Rheological Behavior of Lubricating Systems in Polypropylene/Seaweed Composites

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ABSTRACT: The present article summarizes an experimental study on the effects of two additives on polypropylene/seaweed (PP/SW) biocomposites by dynamic rheological characterization. Storage and loss moduli as a function of frequency were obtained by small-amplitude shear oscillation tests in parallel-plate mode. Maleic anhydride-grafted polypropylene (MAPP) was found to provide good external lubrication, while CNT masterbatch (CESA) promoted fiber–fiber interaction. Han plot and Cole-Cole plot visibly present the difference between the two interaction mechanisms. A synergistic effect was also observed when MAPP and CESA were simultaneously used in biocomposites. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 2143–2148, 2011

Key words: PP/SW biocomposites; rheological properties; lubricating effect

INTRODUCTION

Natural fiber composites (NFCs) have attracted significant attention as an effective method of utilizing renewable resources together with polymer. Besides enhanced awareness of environmental requirements, biocomposites represent a new material with characteristics from both polymer matrix and natural fibers. Because of reduced cost, variable specific gravity, as well as recyclability, NFCs are currently under investigation and have already been used as exterior non-structural building products as well as in the automobile industry.[1–4]

Many technical issues regarding NFCs have been well studied, such as mechanical properties, thermal stability, and water absorption.[5,6] The main issue with preparation and application of NFCs is the incompatibility of hydrophilic cellulose and hydrophobic polyolefin. Also, a poor level of dispersion of the blend components reduces mechanical properties, and hence compatibilizers such as lubricants and elastomers were explored in view of their potential for improvement of processability and mechanical properties. It is reasonable to regard a natural fiber reinforced polymer composites therefore as a three-phase system. Ideal additives are expected to create a deformable, tough, and flexible interfacial layer. Enhanced adhesion leads to better transfer of applied stresses providing NFCs with superior performance.[5]

The rheological phenomena resulting from the high filler contents (high viscosity and complex stress-strain rate dependence) must be understood for proper formulation design and process control. Rheology can interpret the degree of dispersion of natural fibers in the matrix polymer, the properties of the interfacial region, as well as the affinity of polymer and natural fiber, and plays a vital role in optimization of processing of NFCs.[7,8] Capillary rheometry has been widely used, but it is difficult to apply because of poor flowability of NFCs, fiber migration from die wall to center, and breaking of natural fibers because of high shear rates in capillary rheometers.[9,10] For highly filled NFCs, small amplitude dynamic oscillation tests are believed to be the most suitable method for assessing the internal structure as well as the dispersion state of the filler, because small amplitude strain does not lead to a change of the internal structure. Therefore dynamic rheological characterizations were recently used to obtain detailed information on elastic and viscous properties of the NFCs blend formulations.[11–14]

The addition of natural fibers into a polymer matrix induces two different interactions: fiber–fiber interaction (internal) and fiber–matrix interaction (external), and together affect the flow behavior and the mechanical performance of the composites.[13] It was found that a strong fiber–fiber interaction causes an increase of the steady shear viscosity and

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a higher zero-shear viscosity, while a strong coupling effect between polymer and fiber (fiber–matrix interaction) results in an enhanced shear thinning behavior starting at lower shear rates.[15]

Suitable additives are vital for both manufacturing and application of NFCs. Schemenauer reported that maleated polypropylene used as coupling agent does not influence the melt flow behavior of 30 wt % natural fiber filled polypropylene.[16] However, several authors have observed an increase of the complex viscosity. The melt rheological behavior of short sisal fiber reinforced polymer systems were reported by Joseph and coworkers.[12,17] Wolcott found that a coupling agent increased the shear viscosity of wood filled HDPE.[11] The effects of mesh size, filler loadings, and coupling agent of PP/wood flour composites were reported by Azizi.[14]

We have reported interesting results on seaweed fiber as a novel biofiller for polypropylene.[18] The subject of this article is to study the mechanism of lubricating systems, and the effects on fiber–fiber and fiber–matrix interactions in PP/seaweed biocomposites by use of rheological characterisations.

EXPERIMENTAL

Materials

Polypropylene (PP) was supplied by Sabic (PP 579S; density = 0.905 g/cm^3; MFI = 47 g/10 min). Seaweed fiber (SW) was obtained from Natural Garden (Birmingham, GB). Maleic anhydride polypropylene was obtained from Aldrich (MAPP; MA% = 8–10%), and a CNTs containing masterbatch (CESA, CESA®-conductive CNT OC90025520) was supplied by Clariant.[17] Based on FTIR and TGA analysis (not show here), CESA is a masterbatch based on polypropylene matrix.

Sample preparation

All the raw materials were dried at 60°C over 48 hr with vacuum oven to remove moisture. Melt compounding was carried out by extrusion (L/D = 20, Collin GmbH, Germany). The temperature was 180°C, and the screw speed was fixed at 60 rpm. The compositions are listed below in Table I. Then, samples (25 mm in diameter) were prepared by compression moulding at 180°C, 20 MPa for 10 min.

Characterization

All samples were dried before measurement. Oscillatory shear tests were performed with a stress-controlled Rheometer (MCR301 Anton Paar, Germany) under nitrogen atmosphere to avoid oxidation. A plate-plate system was used with diameter of 25 mm and a gap size of 1.0 mm for all tests. A fresh sample was used for each test for consistency.

TABLE I
Compositions of PP/SW Biocomposites

Sample	PP (wt %)	SW (wt %)	MAPP (wt %)	CESA (wt %)
PP	100			
SW20	80	20		
SW30	70	30		
SW40	60	40		
SW20MAPP	80	20	2.5	
SW30MAPP	70	30	2.5	
SW40MAPP	60	40	2.5	
SW20CESA	80	20		5
SW30CESA	70	30		5
SW40CESA	60	40		5
SW20MC	80	20	2.5	5
SW30MC	70	30	2.5	5
SW40MC	60	40	2.5	5

Strain sweep tests at 180°C were performed at the 10 rad/s frequency by increasing the nominal shear amplitude from 0.01% to 100%.

Frequency sweep tests were performed at 180°C, 7 point/decade intervals from 500 to 0.1 rad/s under 0.1% shear amplitude.

Frequency-temperature sweep tests were applied from 180 to 210°C with temperature intervals of 10°C in the frequency range from 500 to 0.1 rad/s for each temperature. Horizontal shifting was performed based on storage modulus (G') and loss modulus (G''); the influence of $\rho_0 T_0/\rho T$ [eq. (1)] is neglected owing to the narrow temperature range of interest.[11]

$$G'[\omega, T_0] = \frac{\rho_0 T_0}{\rho T} G'[\omega_{aT}, T] \quad (1)$$

RESULTS AND DISCUSSION

The strain sweep of PP/SW biocomposites

The variations of storage modulus (G') and loss modulus (G'') with SW loadings from strain sweep tests are illustrated in Figure 1. SW filled PP presents higher moduli as compared to the PP matrix and the moduli are rising with SW loading. This trend indicates strong filler-matrix interactions in natural fiber reinforced composites.[11,13] Additional, the width of linear-viscoelastic regions remains nearly unchanged that implies the fine dispersion of SW fiber in the PP matrix,[18] as severe agglomerations would induce an obvious shift of the nonlinear viscoelastic region to lower strain.[19]

Figure 2 compares the effect of two additives separately on the strain sweep, while the SW content is fixed at 40 wt %. MAPP leads to a slight decrease of G' and G'' compared to raw SW filled PP. In contrast,

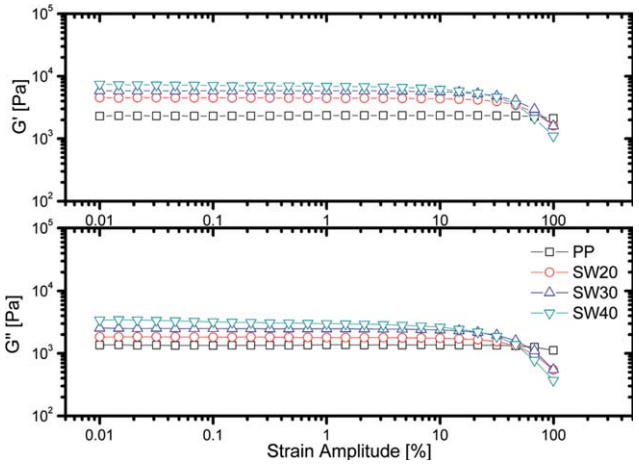

Figure 1 Effect of SW loadings on dynamic strain sweep. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

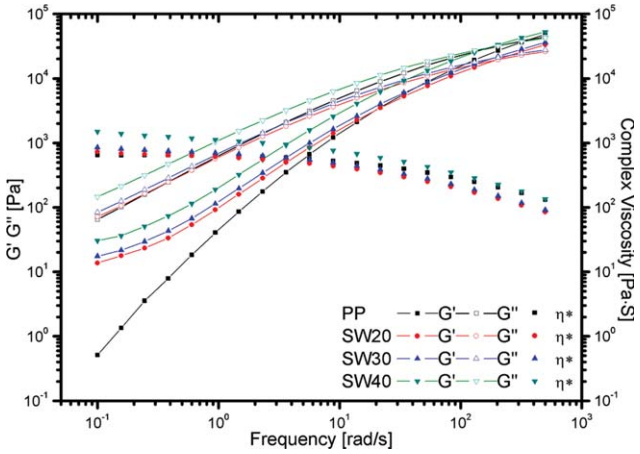

Figure 3 Effect of SW loadings on dynamic frequency sweep. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CESA introduces an increase of the moduli. Judged from these two diverse tendencies, it is reasonable to assume the distinct effects of the two additives studied in this work. As the linear-viscoelastic behavior of the biocomposites is of interest here, it can be seen from Figures 1 and 2 that the results of the frequency sweeps measured at a strain level of 0.1% are clearly within the linear-viscoelastic regime.

The frequency sweep of PP/SW biocomposites

The comparison between storage modulus (G') and loss modulus (G'') of PP/SW biocomposites without additives as obtained by dynamic frequency sweep is illustrated in Figure 3. It is obvious that both G' and G'' increase with frequency, and also that the moduli increase with increasing SW loadings, thus revealing the filling effect. The formation of a plateau in G' at very low frequencies after adding SW is obvious, which is the result of the formation of a physical network structure, which might eventually cause an apparent yield stress.[12]

In all the cases, the loss modulus (G'') is larger than the storage modulus (G') except for high frequencies, which represents the highly viscous nature of biocomposites in the molten state.

A similar trend as in the case of the strain sweep test is observed: Neat PP shows the lowest complex viscosity. The high value of complex viscosity reflects the viscoelastic resistance of the polymer melt against flow, and by the incorporation of SW in the PP matrix, friction in the melt is raised; rigid SW particles disturb and create obstructions to flow of the matrix melt, which results in the remarkable increase in viscosity.

It can be seen in Figure 3 that the storage modulus G' also increases with SW content, especially in the low frequency regime. The storage modulus of SW filled PP tends to reach a plateau below 0.2 rad/s, and such a low-frequency plateau for filled thermoplastics indicates the presence of a physical network structure because of the interaction among the dispersed particles.[11]

The frequency sweep results also reveal the role of lubricants in PP/SW biocomposites (Fig. 4). A similar trend as recorded by the strain sweeps can be seen, i.e., adding MAPP as coupling agent decreases the complex viscosity and the storage modulus. Judging from the limited decline after adding MAPP, it can be assumed that MAPP in this investigation partly reduces interfacial disordering. It is known that maleated polyolefins have an external compatibilization function and improve the interfacial balance between fiber and matrix.[11]

In contrast, the values of storage modulus G' and complex viscosity η^* are remarkably raised by

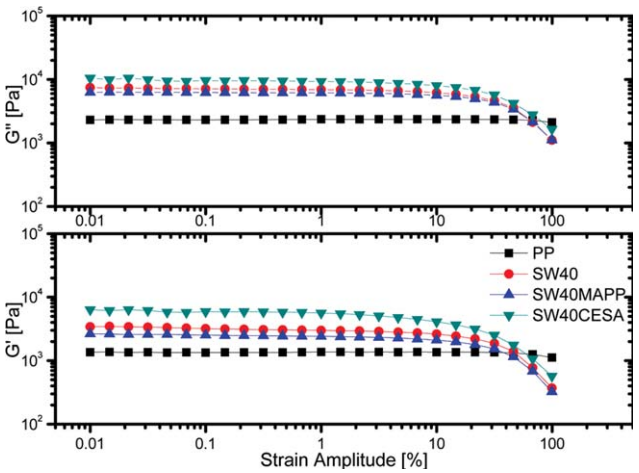

Figure 2 Effect of lubricant systems on dynamic strain sweep. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

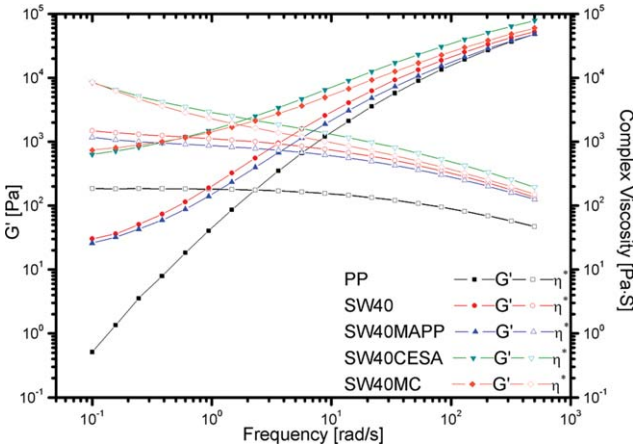

Figure 4 Effect of lubricant systems on dynamic frequency sweep. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

adding CESA, especially in the low frequency range. This could be understood as an indication of the forming of an interfacial layer that enhances the fiber–fiber interaction. This coating layer greatly reduce the surface energy differences between SW fiber and PP matrix that achieve better miscibility that lead to the higher yielding plateau.

Further, adding MAPP and CESA simultaneously to the blend leads to lower viscosity and storage modulus than in the case of CESA used alone except at low frequencies. This implies a certain synergistic effect of these two lubricants, which results in an enhanced shear thinning behavior. It could be assumed two fiber–fiber interactions exist in this system, SW–SW and SW–CNTs interactions. The above results indicate the dominance of SW–SW interaction in this work; this could be explained the large surface energy difference between SW fiber and CNTs.

The temperature-frequency sweep of PP/SW biocomposites

The effects of the two additives are further illustrated by the comparison between master curves obtained from temperature-shifted frequency sweeps, and the frequency sweeps at 180°C. The master curves were generated by use of the well-known Arrhenius equation,

$$\log a_T = \log \frac{\eta_0(T)}{\eta_0(T_0)} - \frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \qquad (2)$$

where E_a is the activation energy, T is the temperature, T_0 is the reference temperature, and R is the universal gas constant. The master curves of the formulation in comparison with frequency sweep tests are displayed in Figure 5, and the shift factors are displayed in Figure 6 as Arrhenius plot.

A certain variance in the master curve and a difference between the master curve and the frequency sweep data obtained at 180°C could be observed in the case of raw SW filled PP. This indicates thermorheological complexity and may be because of the fact that the low frequency data in the master curve are obtain at higher temperatures which could induce variations in the interaction between fiber and matrix.[12] In contrast, better agreement between the frequency sweep results and the master curves was achieved after using the lubricants either alone or together, indicating enhanced thermorheological simplicity because of temperature-independent fiber–fiber or fiber–matrix interaction.

Figure 5 also reveals the difference between the lubricating mechanisms of MAPP and CESA: MAPP used alone leads to a limited decrease in both the storage modulus G' and the complex viscosity η*, and the agreement between frequency sweep data and master curve is highly improved. This effect clearly confirms the compatibilizing efficiency of MAPP. However, a limited difference can still be observed, which may be attributed to the random nature of the bonding between fiber and matrix created by maleated polyolefin. CESA used alone eliminates the low frequency thermorheological complexity, while the storage modulus G' and the complex viscosity η* are much higher than in the case of both SW40 and SW40MAPP.

The difference between the two additives when used alone is now becoming clearer: MAPP acts as external lubricant improving the fiber–matrix interaction, while CESA induces a remarkable increase in the yielding stress by enhanced fiber–fiber interaction. For the MAPP/CESA system, the blend behavior is dominated by CESA resulting in an increased yielding plateau.

Han plot and Cole-Cole plot

Additionally, two different techniques were used to visualize the difference between the internal and external lubricating effect. The Han plot (log–log plot of G'' versus G') indicating the sensitivity to composition and temperature has been widely used to investigate miscibility of polymer blends,[20–22] and has also been applied to explore the compatibility of NFCs recently.[14,23] The Han plot at 180°C of the two additives used alone and together with fixed SW loading (40 wt %) is illustrated in Figure 7. As clearly observed, SW fiber induces a higher loss modulus in comparison to neat PP at the same storage modulus. The curves for SW40 and SW40MAPP are almost indistinguishable, while CESA used alone increases dramatically the loss modulus. This again confirms the distinctive interaction mechanisms of MAPP and CESA.

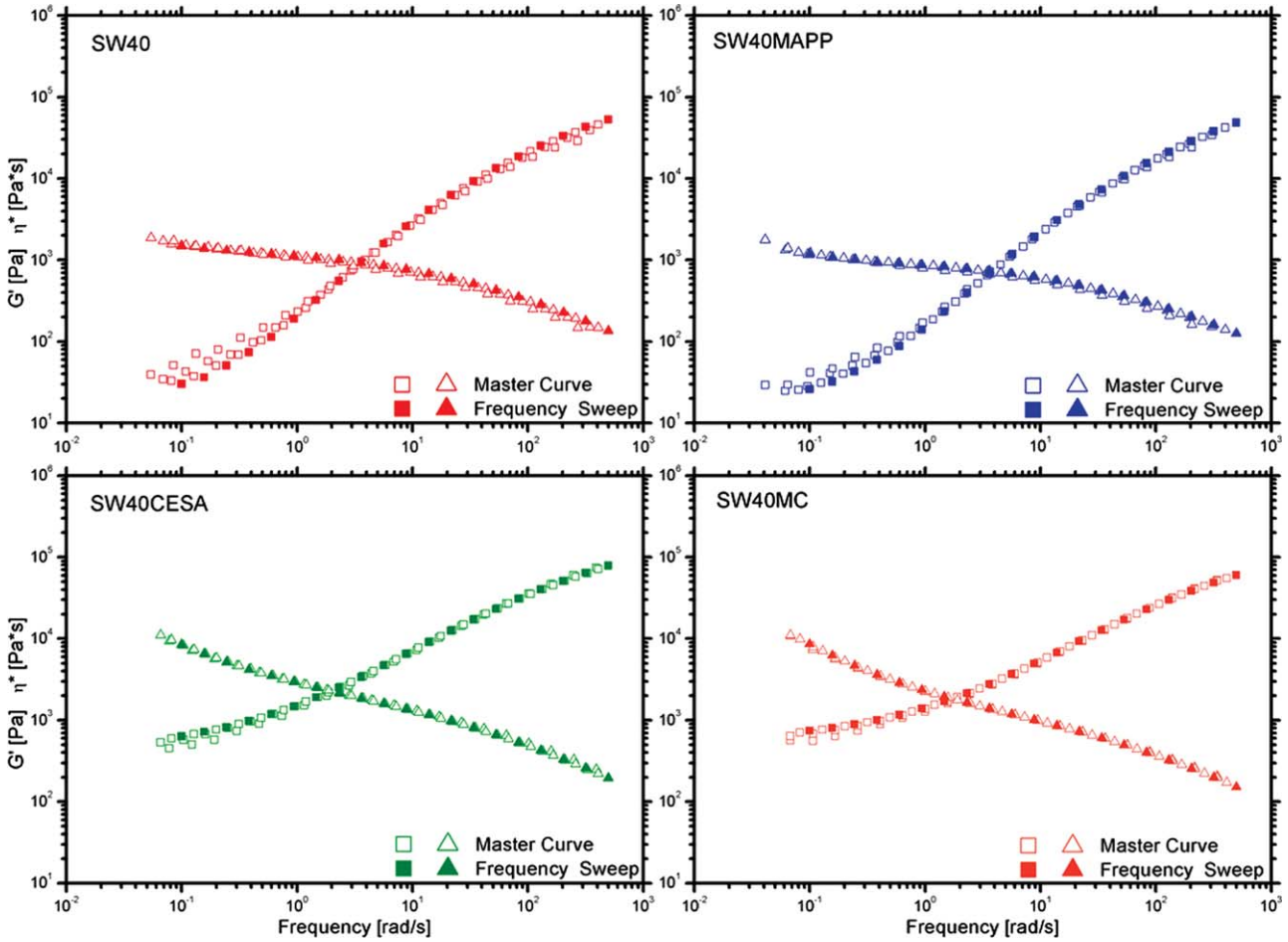

Figure 5 Comparison of master curves and frequency sweep results. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As proposed above, the interactions may be classified into a fiber–fiber (internal) part and a fiber–matrix (external) part. All the result indicates that the lubricating function of MAPP is because of enhanced fiber–matrix interaction, while CESA increases the fiber–fiber interaction.

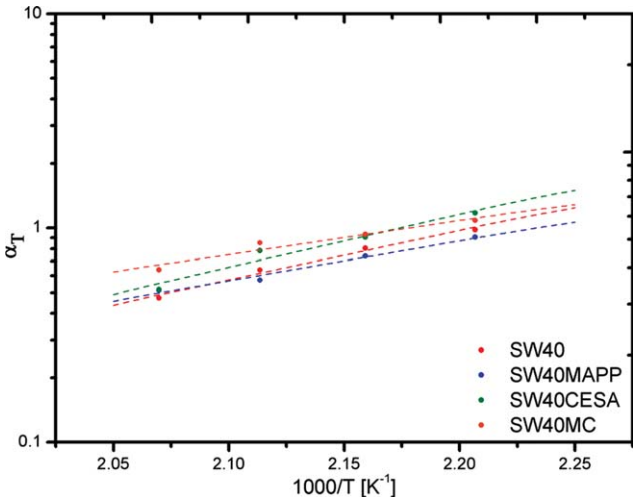

Figure 6 Shift factors for obtaining mater curves. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

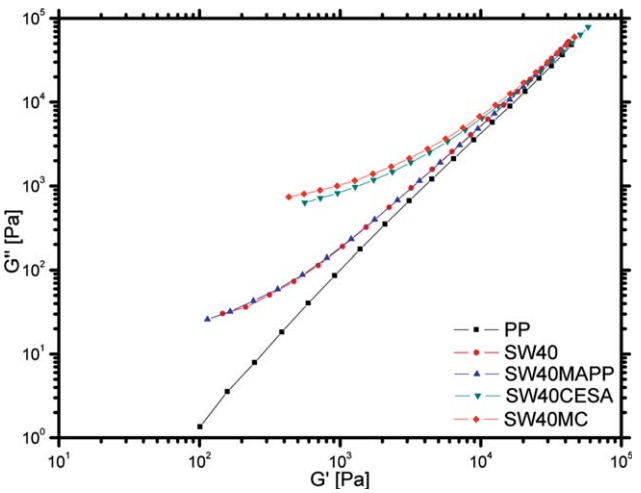

Figure 7 Effect of lubricating systems on the Han Plot. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

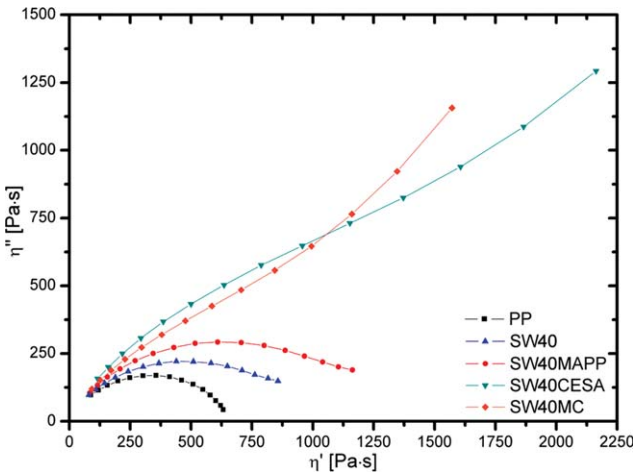

Figure 8 Effect of lubricating systems on the Cole-Cole Plot. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The Cole-Cole plot (Fig. 8) further confirms the two mechanisms. A smooth, semicircle shape of the Cole-Cole plot suggests phase homogeneity in the melt and good compatibility and fine dispersion of the blend.[13] Good distribution of SW fiber within the PP matrix is reflected from the plot; and after coupling by MAPP, the shape of the curve remains semicircle. Addition of CESA shows total deviation from a semicircular curve, indicating strong fiber–fiber interaction.

CONCLUSIONS

The rheological properties of PP/SW biocomposites have been characterized by small-amplitude oscillatory shear measurements. Incorporation of SW fiber into PP matrix leads to a remarkable increase in the storage modulus G', loss modulus G'', and complex viscosity η^* with increasing SW loadings. The results demonstrate the efficiency of MAPP in enhancing filler-matrix interaction in terms of promoting SW fiber dispersion and internal lubricating. In contrast, the values of storage modulus G' and complex viscosity η^* are remarkably raised by adding CESA, especially in the low frequency range. This could be understood as an indication of the forming of an interfacial layer that enhances the fiber–fiber interaction, thereby improving the yield stress of the blend. A certain synergistic effect of MAPP and CESA was also observed with the blend behavior being dominated by CESA.

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