Study on compatibility of hydroxypropyl guar gum/ultrafine powder of bagasse blends

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Abstract: The influence of the concentration of bagasse ultrafine powder on the compatibility of hydroxypropyl guar gum solution/bagasse ultrafine powder blend system was investigated by Hakke MARSIII rheometer from Germany. According to Utraki principle, composite viscosity, storage modulus and loss modulus analysis, cole-cole curve and other theories, the stable and dynamic scanning data of the blends were processed and analyzed. It was found that when hydroxypropyl guar gum/bagasse ultrafine powder = 40/100 (m/m), the compatibility between the two was good. SEM also confirmed this conclusion.

1. Introduction
The compatibility of raw materials in polymer blend system, which is closely related to the physical and mechanical properties of materials, is the key link of polymer blend materials research. Compatibility is related to dispersion morphology of dispersed phase, interface condition and interface interaction. Rheological properties of materials have attracted much attention in recent years, because they can’t only guide the processing and forming of materials, but also provide sensitive information about the internal structure of materials. Compared with FTIR, SEM and other characterization methods, rheological study has the following advantages: A wide range of determination, most of the multi-component polymer blends are studied accurately and reliably, high sensitivity, sensitive perception of phase morphological characteristics of the blending system changes.

Utraki has proposed the logarithmic sum formula for the shear viscosity of "ideal" blends, which has certain practical significance [1]. The formula:

\[ \lg \eta_m = \omega_1 \lg \eta_1 + \omega_2 \lg \eta_2 \]  

\( \omega_1, \omega_2 \) as the mass fraction of two phase, \( \eta_1, \eta_2 \) for two phase viscosity. According to this formula, the simple blend shear viscosity should be \( \lg \eta_1 \) to \( \lg \eta_2 \) in a straight line. Although there is no ideal blend that can strictly meet this formula, the actual shear viscosity of two-phase blends can be compared with this line as a reference to judge the degree of deviation from the ideal blend. Deviation modes include positive deviation, negative deviation and positive and negative deviation. The positive deviation curve contains a maximum value, indicating that the interaction between the two phases is large and the viscosity increases at this concentration. Conversely, the interaction is small and the viscosity decreases.
The rheological behavior of the material has nothing to do with the stress and strain within a fixed range, the material is in the linear viscoelastic interval. While it shows nonlinear viscoelastic behavior beyond this range. That is due to the orientation and orderly arrangement of molecular chains in the system with shear action, which leads to the reduction of resistance in the system and the decrease of modulus with the increase of stress or strain. Therefore, the dynamic scanning stress or strain should be determined in the linear viscoelastic interval [2]. It is necessary to determine the linear viscoelastic interval of viscoelastic material by stress or strain scanning before dynamic scanning.

According to the classical linear viscoelastic theory:

\[
G' (f') \big|_{f \rightarrow 0} = \frac{J^0}{\eta_d} (2\pi f')^2 \\
G'' (f') \big|_{f \rightarrow 0} = \eta_d (2\pi f')
\]  

(2)

In the formula, \(J^0\) is the steady-state shear flexibility, \(\eta_d\) is the zero shear viscosity, and \(f\) is the frequency. According to the formula, the slope of the logarithmic curve of the sum and frequency of a single sample should be 2 and 1 respectively in the low frequency region [3]. The blending system is more consistent, the blending system is closer to monodisperse single component system, so the compatibility is better [4].

Cole–cole diagrams are \(\eta'\) (\(\eta' = G' / \omega\)) tan' (\(\eta' = G' / \omega\)), Havriliak etc thought that the complex viscosity(\(\eta^*\)), frequency(\(\omega\)) and relaxation time(\(\tau\)) are expressed as the relationship:

\[
\eta^* = \eta_0 \frac{1 + (i\omega \tau)^{1-\alpha}}{1 + (i\omega \tau)^{1-\beta}}
\]

(3)

In the formula, \(\alpha\) and \(\beta\) are parameters. So, \(\eta'\) of imaginary part (\(\eta''\)) and real (\(\eta'\)) can be represented as respectively:

\[
\eta'' = \eta_0 r^{-\beta} \sin \beta \theta
\]

(4)

\[
\eta' = \eta_0 r^{-\beta} \cos \beta \theta
\]

(5)

\(r = (a^2 + b^2)^{1/2}\), \(\theta = \arctan(b/a)\), \(a = 1 - (\omega \tau)^{1-\alpha} \sin(\alpha \pi / 2)\), \(b = (\omega \tau)^{1-\alpha} \cos(\alpha \pi / 2)\).

Then \(\eta'\) curve is half arc for the polymer system with single peak distribution of molecular weight.

According to Gross’s method, the frequency relaxation spectrum (\(HG(\omega)\)) is obtained by \(G^*\):

\[
H_G(\omega) = \pm (1/\omega \tau) \text{Im} G^*(\omega e^{2\pi i})
\]

(6)

So, \(\text{Im} G^*\) is the imaginary part of \(G^*\), for \(\eta'' = G^* / \omega\):

\[
\eta'' = \pi \text{Im} H_G(\omega)
\]

(7)

Relaxation occurs in the separation of blends. According to the formula [5][6], Cole-Cole diagram can represent the relaxation state of blends, so Cole-Cole diagram can also represent the compatibility of blends. The determination method is as follows: the more the Cole-Cole curve deviates from the semi-arc, the more serious the phase separation of blends is.

The study of the compatibility of guar gum solution/ultrafine powder of bagasse according to the rheological theory of the composite materials and the conventional SEM detection is meaningful.

2. Experimental Section

2.1 Materials
Sugarcane bagasse was obtained from a local sugar factory (Zhanjiang, China). Hydroxypropyl guar gum was purchased from guangrao liuhe chemical co. LTD, it was industrial grade.

2.2 Preparation of ultrafine powder samples of bagasse (short for BP)
The cleaned and dried bagasse was ground by vibrating ultra-micro mill (WZJ6) with the power of 1.1kw. The temperature of grinding chamber should not exceed 25°C to prevent other reactions during vibration during crushing.
2.3 Preparation of rheological test sample
The ultra-fine powder of bagasse and hydroxypropyl guar gum were evenly mixed in accordance with mass ratios of 30/100, 40/100, 50/100, 60/100 and 70/100, a certain volume of water was added to dissolve and stir quickly, the ultrasonic was used for 20 min before incomplete hydration, and the test was started after standing for half an hour.

2.4 Characterization
The rheological test samples were analyzed with rheometer (MARSIII, HAAKE, Germany) for combined structure, SEM (S-4800, HITACHI, Japan) for surface morphology.

3. Results and Discussion

3.1 The steady-state scanning
As shown in figure 1, the sample compatibility reached the best, when the BP concentration was 40%. This should be due to the increase in phase interaction and viscosity. As the BP itself had no viscosity, the interaction between the two phases of the blend gradually decreased with the increased BP dominated in the blend, and the sample viscosity decreased.

![Figure 1 The shear viscosity of composite](image)

3.2 Determination of linear viscoelastic zone
Before dynamic scanning, the samples should be scanned by stress or strain to determine the linear viscoelastic zone. The linear viscoelastic intervals of 30%BP, 40%BP, 50%BP, 60%BP and 70%BP samples were shown in the following table 1 (the complete scan curve was not shown in the paper, and only the initial and yield stress values were recorded). The original sinusoidal waveform fitted well with the standard waveform, which confirming the test results reliable. Therefore, the fixed stress was determined to be 500 mPa during dynamic scanning.

| Sample | Value (mPa) |
|--------|-------------|
| 30%BP  | 306.9-1000  |
| 40%BP  | 300.2-903.5 |
| 50%BP  | 372.7-800.2 |
| 60%BP  | 368.1-975.9 |
| 70%BP  | 108.8-753.2 |
3.3 Dynamic scanning analysis

3.3.1 Dynamic storage modulus and loss modulus. In the figure 2, the hydroxypropyl guar gum had a good compatibility with bagasse ultrafine powder, when the content of bagasse ultrafine powder was 40%. As the concentration of the ultrafine powder of bagasse was 40%, the distribution of the two phases was more uniform and the interaction was stronger. When the content of bagasse ultrafine powder reached 70%, the slope of the storage modulus and loss modulus curves were seriously deviated from 2 and 1 at the low frequency end, which indicated appearing serious phase separation. The excessive bagasse powder was difficult to disperse in the viscous liquid, resulting in serious agglomeration phenomenon, and the hydroxypropyl molecular chain was difficult to "wrap", so the interaction destroyed between hydroxypropyl guar gum molecules.

![Figure 2 Dynamic modulus](image)

3.3.2 The composite viscosity. It was shown in the figure 3 that the change curve of composite viscosity with frequency of hydroxypropyl guar gum/bagasse ultrafine powder blend system at 25℃. The five samples showed the pseudoplastic fluid characteristics of shear thinning. The composite viscosity of 40%BP sample was the highest and 70%BP sample was the lowest. That was due to the moderate content of bagasse ultrafine powder in 40%BP sample, and the close entanglement of molecular chains, which increased the flow resistance and viscosity. While the composite viscosity reduced, and the curve of change with frequency wasn't a straight line at 70%. The reunion of excessive bagasse superfine powder was serious in the hydroxypropyl guar gum solution, and the molecular interaction of hydroxypropyl guar gum was weak, which destroyed the hydroxypropyl guar gum molecular interaction force and reduced the molecular chain entanglement degree, so the viscosity of mixture was lower.

![Figure 3 Compound viscosity](image)
3.3.3 The Cole - Cole curve. As shown in figure 4, the Cole-Cole curve presented a relatively neat semicircle with the bagasse content of 40% at 25°C, while the other four samples which had certain depressions on the arc, it could be vividly called "small tail". This "small tail" deviating from the low-frequency end arc corresponded to another phase deviating from the low-frequency end arc, which indicated that the blending system had obvious phase separation at this time. The sample containing 70% bagasse had the most serious phase separation phenomenon, which could be due to too much phase agglomeration with large particle size in the solution, making it difficult for the two phases to be closely bound together and causing serious phase separation.

![Figure 4 Cole-Cole curve](image)

3.4 Surface morphology observation
The SEM images of 40%BP, 50%BP and 60%BP samples were shown in the figure 5, which presented different blend phase morphology with different content, the two-phase interface was more and more clear and the compatibility became worse with the increasing content, according to the bagasse reunion phenomenon became more serious and the aperture of the bagasse granules got more. The results were consistent with rheological results.

![Figure 5 SEM image of sample](image)

4. Conclusions
The compatibility of bagasse/hydroxypropyl guar gum blends was studied by rheology combined with SEM, the viscoelastic behaviors were systematically studied with different blends of bagasse/hydroxypropyl guar gum in homogeneous and phase separation zones. The results showed that the compatibility of bagasse/hydroxypropyl guar gum was the best when it was 40/100 (m/m). The separation of bagasse and guar gum gradually occurred with the increase of bagasse content, and SEM also proved this conclusion.

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References
[1] Wu, Q. Y., Wu, J. A. (1994) Introduction to Rheology of Polymer Materials. Chemical Industry Press, Beijing.
[2] Lu, J. J., Bai, H. Y., Wang, W., et al. (2016) Study on the compatibility of PVDF/PTW blends by dynamic rheology. Acta Polymerica Sinica, 3:315-323.
[3] Yang, Y. L., Qiu, F., Tang, P., et al. (2006) Polymer systems phase separation kinetics with pattern generation and selection. Progress in Chemistry, 18: 363-381.
[4] Jang, X. L., Zhang, H. D., Zhang, Z. L., et al. (2003) Study the effect of viscosity to the kinetics of polymer blends phase separation. Chem. J. Chin. Univ., 24: 532-536.
[5] Zhang, J. N., Jang, X. L., Zhang, H. D., et al. (2002) Viscoelastic effect on the kinetics of polymer mixtures phase separation. Journal of Fudan University (Natural Science)., 41: 301-308.
[6] Chopra, D., Vlassopoulos, D., Hatzikiriakos, S. G., (1998) Shear-induced mixing and demixing in poly(styrene-co-maleic anhydride) poly(methyl methacrylate) blends. J. Rheol., 42: 1227-1247.