

Blended Graft Copolymer of Carboxymethyl Cellulose and Poly(vinyl alcohol) with Banana Fiber

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ABSTRACT: Conducting hydrogel copolymer was prepared by graft copolymerization of carboxymethyl cellulose (CMC) and boric acid onto poly(vinyl alcohol) (PVA). The dielectric properties of CMC-g-PVA/prehydrolyzed banana blend have been investigated as a function of frequency, with special reference to pure prehydrolyzed banana. Also, the static bending for the blend was determined and no abrupt failure was observed. The dielectric properties measured were dielectric constant (ϵ'), dissipation factor ($\tan \delta$), and loss factor (ϵ''). At high frequencies, a transition in the relaxation behavior was observed, whereby the dielectric constant, loss tangent, and loss factor decreased with frequency. Experimental ϵ' values of the blend are greater than those of prehydrolyzed banana. The dielectric behavior de-

pends greatly on the nature of the present group, the crystallinity of the system, and the degree of hydrogen bonding between the different chains. The variation of the dielectric properties was correlated with blend morphology and also to the possibility for interfacial polarization that arises because of the differences in conductivities of the two phases. It was found from the infrared spectra that the incorporation of CMC-g-PVA copolymer decreases the crystallinity of the blend and also decreases the degree of hydrogen bonding, which results in a high dielectric constant. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1842–1848, 2006

Key words: graft copolymer; blend; dielectric properties

INTRODUCTION

In the past 20 years, a considerable amount of research has been focused on polymer hydrogels that can undergo volume transitions in response to external physical or chemical stimuli such as pH,^{1,2} pressure,^{3,4} ionic strength,^{5,6} electric field,⁶ and temperature.⁷ These materials have been studied extensively because of their applications in various technologies.^{8–12} There has been a tremendous growth in polymer matrix composites containing fibers. These composites provide a unique combination of properties (including high specific strengths and moduli) and therefore substitute other conventional materials.¹³

During the last few decades, thermoplastic elastomers (TPEs) have replaced usual thermoset rubbers in many areas like the automotive and electrical sector.¹⁴ By blending suitably selected plastics with elastomers, materials with desirable final properties can be prepared. However, in recent times, natural fibers are threatened by plastics. In addition, natural fibers have attracted the attention of scientists because of their easy availability, renewable resource, low price, and low density leading to high specific strength.¹³

Natural fibers, particularly banana plant fibers, do not appear much in the list of applications, because their use in reinforcement is minimal, compared with the consumption of glass and synthetic fibers. Thus, there is a need to develop new uses for these fibers. Electrical properties of various polymer blends have been investigated by different researchers.^{15–21} In their publications, it has been shown that the dielectric properties of polymers and blends in general depend on the structure, crystallinity, morphology, and the presence of fillers or other additives. The dielectric constant of the blends is found to increase with an increase in the effective dipole moment. In the present article, carboxymethyl cellulose-*graft*-poly(vinyl alcohol) copolymer (CMC-g-PVA), in presence of boric acid, was prepared, and dielectric constant, dissipation factor, and loss factor for CMC-g-PVA/prehydrolyzed banana blend were investigated. Boric acid was used in graft copolymerization for its use in electrical condensers.²² Additional measurements of infrared spectroscopy have been carried out.

EXPERIMENTAL

Carboxymethyl cellulose-*graft*-poly(vinyl alcohol), in presence of boric acid, was prepared. First, 0.5 g PVA (SD Fine-Chem Ltd., Mumbai, India) was dissolved in 20 mL of dimethyl sulfoxide (DMSO) (BDH, UK), and then 0.5 g sodium carboxymethyl cellulose (CMCNa)

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(Fluka, Buchs, Switzerland), boric acid, and potassium persulphate-sodium bisulphate initiator (SD Fine-Chem Ltd.) were dissolved in the DMSO solution. After nitrogen was introduced into the DMSO solution for 1 h, where CMCNa and PVA were physically crosslinked, the reaction was continued at 40°C for 3 h with shaking. After the desired period, the mixture was poured into excess of acetone. The hydrogel copolymer membrane was prepared by pouring the copolymer solution into a flat laboratory dish, and by allowing the solvent to evaporate. The membrane was removed from the dish and stored for further experiment.

Banana pseudostem was used specifically as a source of the natural fiber. Prehydrolyzed banana pulp was prepared from banana pseudostem on an electrically heated rotary autoclave with water. Water to fiber ratio was 6 : 1, and time for hydrolysis at 100°C was 2 h. Prehydrolyzed banana were then granulated using a Retsch GmbH 5657 HAAN (West Germany) having a 3-mm screen. Blend of CMC-g-PVA/prehydrolyzed banana was prepared by mixing CMC-g-PVA (based on dry weight of prehydrolyzed banana) with the calculated quantity of the prehydrolyzed banana, using Paul Weber Maschinen-u. Apparatebau, at a temperature of 160°C for 10 min. The binary blend was denoted CP₃₀, after preliminary experiments, where the subscript indicate the weight percentage of CMC-g-PVA in the blend.

Static bending [modulus of rupture (MOR) and modulus of elasticity (MOE)] for the blend CP₃₀ was determined according to ASTM D790–90.²³ For testing flexural properties, a three-point loading system was used, and the span-to-depth ratio was found to be 16 : 1. The sample was conditioned at 30% relative humidity before mechanical testing. Five specimens were tested and the results averaged.

The samples for electrical property measurements were prepared by compression molding the samples into 2.8-mm-thick sheets in a hydraulic press at room temperature. The dielectric constant (ϵ') and dielectric loss (ϵ'') of the blend were measured at frequencies ranging from 1 kHz to 5 MHz at room temperature, using a 3532 LCR HiTESTER. The dissipation factor $\tan \delta$ was obtained from ϵ' and ϵ'' using

$$\epsilon'' = \epsilon' \tan \delta$$

The degree of crystallinity and hydrogen bonding of the blend CP₃₀ and prehydrolyzed banana were determined by IR spectra. The fourier transform infrared (FTIR) spectroscopy of CP₃₀ blend and prehydrolyzed banana was performed using a Bruker Vector 22 instrument.

RESULTS AND DISCUSSION

The IR spectra of CMC graft copolymer of PVA (Fig. 1(a)) showed absorption bands at 3418, 2364, 1652, and 1121 cm^{-1} , characteristic of CMC,²⁴ and additional bands at 3004, 1022–953 cm^{-1} ($=\text{C}-\text{H}$ stretch and out-of-plane), and 1435–1409 cm^{-1} (CH_2 stretch) that belong to the spectrum of PVA.

In prehydrolyzed banana [Fig. 1(b)] the peak in the area of 3420 cm^{-1} is due to hydrogen-bonded $\text{O}-\text{H}$ stretching vibration. The peak at 2921 cm^{-1} is due to the $\text{C}-\text{H}$ stretching vibration in cellulose and hemicellulose. Kolboe and Ellefsen²⁵ suggested that the bands in the 1632 cm^{-1} region for cellulose may be attributed to $\text{C}=\text{O}$ stretching vibration of the α -keto carbonyl. The bands from 1457 to 1321 cm^{-1} are associated with CH in the plane deformation of CH_2 groups. The bands in the region 1250–1056 cm^{-1} involve the $\text{C}=\text{O}$ stretching vibrations of aliphatic primary and secondary alcohols in cellulose, hemicellulose, lignin, and extractives.^{25–27} The peak at 897 cm^{-1} is due to β -glucosidic linkage,^{28,29} while peaks at 666 and 614 cm^{-1} are due to out-of-plane bending vibration of intermolecular $\text{H}-\text{bonded}$ $\text{O}-\text{H}$ group and out-of-plane $\text{O}-\text{H}$ bending.^{28–31} The other peak at 520 cm^{-1} is due to torsional vibration of pyranose ring.^{28–31}

In comparison to prehydrolyzed banana [Fig. 1(b)], CMC-g-PVA/prehydrolyzed banana blend [Fig. 1(c)] showed new absorption bands at 2854 and 953 cm^{-1} ($=\text{C}-\text{H}$ stretch and out-of-plane) and 1107 cm^{-1} (characteristic of CMC) that belong to the spectrum of CMC-g-PVA copolymer. The presence of these bands is attributed to the dispersion of the graft copolymer in the prehydrolyzed banana fiber matrix.

With respect to the fracture event of bending test, the failure mode of neat CMC-g-PVA and CMC-g-PVA/prehydrolyzed banana blend shows no abrupt failure, as sketched in Figure 2(a), which means that the blend shows elastic properties during the time of the bending test, as can be seen from Figure 2(b), and its MOE was 253.0 MPa.

The dielectric constant and loss tangent are important parameters in the selection of an insulating or conducting material. The variation in dielectric constants of pure prehydrolyzed banana and the blend of CMC-g-PVA/prehydrolyzed banana (CP₃₀) as a function of frequency is shown in Figure 3. The dielectric constant values of pure prehydrolyzed banana and the blend CP₃₀ were decreased with increase in frequency. Generally, the dielectric constant of a material arises because of polarization of molecules, and the dielectric constant increases with increase in polarizability. The different types of polarizations possible in a material are the polarizations arising from (1) electronic polarization, (2) atomic polarization, and (3) orientation polarization due to the orientation of dipoles parallel

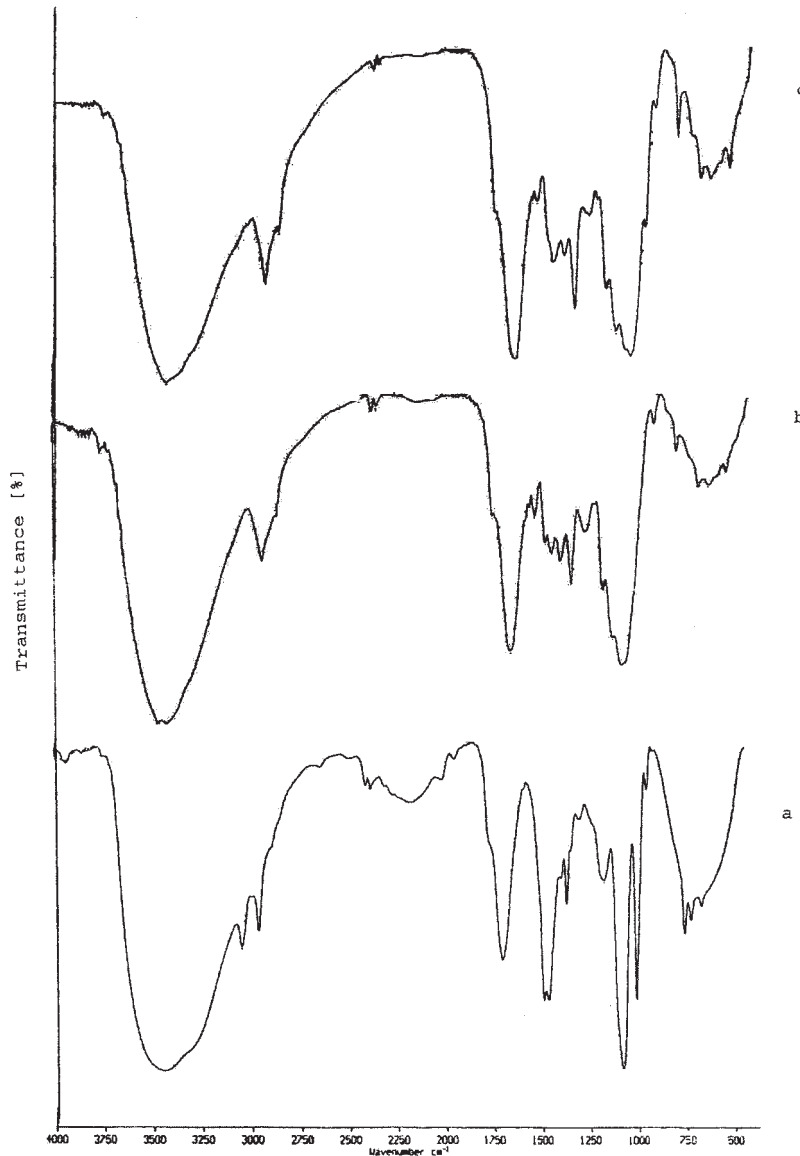


Figure 1 FTIR spectra of (a) CMC-g-PVA, (b) prehydrolyzed banana, and (c) CMC-g-PVA/prehydrolyzed banana blend.

to the applied field.³² For heterogeneous materials, there is also the possibility for interfacial polarization that arises because of the differences in conductivities of the two phases.³³

The time required for each type of polarization to reach the equilibrium level varies with the nature of the polarization. The orientation polarization requires much more time, compared with electronic and atomic polarization, to reach static field value.¹⁴ Therefore, the orientation polarization decreases with increase in frequency, at a lower frequency region, compared with electronic and atomic polarization.¹⁴ Interfacial polarization generally occurs at still lower frequencies.¹⁴ In the dielectric constant vs. frequency plot of CMC-g-PVA/prehydrolyzed banana blend, it is seen that the reduction in ϵ' occurs in three stages. In the first stage, the high values of dielectric constant

can be attributed to the interfacial polarization effects. In the case of blend, because of the presence of two phases of prehydrolyzed banana and CMC-g-PVA copolymer with different conductivities, interfacial polarization occurs leading to an increase in dielectric constant. Because interfacial polarization decreases with an increase in frequency, as the frequency increases to 3×10^4 Hz, the dielectric constant decreases considerably. In the region $6\text{--}300 \times 10^4$ Hz frequency, the dielectric constant has contribution from orientation and atomic and electronic polarization. Above 300×10^4 Hz frequency, the ϵ' further reduces, which may be due to the drop in orientation polarization.

Banana plant is a natural fiber composed mainly of cellulose, hemicellulose, and lignin. The dielectric properties of cellulose depend on the free OH groups, and hence the dielectric constant of cellulose can be

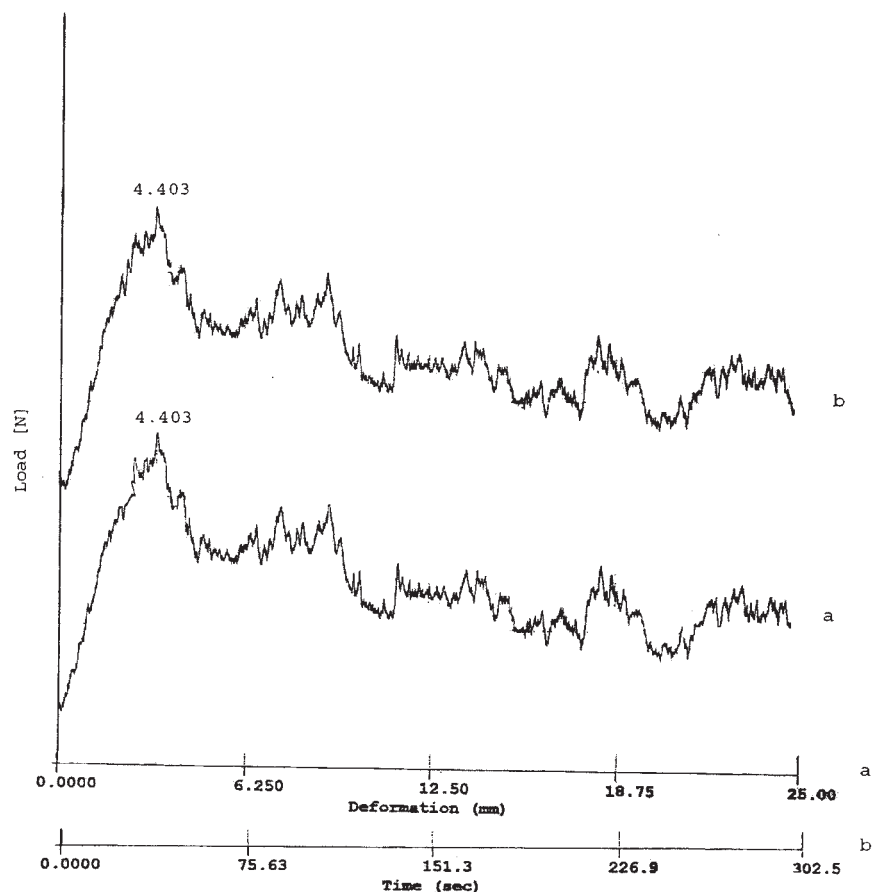


Figure 2 Schematic of the load vs. (a) deformation curve and (b) time curve displaying (a) that there is no abrupt failure observed for the CMC-g-PVA/prehydrolyzed banana blend in bending test and (b) the elasticity observed for the blend in the same test.

explained by assuming that the dielectric constant is of two component system: the ordered and the disordered fraction. The latter fraction contains the accessible OH groups responsible for the dielectric behavior.³⁴ It was pointed out by many investigators^{35–37} that a decrease in crystallinity is accompanied by an increase in the dielectric constant. This is because a decrease in the degree of crystallinity or an extension and formation of disordered regions in the crystalline cellulose results in an increased freedom of movement of the OH groups and portions of the cellulose molecules.³⁴ IR spectra have been used to determine the degree of crystallinity and crystalline modification of pure celluloses.^{37–40} The intensity of certain bands in IR spectra have been found to be sensitive to variations in cellulose crystallinity or crystalline form. Such variation may be determined using the ratio of a band that is affected by cellulose crystallinity to that of a band that is comparatively insensitive to crystallinity changes. The ratio of the absorbency of the peaks at 1372 cm^{-1} to those at 2900 cm^{-1} (A_{1372}/A_{2900})^{38,39} have been used to measure the relative cellulose crystallinity.

Table I shows the crystallinity index (CrI) of prehydrolyzed banana and CMC-g-PVA/prehydrolyzed

banana blend calculated using the aforementioned measures. As shown in the table, there is a decrease in the CrI of the blend sample. This should mean that the dielectric constant of the blend will be higher than that for the prehydrolyzed banana. Moreover, the increase in ϵ' with the incorporation of CMC-g-PVA copolymer is due to an increase in dipoles, which increase the orientation polarization, and also due to the presence of interfacial polarization. Again, the orientation of dipoles depends on the crystallinity of the medium. Upon the introduction of CMC-g-PVA copolymer, the crystallinity of the system decreases (Table I). As the crystallinity decreases, the dipoles can orient more easily. This is because in the disordered regions the dipoles or molecular polarization is influenced by the proximity and configuration of adjacent molecules; consequently, a decrease in crystallinity results in a greater chance for the disordered chain to achieve random disorder and, therefore, a higher dielectric constant results. Such an increase in dielectric constant on incorporation of polar polymers was reported.⁴¹ On the other hand, an increase in the degree of hydrogen bonding between the chains or a blocking of the free OH groups by a substituent group of less

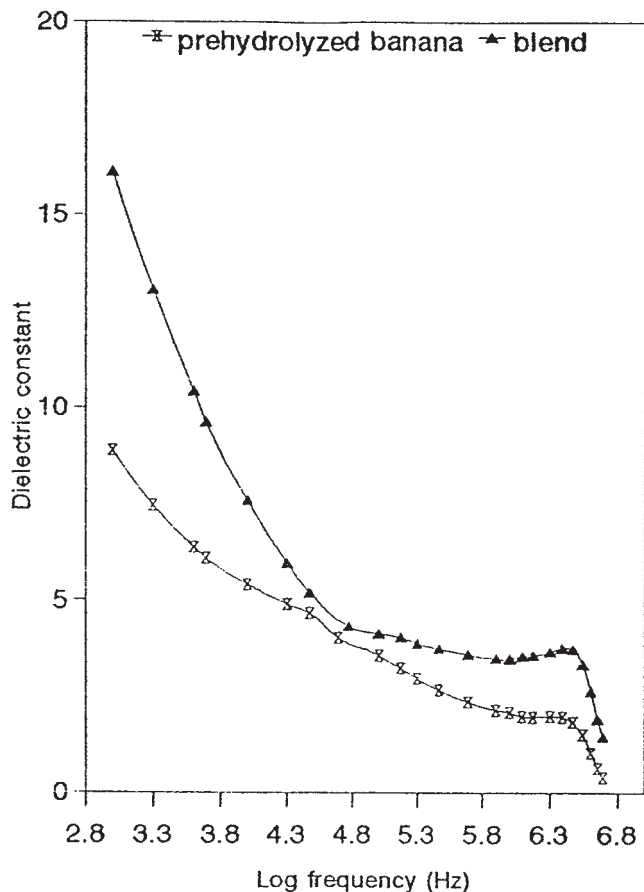


Figure 3 Variation of dielectric constant of CMC-g-PVA/prehydrolyzed banana blend with frequency.

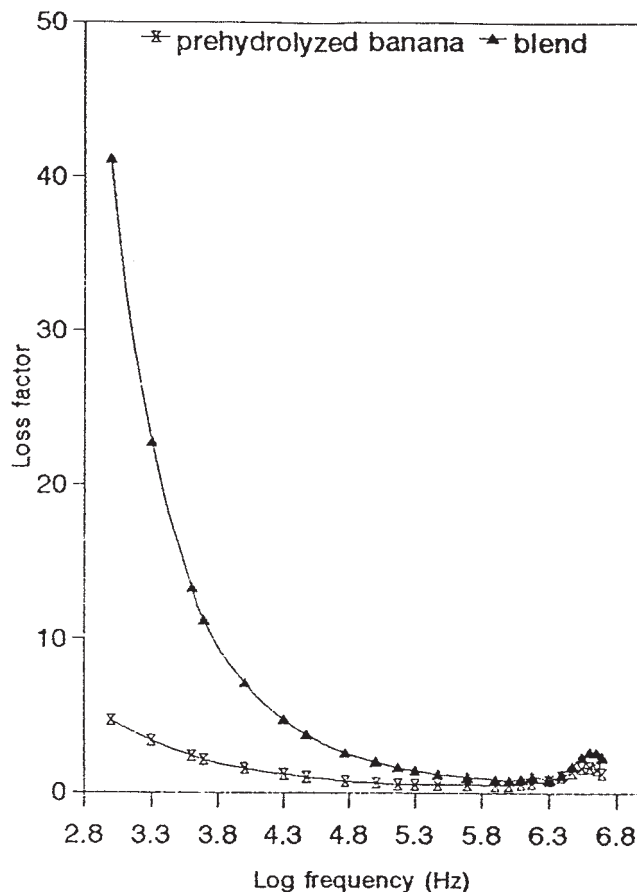


Figure 4 Variation of loss factor ϵ'' of CMC-g-PVA/prehydrolyzed banana blend with frequency.

polar character would hinder the absorption and, therefore, a decrease in ϵ' occurs.³⁴

In view of the above explanation, the higher dielectric constant obtained with the blend compared with prehydrolyzed banana may indicate a decrease or a weakening of the degree of hydrogen bonding between different chains. For cellulosic substances, the group responsible for the hydrogen bonding is the OH group. Several infrared investigations have been carried out on this subject.^{37,42-44} The spectra of the prehydrolyzed banana and the blend [Fig. 1(b,c)] showed that the band of the OH stretching vibration occurs at 3420 and 3419 cm^{-1} , respectively. When a hydrogen bond is formed between a hydroxyl group and a neighboring oxygen atom, the bond length of the OH increases and the force constant decreases.³⁴ In case of

the blend, the highest dielectric constant obtained would be expected. That is to say, blending CMC-g-PVA copolymer to prehydrolyzed banana leads to a decrease in the bond length of the hydrogen bonded region, which results in a weakening of the degree of hydrogen bonding. Thus, the polarization of the blend increases resulting in a higher dielectric constant than that of prehydrolyzed banana.

The measurement of dissipation factor ($\tan \delta$) and loss factor (ϵ'') is important because the loss tangent is a measure of the alternating current electrical energy that is converted to heat. This heat raises the temperature and accelerates deterioration.¹⁴ The variation of loss factor and dissipation factor with frequency of prehydrolyzed banana and CMC-g-PVA/prehydrolyzed banana blend are shown in Figures 4 and 5. Frequency decreases the dissipation factor and the loss factor for both prehydrolyzed banana and the blend. A relaxation region is observed in the frequency of 2×10^6 Hz, which may be due to a lag in dipole orientation behind the alternating electric field. In case of the blend, during the incorporation of CMC-g-PVA copolymer, dipoles are introduced into the system and this leads to a lag in orientation of dipoles on the application of the electric field.

TABLE I
Effect of Incorporation of CMC-g-PVA Copolymer on CrI

Sample	CrI A_{1372}/A_{2900}
Prehydrolyzed banana	0.5
CMC-g-PVA/prehydrolyzed banana blend	0.294

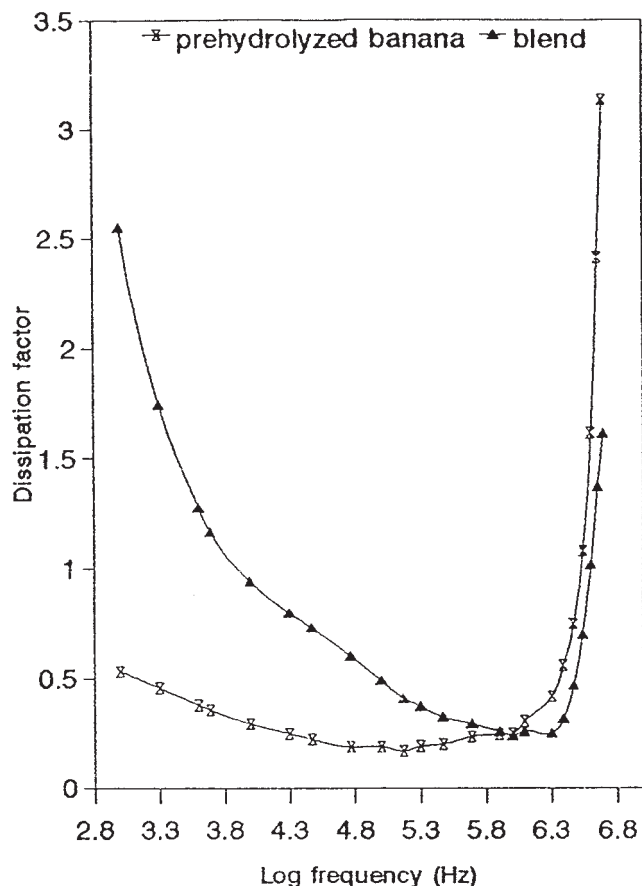


Figure 5 Variation of dissipation factor $\tan \delta$ of CMC-g-PVA/prehydrolyzed banana blend with frequency.

In polar polymer, it was reported that the increase in crystallinity reduces the $\tan \delta$ values and also leads to an increase in relaxation time (i.e., their peaks corresponding to α and β relaxation process shifted to lower frequency).¹⁴ In CP₃₀, the incorporation of CMC-g-PVA copolymer decreases the crystallinity of the blend. Hence, the observed shift in relaxation frequency (to higher frequency) or reduction in relaxation time is due to the reduction in crystallinity. As the crystallinity of the system decreases, the rotatory motion of the dipoles becomes more easy, which leads to higher values of $\tan \delta$.

CONCLUSIONS

CMC-g-PVA copolymer was prepared physically by graft copolymerization of CMC and boric acid onto PVA in DMSO. The graft copolymer CMC-g-PVA showed elastic properties as well as electrical properties when used in blend with prehydrolyzed banana. The dielectric properties of CMC-g-PVA/prehydrolyzed banana were investigated over a wide range of frequencies. The dielectric constant of both prehydrolyzed banana and the blend decreases with an increase

in frequency. Variation in dielectric constant for the blend is in three stages because of the relaxation in interfacial and orientation polarization. Upon the incorporation of CMC-g-PVA copolymer, the dielectric constant showed high values compared with pure prehydrolyzed banana. The increase in ϵ' with the incorporation of CMC-g-PVA copolymer is due to an increase in dipoles, which increase the orientation polarization, and also due to the presence of interfacial polarization. The orientation of dipoles depends on the crystallinity of the system. The introduction of CMC-g-PVA copolymer decreases the crystallinity of the blend and hence the dipoles can orient more easily. Also, the incorporation of CMC-g-PVA copolymer leads to a decrease in the degree of the hydrogen bonding in the blend, and thus the polarization of the blend increases resulting in a high dielectric constant. The dissipation factor and loss factor values also increased in the blend depending on the crystallinity of the system.

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