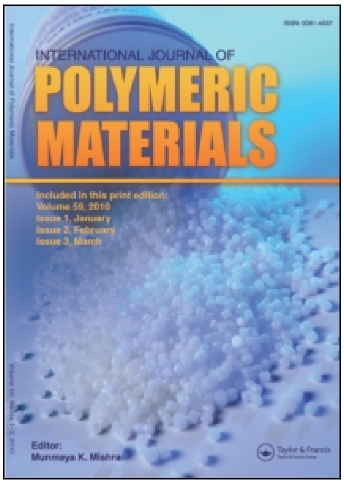

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Dynamic Mechanical Analysis of PMMA-Cellulose Blends

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Dynamic mechanical analysis (1–30 Hz, 274–414 K) is employed to study the inter- and intramolecular dynamics in a set of PMMA-CELL blends. Two relaxation processes are observed, the dynamic glass transition (α-relaxation) being characterized by WLF law and secondary transition (β-relaxation). The α-relaxation is strongly influenced by the composition of the blends and shows a rapid slowing down with increasing cellulose (CELL) intake. Increasing the content of the latter reduces the strength of the β-relaxation strongly and increases its activation energy by more than 60%. This proves that owing to the interactions between the cellulose hydroxyl group and PMMA ester group, the β-relaxation no longer has a local character only. By fitting the T_g data for the blends to T_g-composition models proposed by Gordon and Taylor and by Jenckel and Heusch, it is shown that the strength of the interaction increases strongly beyond 72% of CELL intake.

Keywords cellulose, curve fitting, dynamic mechanical analysis, glass transition temperature, mechanical relaxation parameters, poly(methylmethacrylate)

INTRODUCTION

During the past three decades, intense interest has been focused on polymer blends in which both components are synthetic polymers [1–3]. In contrast, few studies [4–6] have been made on blends in which one component is cellulose. Nevertheless, cellulose/synthetic polymer blends are attractive and important not only because of potential applications but more especially as models for the investigation of blends containing polymers with functional

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groups that can engage in strong intermolecular interaction such as hydrogen bonding.

Many studies have focused on the secondary relaxation of polymers [7–9]. Part of the impetus was to establish a relationship between these secondary relaxations and mechanical properties. In the case of PMMA, Heijboer [1,10] believed that the secondary relaxation was associated with the rotation of the methoxy-carbonyl side group about the bond linking the group to the main chain. When the rotation of the side group was restricted by systematically attaching bulkier and stiffer groups, the secondary loss peak was depressed [11]. Heijboer had strong evidence that the side group contributes to the secondary relaxation in PMMA but the extent to which the main chain participates in the side chain was speculative.

In this paper, we are interested in determining the changes in molecular motion that result directly from the variation in environment with respect to hydrogen bonding.

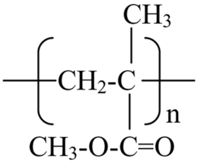
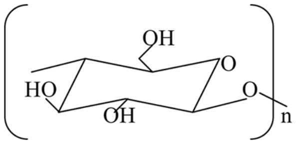
EXPERIMENTAL

Materials

The cellulose sample was solidified cell sap from eucalyptus (blue gum) with a degree of polymerization of 850. PMMA (molecular weight 78,000), dimethyl sulfoxide (DMSO) and paraformaldehyde were purchased from Aldrich Chemical Co. (New York, USA).

The chemical structures of PMMA and cellulose used in this investigation and their thermal properties are given in Table 1.

Table 1: Structures of PMMA and cellulose units and glass transition temperatures (T_g).

Polymer	**Repeat unit**	**T_g (K)**
PMMA	 $\left[CH_2\text{-}\overset{CH_3}{\underset{CH_3\text{-}O\text{-}C=O}{C}} \right]_n$	330.6
Cellulose		525

Preparation of Samples

Cellulose was stirred in the presence of paraformaldehyde in DMSO at 65–70°C whereas PMMA was stirred in the presence of paraformaldehyde in DMSO at room temperature. The cellulose and PMMA solutions were mixed in appropriate ratios (PMMA:CELL denoted as P:C) to produce blends with composition ranging 100:0 to 23:77. The cast films were dried at 125°C in vacuo for 24 h. The resulting films were 0.25 mm thick.

Dynamic Mechanical Experiment

The films were cut giving rectangular strips of 8 mm width and 20 mm gage length. The DMS tests were performed using a DMA 2890 TA Instruments in tensile mode. An oscillating amplitude of 2 μm static force of 0.5 N and a sampling rate of 2 sec per point were applied at frequencies of 1, 10, 20, and 30 Hz. The specimens were run in an iso-step mode from 0 to 141°C in 2°C intervals.

To describe the mechanical spectra quantitatively, a superposition of model function [12] was used:

$$E(T) = \sum_{i=1}^{2} A_i \exp\left\{-\frac{W_i}{kT} - \frac{T^2}{T_{m_i}^2}\exp\left[\frac{W_i}{k}\left(\frac{1}{T_{m_i}} - \frac{1}{T}\right)\right]\right\} \tag{1}$$

In this model function, A is a constant, W is the activation energy and *i* refers to different processes which contribute to the mechanical response.

RESULTS AND DISCUSSION

α-Relaxation

Figure 1 shows isochronal plots of the storage and loss modulus of the relaxation peaks in PMMA and PMMA-CELL blends at 20 Hz. Two relaxation processes can be distinguished. The high-temperature peak is the α-relaxation which is assigned to the main chain motion (the low temperature peak will be discussed in the next section). It is shifted to higher temperature with increasing CELL content. It should be noted that in going from PMMA to PMMA-CELL the mole fraction of the hydroxyl groups increases. Also, due to the hydrogen bonding between the hydroxyl groups, steric hindrance to chain motion is possible which may slow the relaxation frequency. The shift is stronger at CELL intakes above 72%.

The temperature dependence of mean relaxation times (Figure 2) for the α-relaxation for all samples investigated follows WLF law [13]

$$\ln\left(\frac{\tau}{\tau_{Tg}}\right) = \frac{C_1(T - T_g)}{C_2 + T - T_g} \tag{2}$$

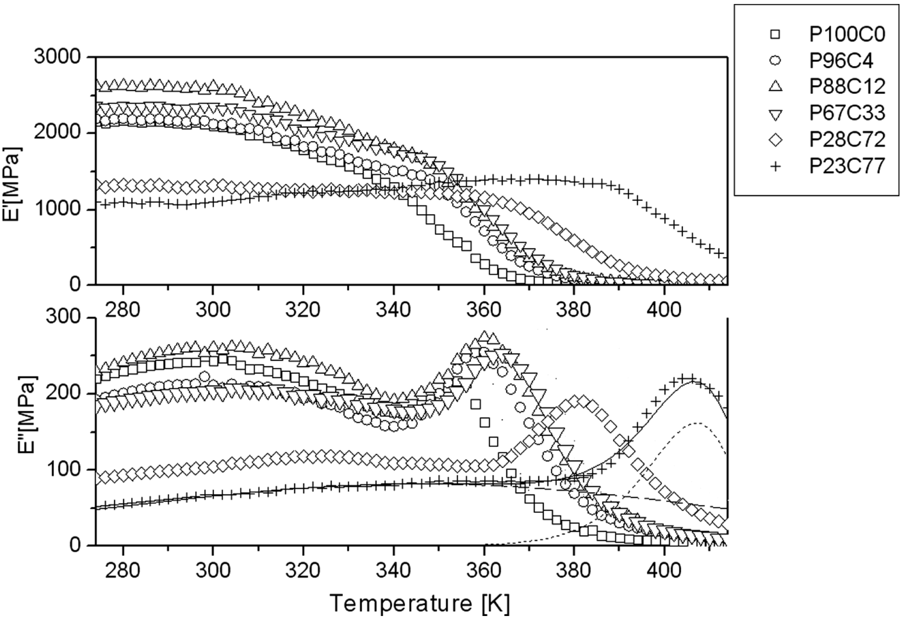


Figure 1: (Top) Storage modulus E′ and (Bottom) loss modulus E′′ as a function of temperature for P100C0 (□), P96C4 (O), P88C12 (Δ), P67C33 (▽), P28C72 (◇) and P23C77 (+). The solid, dotted and dashed lines are fits according to Eq. (1). The limit of experimental accuracy is smaller than the size of the symbols.

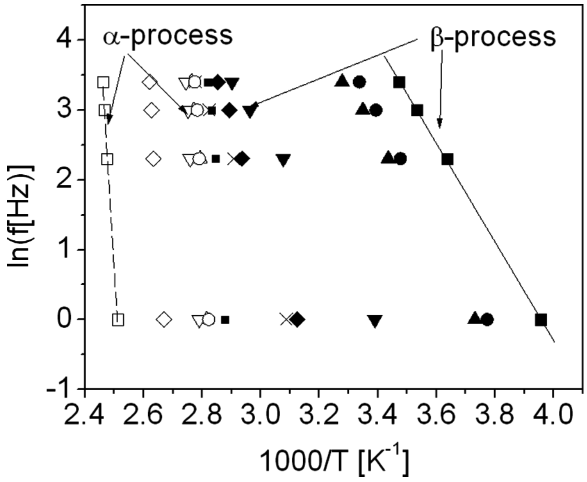


Figure 2: Temperature dependence of the relaxation frequency for the α- and β-processes for the blends. The symbols correspond to P100C0 (□, ■), P96C4 (○, •), P88C12 (△, ▲), P67C33 (▽, ▼), P28C72 (◇, ◆) and P23C77 (+, ×) where open and cross symbols denote α-process and solid and cross symbols denote β-process.

Table 2: WLF parameters of the α-relaxation for the PMMA-CELL blends.

Polymer/Blend PMMA:CELL	C_1	C_2 (K)	T_g (K)
100:00	−13.2	6.9	343.8
98:02	−15.9	8.2	345.5
96:04	−15.5	9.4	350.3
88:12	−10.0	3.2	352.8
83:17	−12.0	6.2	354.0
67:33	−16.3	10.5	354.3
33:67	−14.3	9.0	352.7
28:72	−20.0	19.4	368.7
23:77	−27.0	38.3	390.6

where C_1 and C_2 are constants and τ_{Tg} is the relaxation time corresponding to the dynamic glass transition temperature (T_g) which is approximately 100°C.

Table 2 gives a summary of WLF parameters obtained for the samples investigated. The T_g values of PMMA as measured dielectrically (Table 1) and mechanically (Table 2) do not coincide within the limits of experimental accuracy. This is due to the fact that the dielectric method senses the fluctuations of the dipolar units only, whereas the mechanical method senses the dissipation and storage of the input energy in a viscous flow.

β-Relaxation

The low-temperature peak in Figure 1 is the β-relaxation, assigned to the rotation of the methoxy-carbonyl side group about the bond linking the group to the main chain. It is broad, indicating a wide distribution of relaxation times. Both the temperature position and width is weakly affected by the CELL intake below 72% above which it is strongly influenced. This is an indication of strong interactions between the carbonyl and hydroxyl groups.

The temperature dependence of mean relaxation times (Figure 2) for the β-relaxation for all samples investigated follows the Arrhenius law [12]

$$f = f_o \exp\left[\frac{-E_a}{kT}\right] \tag{3}$$

where f_o is the pre exponential factor and E_a is the activation energy. Table 3 gives a summary of Arrhenius parameters obtained for the samples investigated.

In blends with CELL intakes of 72% and above, the activation rises significantly. Such a process seems to be possible only if both the carbonyl and hydroxyl units move cooperatively together. It should have a higher activation energy than a local one, as observed by an increase in activation energy by more than 60%.

Table 3: Activation energies (E_a) and characteristic frequencies (f_o) for the β-relaxation for the PMMA-CELL blends.

Polymer/Blend PMMA:CELL	B (ln(f_o (Hz))	E_a (kJ/mol)
100:00	27.7	58.2
98:02	25.0	53.2
96:04	28.0	61.5
88:12	28.0	62.3
83:17	23.0	51.5
67:33	22.7	55.5
33:67	27.3	67.7
28:72	37.5	99.7
23:77	35.1	94.7

T_g-Composition Relationships

Several semiempirical equations have been used to model the variation of T_g as a function of blend composition [14–16]. Among these, three equations contain a parameter that can be related to the strength of the interaction between the constituent polymers of the blends. From the calculation of these parameters it is possible to compare the relative strength of interaction between the constituent polymers of the blends.

To explain the lowering of T_g by the plasticizers, Jenckel and Heusch proposed the expression

$$T_g = W_1T_{g1} + W_2T_{g2} + W_1W_2b(T_{g1} - T_{g2}) \tag{4}$$

where W_i and T_{gi} are the weight fraction and glass transition temperature of the respective polymers. The constant b originally characterized the efficiency of the plasticizer to depress T_g of the pure polymer, i.e., the interaction between the plasticizer and the polymer. Such a reason can very well be applied to characterize polymer blends. The constant b can then become a measure of how well two polymers interact with one another, b being inversely proportional to the strength of interaction between the polymers [18,19].

Similarly, Gordon and Taylor proposed the expression [20]

$$T_g = (W_1T_{g1} + hW_2T_{g2})/(W_1 + hW_2) \tag{5}$$

to predict the T_g behavior in random copolymers, the constant h being defined as $\Delta\beta_2/\Delta\beta_1$, where $\Delta\beta_i$ is the cubic expansion coefficient of component i. The equation was subsequently used to explain the T_g-composition dependence of polymer blends, with h proportional to the strength of the interchain interaction [15,19,20].

Table 4: Gordon-Taylor, Jenkel-Heusch and Kwei parameters for the PMMA-CELL blends.

Gordon-Taylor	**Jenckel-Heusch**	**Kwei**	
h	***b***	**h**	***q***
0.33	0.7	0.55	−23

Later Kwei proposed a modification to the Gordon-Taylor equation to account for hydrogen bonding between the blend components [21]

$$T_g \cong (W_1T_{g1} + hW_2T_{g2})/(W_1 + hW_2) + qW_1W_2 \tag{6}$$

where the qW_1W_2 term can be taken as the contribution of hydrogen bonds, q proportional to the strength of the hydrogen bond. When $h = 1$ this equation is identical with the Jenckel-Heusch equation with $q = b(T_{g1} - T_{g2})$. The h value of the Gordon-Taylor equation, the b value of the Jenckel-Heusch equation, and the q value of the Kwei equation have all been used to compare the strength of interchain interaction in blend systems.

In Table 4 we show the parameter values obtained with the various equations, to get the best fit to the T_g experimental data in Figure 3, using the loss modulus of the PMMA-CELL blends.

The T_g of the blends falls below the weight-average values of the T_g's of the components (negative deviation). A positive deviation has been interpreted as

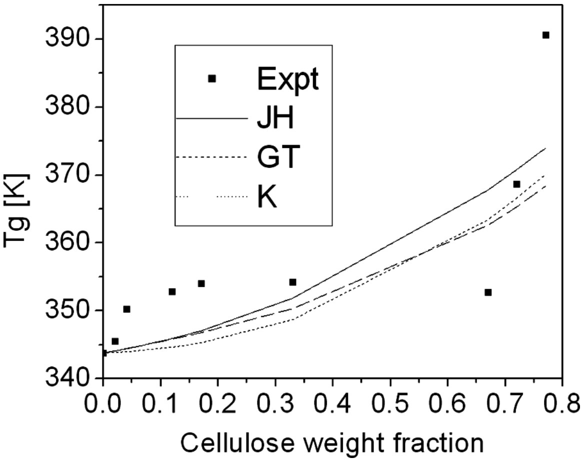


Figure 3: Experimental glass transition temperature (■) versus the weight fraction of cellulose for the blends. The solid, dotted and dashed lines are fits according to Jenckel-Heusch, Kwei and Gordon-Taylor models.

an indication of very strong interactions [15,16]. In the present study, the trends revealed by the *h, b* and *q* values in the Gordon-Taylor, Jenckel-Heusch and Kwei equations, respectively, suggest that stronger interactions lead to better miscibility.

CONCLUSION

DMA has enabled us to elucidate the molecular dynamics in PMMA-CELL blends. The mean relaxation times and strengths of the dynamic and secondary relaxation are strongly affected by CELL intakes above 72% owing to the strong hydrogen bonding between the hydroxy groups as well as the interactions between the carbonyl and hydroxyl groups. Fitting parameters obtained in Gordon-Taylor, Jenckel-Heusch and Kwei models suggest strong interactions between carbonyl and hydroxyl groups.

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