] The (E-CE)C/polyacrylic acid (PAA) composites with cholesteric structure have been prepared by photopolymerization. In this article, the effects of the cholesteric order on mechanical properties are discussed.

## EXPERIMENTAL

### Raw Materials

The ethyl-cyanoethyl cellulose [(E-CE)C] was obtained by the reaction of ethyl cellulose and acrylonitrile. The degree of substitution for ethyl was 2.1, and for cyanoethyl, was about 0.43. The molecular weight, $M_n$, of (E-CE)C, measured by gel permeation chromatography (GPC) (HPLC, Waters-209), was $7 \times 10^4$. The molecular formula of (E-CE)C is as follows:



R =H, CH₂CH₃, CH₂CH₂CN
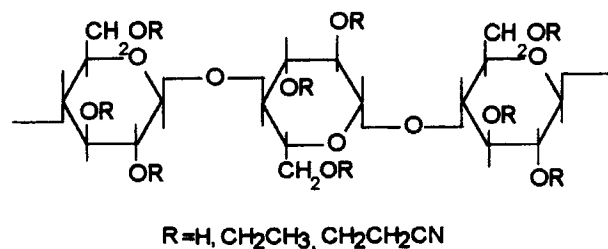
The acrylic acid (AA) was a chemically pure reagent and was distilled in vacuum before using.

### Preparation of the Composites

(E-CE)C/AA solutions for polymerization were prepared in glass vials by weighing the desired amount of (E-CE)C, AA and 2 wt % initiator (with respect to the solvent AA), benzoin ethyl ether, into a vial and mechanically mixing with a spatula for several minutes. The mixtures were allowed to sit for 1 more week, and the resulting homogeneous and transparent solutions were then stored in the dark until used. The solution was put into the mold described in Figure 1, then it was sandwiched with two glass slides. After being stored quietly for 2 h, the sample was inserted into the ultraviolet chamber equipped with a 250 W high-intensity mercury arc lamp until completely polymerized.

### Measurement

The tensile testing of (E-CE)C/PAA composites was conducted with a tensile tester (MONSANTO P-10, USA). The samples were equilibrated in an
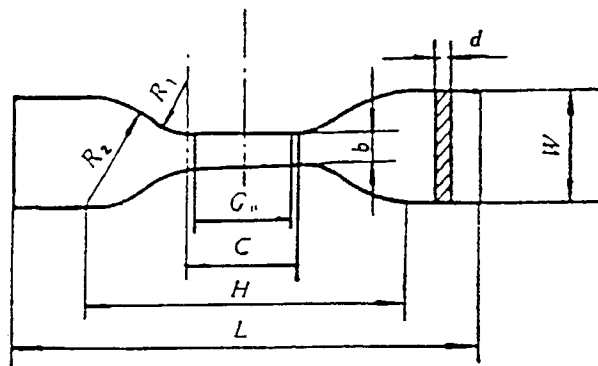


L=110 mm, C=26 ± 0.5 mm, b = 6.5 ± 0.1 mm, w = 25 mm,
G = 25 ± 0.2 mm, H = 76 mm, d = 0.30 mm, R₁= 14, R₂ = 25.

**Figure 1** The specimen mold used for the measurement of mechanical properties of composites.

environment, in which the temperature was 25°C and the relative humidity was 80%, for 48 h before measurement. The stretch speed was 5 mm/min. The broken sections of the composites were observed by using a scanning electron microscope (SEM) (S-430, Hitachi, Japan). The phase structure of the composite sections were observed by a transmission electron microscope (TEM) (JEOL-100CX/II, Japan).

## RESULTS AND DISCUSSION

The mechanical properties of polymer blends are greatly affected by their morphology and structure. (E-CE)C can be dissolved in AA and forms cholesteric liquid crystals when its concentration is over a critical value.[10] The (E-CE)C/PAA composites prepared from the solution by photopolymerization retain the original morphology and structure of solution.[6] Hence, the composites with different (E-CE)C contents have different morphologies and structures, which may influence their mechanical properties. Figure 2 shows the ultimate tensile strength of the photopolymerized (E-CE)C/PAA composites as a function of the (E-CE)C content. According to the (E-CE)C content, the curve can be divided into three parts: (a) when (E-CE)C content is less than about 34%, the ultimate tensile strength is almost unchanged with increasing (E-CE)C content; (b) when the (E-CE)C content is in the region between about 34–42.5%, the ultimate tensile strength abruptly increases with increasing (E-CE)C content. In this narrow region, the tensile ultimate strength increases from 22 MPa to 67 MPa,
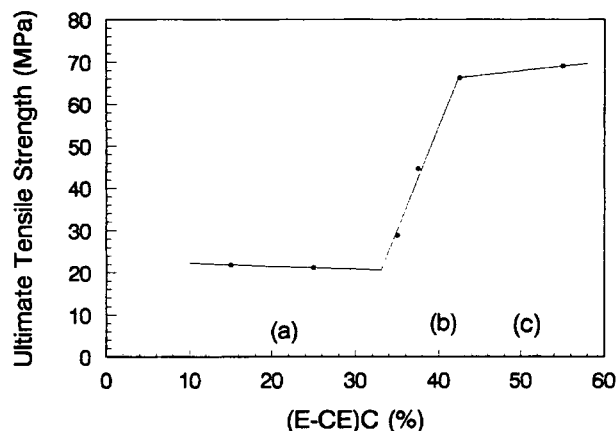
**Figure 2** Ultimate tensile strength as a function of the (E-CE)C content for (E-CE)C/PAA composites.

or about threefold; (c) when the (E-CE)C content is over 42.5%, the ultimate tensile strength increases with increasing (E-CE)C content, but the rate of increase is much lower than that in region (b).

The cholesteric liquid crystalline phase in the (E-CE)C/AA solution begins to appear at the concentration of 33.8 wt %. At this time, the mesophase and the isotropic phase coexist in the solutions that are biphasic. When the (E-CE)C concentration is above 42.5 wt %, the solutions are completely anisotropic. The morphology and structure of the solutions can be retained in the (E-CE)C/PAA composites, which are prepared by photopolymerization with a high rate of polymerization.[6] Hence, the (E-CE)C/PAA composites with (E-CE)C less than 33.8% are isotropic and those with (E-CE)C content between 33.8–42.5% are biphasic. Those with (E-CE)C above 42.5% are completely anisotropic. From the variation of the ultimate tensile strength of (E-
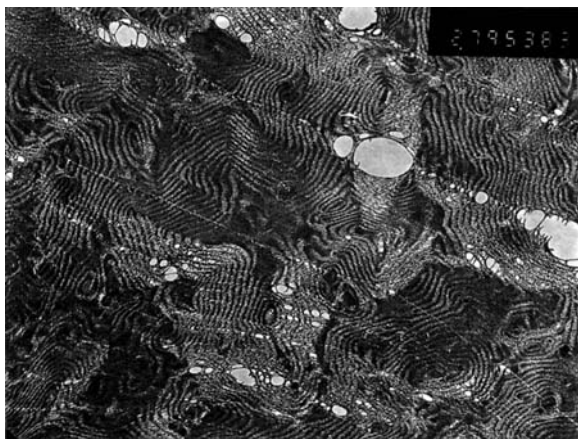


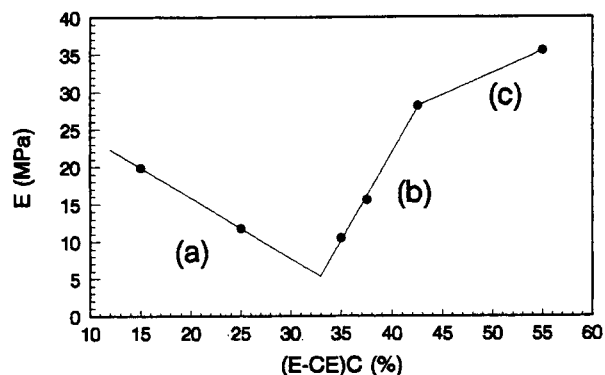**Figure 3** The transmission electron micrograph of the (E-CE)C/PAA composite with 45 wt % (E-CE)C.



**Figure 4** The relationship between the elastic modulus and the (E-CE)C content of (E-CE)C/PAA composites.

CE)C/PAA composites with (E-CE)C content, it can be concluded that the changes in the ultimate tensile strength correspond to the variation of the structure and morphology of the composites. That is, in region (a), the (E-CE)C/PAA composites with (E-CE)C content less than 33.8% are completely amorphous. The (E-CE)C in the composites does not act as an enhancing element and, therefore, the ultimate tensile strength of the composites does not change significantly with an increase in (E-CE)C. In region (b), there exist both the amorphous phase and cholesteric order in the composites. With increasing (E-CE)C content, the ratio of the cholesteric liquid crystalline phase to the amorphous one increases rapidly until the system becomes completely cholesteric at the end of region (b). It is clear that composites with cholesteric order have much higher strength than those with amorphous structure, and the ultimate tensile strength of the composite increases with increasing cholesteric order in composites. Because the ratio of the fraction with cholesteric order to that with amorphous structure increases rapidly with (E-CE)C content in region (b), the ultimate strength rapidly increases with increasing (E-CE)C content in composites. In region (c), the system shows completely cholesteric order. The structure of the composites does not change with increasing (E-CE)C content in region (c). The strength of composites increases very slightly with increasing (E-CE)C. It is suggested that the strength increment of (E-CE)C/PAA composites is attributed to the cholesteric order in the composites.

The elastic moduli of typical composite materials can be calculated from the following two equations[7]:

$$\text{low limit: } E_c = E_1E_2/(E_1V_2 + E_2V_1) \quad (1)$$

$$\text{high limit: } E_c = E_1V_1 + E_2V_2 \quad (2)$$

Where $E_c$ is the modulus of the composites, $V_1$ and $V_2$ are the volume fractions of the two components, $E_1$ and $E_2$ are the moduli of the two components. Equation (1) can be used in the case where the stresses are the same in the two phases when the sample is stretched, such as in a composite with spherular phases. Equation (2) can be used in cases where the strain is the same in the two components, which can often be observed in molecular composites or composites with a fiber phase. Figure 3 shows the transmission electron micrograph of the (E-CE)C/PAA composite with cholesteric structure. The composite shows a lamellar structure extending over the whole specimen. It has been confirmed that lamellation in composites originates from the cholesteric struc-

ture.[6] DSC measurements show that the composites give one $T_g$, which confirms that the (E-CE)C/PAA composites prepared by photopolymerization are homogeneous, and eq. (2) may be adopted for calculation of $E_c$.

Figure 4 presents the variation of the elastic modulus of (E-CE)C/PAA composites with (E-CE)C content. Similar to the variation of the ultimate tensile strength with (E-CE)C content, there are three parts in the curve, and the relationship between elastic modulus and (E-CE)C content is linear in each region. It is clear that both eqs. (1) and (2) cannot describe the variation of the modulus with (E-CE)C content in Figure 4. However, the moduli of the composites in each region can be modeled by eq. (2).
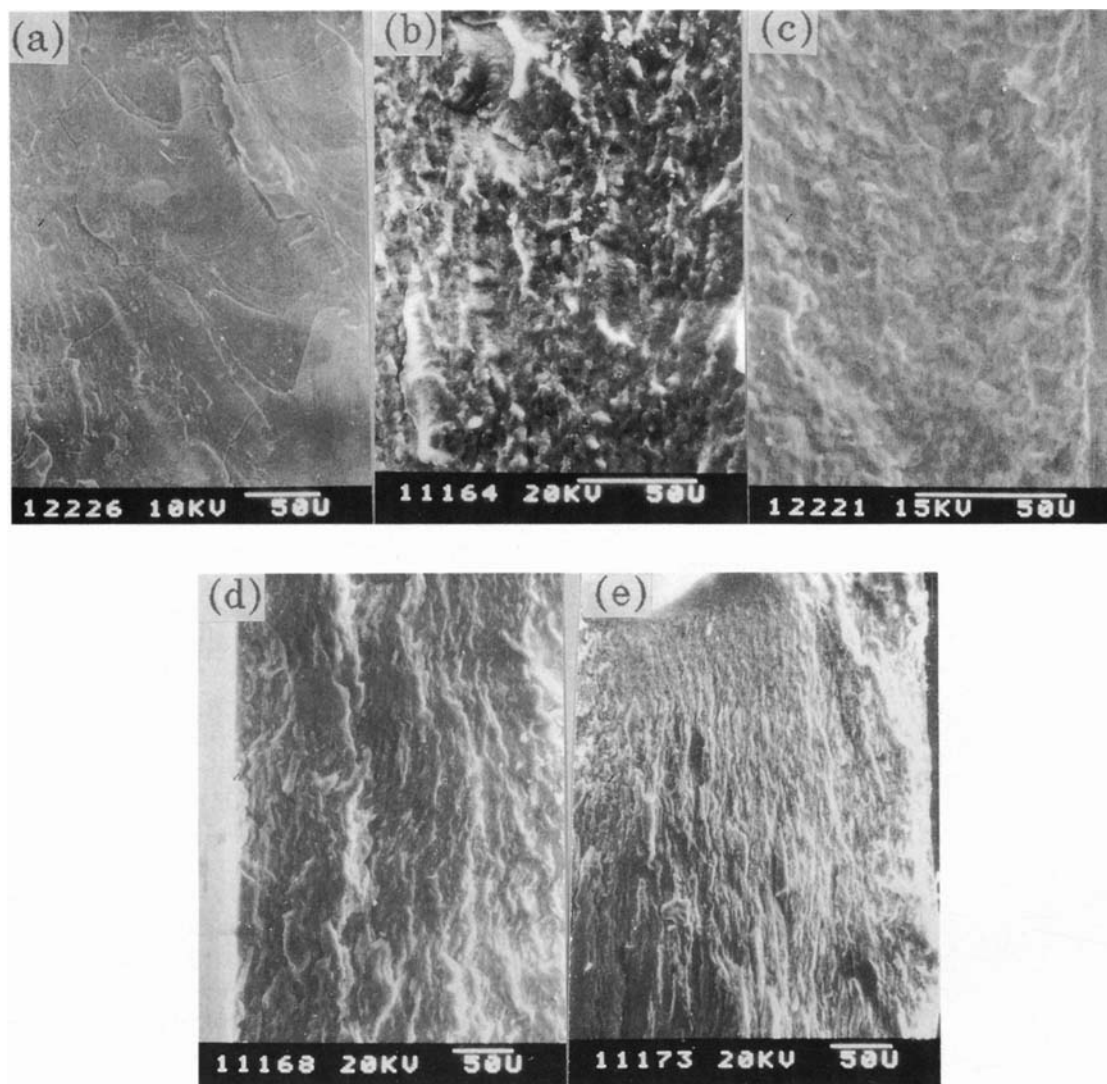


**Figure 5**    Scanning electron micrographs of the broken sections of composites that have been stretched, (E-CE)C content is (a) 15%, (b) 35%, (c) 37.5%, (d) 42.5%, and (e) 55%.
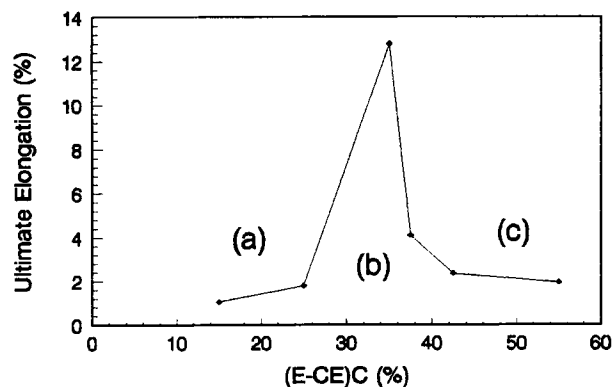
**Figure 6**  The relationship between the ultimate elongation and the (E-CE)C content of (E-CE)C/PAA composites.

In region (a), the elastic modulus decreases with increasing (E-CE)C. In regions (b) and (c), however, it increases with increasing (E-CE)C, although the slope of the straight line in region (c) is smaller than that in region (b). The variation of the elastic modulus with (E-CE)C content suggests that the (E-CE)C with isotropic structure lowers the elastic modulus of the composites. However, the (E-CE)C with cholesteric liquid crystalline order increases the modulus of the composites. This means that the modulus decreases with increasing (E-CE)C in the (E-CE)C/PAA composites with completely isotropic structure, while, when cholesteric order appears in the composites after the (E-CE)C content is more than 33.8%, the modulus of the composites abruptly increases with increasing the fraction of cholesteric order. Consequently, it can be concluded that the increment of the elastic modulus for (E-CE)C/PAA composites is attributed to the cholesteric order in composites. In region (c), there is no isotropic structure in the composites and the increase of the elastic modulus for the composites is slowed.

Figure 5 shows the SEM micrographs of the broken sections of the composites that have been stretched. The lamellar structure, which is parallel to the composite plane, can be observed in the composites with cholesteric structure and cannot be observed in those with amorphous structure. It is clear that the (E-CE)C/PAA composites with this kind of orienting structure have high modulus and ultimate tensile strength.

Figure 6 shows the relationship between the ultimate elongation and the (E-CE)C content of (E-CE)C/PAA composites. PAA is a brittle polymer. When the (E-CE)C content is low, the ultimate elongation increases slightly with the increasing (E-CE)C content, but when the (E-CE)C content is

just over the critical value to form mesophase, the ultimate elongation abruptly increases with increasing (E-CE)C content. This phenomenon cannot be explained only by the increase of the (E-CE)C content, but it can be related to the structural changes of composites. Figure 7 shows the stress–strain curves of the (E-CE)C/PAA composites. The composites with different (E-CE)C content have different tensile properties. In region (a), the (E-CE)C content is low, the composites are brittle. In region (b), both amorphous structure and cholesteric order coexist in the composites; the composites have some toughness, and yield occurs when the composites are stretched. In this region, the composites show larger ultimate elongation. In general, the occurrence of yield is the result of molecular reorientation during deformation. When the composites are stretched, the (E-CE)C with cholesteric order may act as a nucleus to induce orientation of the (E-CE)C with amorphous structure, which leads to increasing the ultimate elongation, and the (E-CE)C/PAA composites become tough. When the (E-CE)C increases continuously, the (E-CE)C with cholesteric order increases, which results in increasing the degree of induced orientation and the composites become tougher with high ultimate elongation. However, when most of the (E-CE)C exists in the cholesteric state, the (E-CE)C that can be oriented becomes smaller and the degree of induced orientation is low for such composites. Therefore, the toughness of the composites decreases. Figure 6 shows that the composites have maximum ultimate elongation when the (E-CE)C content is about 35% in region (b), and Figure 7 shows that the composites are tough when the (E-CE)C content is located in region (b). When the amorphous structure in (E-CE)C/PAA composites completely disappears, the
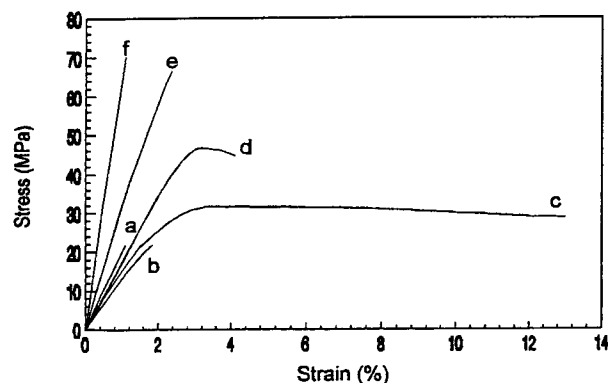


**Figure 7**  The stress–strain curves of the composites, the (E-CE)C content is: (a) 15, (b) 25, (c) 35, (d) 37.5, (e) 42.5, (f) 55.

ultimate elongation decreases slightly with increasing (E-CE)C content and the composites are brittle when the (E-CE)C content is located in region (c).

## CONCLUSIONS

The mechanical properties of (E-CE)C/PAA composites are mainly influenced by their structure. When the (E-CE)C content changes from 33% to 42.5%, the structure in the composites changes from the amorphous state to the cholesteric and the ultimate tensile strength of the composites increases from 22 MPa to 67 MPa. When the (E-CE)C content is less than 33%, the (E-CE)C/PAA composites are a completely isotropic system. When the (E-CE)C content is above 42.5 wt %, the (E-CE)C/PAA composites are systems with completely cholesteric liquid crystalline order and the variation of the (E-CE)C content has no significant influence on the composite strength. The elastic modulus of the composites with completely isotropic structure decreases with increasing (E-CE)C content but increases abruptly with increasing fraction of the cholesteric order in the composites. The (E-CE)C/PAA composites with both amorphous structure and cholesteric order are tough, and yield occurs when they are stretched. The ultimate elongation of the composites is at a maximum with 35% (E-CE)C. The composites with completely amorphous structure or completely cholesteric order are brittle.

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