Study on rheological properties of CMC/Eu-Tb solutions with different concentrations

Z C Fu[1], J Ye[1] and J Xiong[2,3]

[1]State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, 510640, China
[2]School of Food Science and Engineering, South China University of Technology, Guangzhou, 510640, China

E-mail: lcjxiong@scut.edu.cn

Abstract. The rheological properties of polymer solution are sensitive to variations in the polymer structure. Carboxymethyl cellulose (CMC) aqueous solution has been used in many fields, such as food, medicine and paper industry. In this paper, the effects of different concentrations (2% - 6%) of CMC/Eu-Tb on their rheological properties were investigeted, including steady-state flow and viscoelastic response. The results show that, the viscosity of CMC/Eu-Tb is lower than that of CMC, at the same concentrations; the products solutions present a nearly Newtonian behavior at the low concentrations (2% - 3%); while at the higher concentrations (4% - 6%), the products solutions present a pseudoplastic behavior; shear-thinning behavior is due to the polymer chains unravel under the action of flow and the molecular chains are oriented in the flow direction. The results also show that the viscosity of the solutions decreases with increasing temperature. Dynamic rheological tests show that CMC/Eu-Tb has viscoelasticity in the concentrations of 2% -6%. At lower concentrations, the elastic modulus G' is slightly higher than the viscous modulus G", and as the concentrations increase, the elastic modulus G' is significantly higher than the viscous modulus G". It means that at the lower solution concentrations, the solutions tend to be less elastic and easier to flow. Most of the energies are lost through the viscous flow. As the solution concentrations increase, the solutions tend to be more elastic, and the system tends to form a gel.

1. Aims

CMC is an important cellulose ether, obtained by carboxymethylation of cellulose. Carboxymethyl cellulose (CMC) has a very wide range of applications [1]. For example, in the food industry, CMC can be used as an emulsifier and stabilizer in ice cream production; in the medical industry, CMC can be used as a tablet binder and film-forming agent, but also a safe and reliable anti-cancer drug carrier; In the paper industry, CMC can be used as coating colors to improve paper properties.

The rheological properties of CMC have been the subject of many studies [2,3]. Mohamed et al. investigated rheological properties of high concentrations of carboxymethyl cellulose solutions [4]. Mamdouh *et al* studied rheological behavior of 1 to 5% carboxymethyl cellulose solutions [5]. Adel Benchabane *et al* investigated the effect of two critical concentrations on the rheological behavior of carboxymethyl cellulose (CMC) solutions [6].

It was confirmed that carboxymethyl cellulose/Tb (III) nanocomposites possess high fluorescence. With their fluorescent properties, the CMC/Tb nanocomposites could be used in such as food packaging, and biomedical devices for potential application [7]. Under ultraviolet light, the green

fluorescence is a characteristic emission of Tb^{3+} and the red fluorescence is a characteristic emission of Eu^{3+} [8], so we may change the mixing ratio of Eu, Tb in order to get different colors of complexes. Therefore, CMC/Eu-Tb nano-complexes may have more potential in food packaging, and biomedical devices application.

In this paper, CMC/Eu-Tb nano-complexes were synthesized by reacting Eu^{3+} and Tb^{3+} with carboxymethyl cellulose. The effects of different concentrations (2% - 6%) of CMC/Eu-Tb along with fluorescent properties on their rheological properties were investigeted, including steady-state flow and viscoelastic response. The experimental results of CMC and CMC/Eu-Tb were compared, to investigate the differences of CMC rheological properties reacting with Eu^{3+} and Tb^{3+}.

2. Methods

2.1. The preparation of CMC/Eu-Tb complexes
The CMC has the Degree of Substitution (DS) of 0.81, in food grade, and its 1.0% aqueous solution has a viscosity of 8200 mPa s at 25℃ [9], (Brookfield viscometer). It was purchased from WEIYI Technology Company in Chang Shu. 1.000 g of CMC was added slowly into a three-necked flask containing 100 mL of deionized water, then the mixture was stirred at room temperature for more than 4 hours until no air bubbles were left. 15ml $TbCl_3$ solution and 15ml $EuCl_3$ solution were taken into a reagent bottle, Both $TbCl_3$ and $EuCl_3$ concentrations were 0.0318 mol/L The mixture was adjusted to pH = 7.0 with NaOH solution and diluted with about 60 mL of deionized water. Then flask containing CMC solution was put on constant temperature (70 ℃) magnetic stirrer. $TbCl_3$ solution and $EuCl_3$ solution were slowly added to the flask for 9h. After that, the suspension was placed in a dialysis bag, repeatedly soaked in dialysis bag with deionized water; the aqueous solution was tested with $AgNO_3$ solution until no white precipitate was obtained. The product was transferred to a watch glass, placed in an oven and dried to constant weight for milling to spare.

2.2. The preparation of CMC/Eu-Tb solutions
Weigh respectively the mass of 0.2, 0.3, 0.4 0.5, 0.6g CMC/Eu-Tb, gradually added to a beaker containing 10 mL of deionized water with stirring. After stirring for 2 hours, the beaker was sealed with plastic wrap, refrigerated and placed in refrigerator overnight.

2.3. Rheological test of CMC/Eu-Tb solutions
Model of rheometer: HAAKE RS600 rheometer

Test fixture: 60 mm parallel plate

Steady-state flow test: the test spacing is 750 μm; the test temperature is from 20℃ to 60℃; maintain for 15 min after pre-shearing; the range of shear rate: 0.01~50 s^{-1}

Frequency scanning test: the test spacing is 500 μm; the test temperature is 25℃; maintain for 5 min after placing samples; the strain is 15%; the range of frequency scanning: 0.01~10 Hz.

3. Results

3.1. Steady-state flow test
In this test, five temperatures of 20, 30, 40, 50, 60 ℃ were selected. At each temperature, the flow behaviors of CMC/Eu-Tb solutions in the concentration range of 2−6% were investigated. The steady-state flow curves of CMC/Eu-Tb measured at various concentrations at different temperatures are shown in figure 1.

As can be seen in figure 1, there is a shear thinning area for each concentration curve. This phenomenon can be explained from the microstructure. When the shear rate is very low, the rate of polymer molecule rewinding is greater than the rate of shear deformation. However, above a certain shear rate, the polymer chains unravel under the action of flow and the molecular chains are oriented

in the flow direction, making the rearrangement rate is less than the rate of shear deformation, which leads to shear thinning phenomenon.
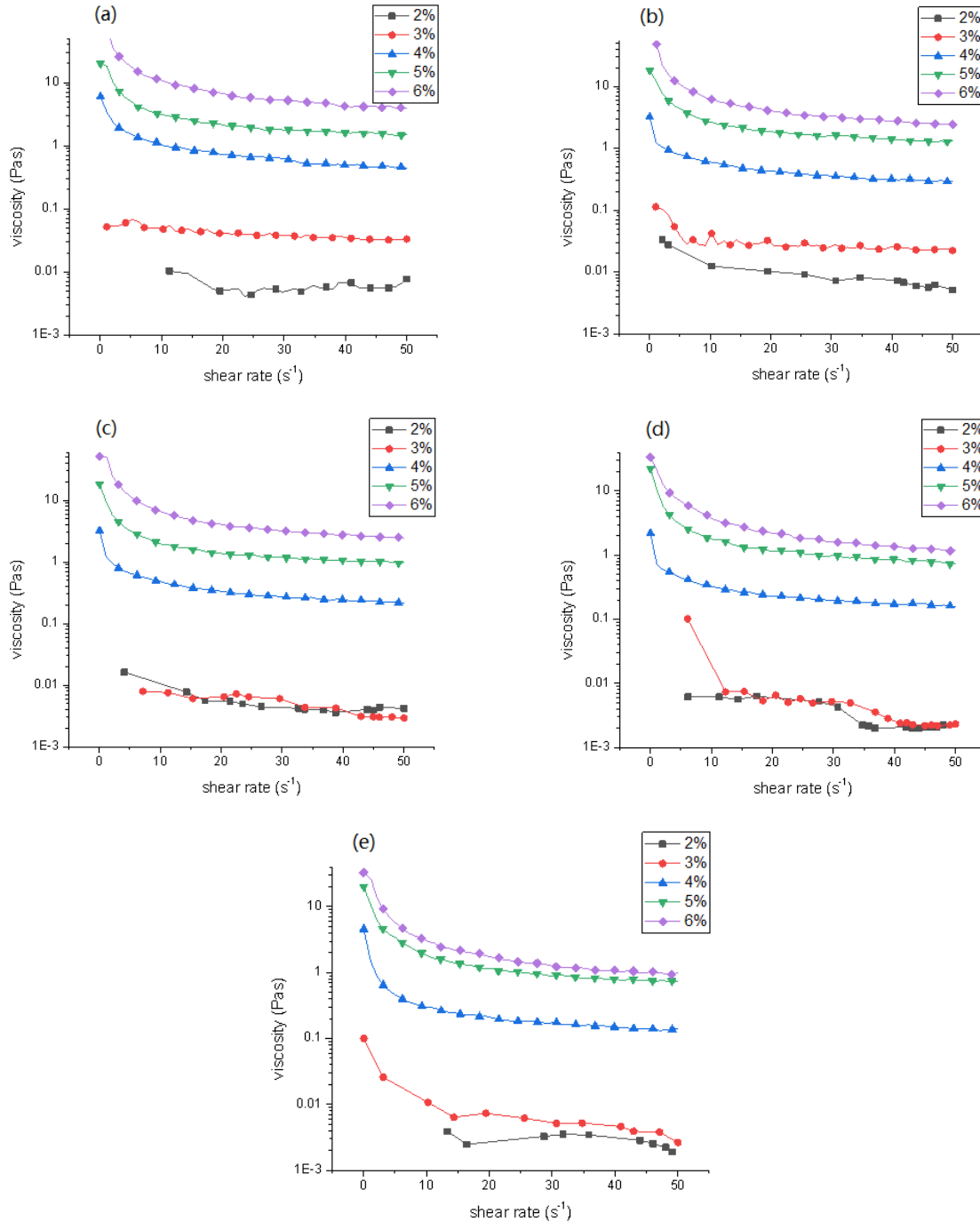

Figure 1. The steady-state flow curves of CMC/Eu-Tb various concentrations at different temperatures. (a)measured at 20℃ (b)measured at 30℃ (c)measured at 40℃ (d)measured at 50℃ (e)measured at 60℃.

The Power-law model fits the relationship between viscosity and shear rate. It can be written as [10]:

$$\eta_0 = K \dot{\gamma}^{n-1} \tag{1}$$

where η_0 (Pas) is apparent viscosity, $\dot{\gamma}$ (s^{-1}) is shear rate, K(Pas^n) is the consistency index, and n is the flow behavior index. When n=1, it is a Newtonian liquid; when n<1, it is a pseudoplastic fluid; when n>1, it is a swelling fluid.

Equation (1) can be converted to the following:

$$\ln \eta_0 = \ln K + (n-1)\ln \dot{\gamma} \tag{2}$$

Plot using the logarithm of viscosity and shear rate, then n value and K value can be calculated by slope and intercept. The values of n and K of CMC/Eu-Tb at different temperatures are shown in tables 1 and 2.

Table 1. The n value of CMC/Eu-Tb of various concentrations at different temperatures.

T(℃) Concentration	n value				
	2%	3%	4%	5%	6%
20	0.8639	0.8042	0.5486	0.5113	0.4715
30	0.7410	0.6441	0.6291	0.5336	0.4773
40	0.7183	0.6693	0.5679	0.5101	0.4301
50	0.8251	0.7897	0.6108	0.4612	0.4194
60	0.6237	0.5010	0.4508	0.4302	0.3659

Table 2. The K value of CMC/Eu-Tb of various concentrations at different temperatures.

T(℃) Concentration	K value				
	2%	3%	4%	5%	6%
20	0.0431	0.0728	2.7879	9.7865	33.1254
30	0.0142	0.0842	1.2870	7.8885	20.0554
40	0.0071	0.0104	1.2131	6.3745	23.4530
50	0.0032	0.0051	0.7559	6.2358	12.6962
60	0.0016	0.0182	1.1126	6.6839	12.0155

As can be seen from the tables 1 and 2, 2% and 3% CMC/Eu-Tb solutions present a nearly Newtonian behavior at 20 ℃. As the solutions concentration increases, the flow behavior index decreases sharply from 0.8639 to 0.4715. 4% to 6% CMC/Eu-Tb solutions present a pseudoplastic behavior. At the same temperature, n value decreases with increasing concentration, and K value increases with increasing concentration. However, under the same concentration, n value and K value are not significantly changed with the increase of temperature, but the trend is declining overall.

3.2. Frequency sweep test
Each concentration of CMC/Eu-Tb solutions was doing frequency sweep test. We worked in the linear viscoelastic regime when performing the frequency sweeps. The strain is 15%. The results are shown in figure 2.
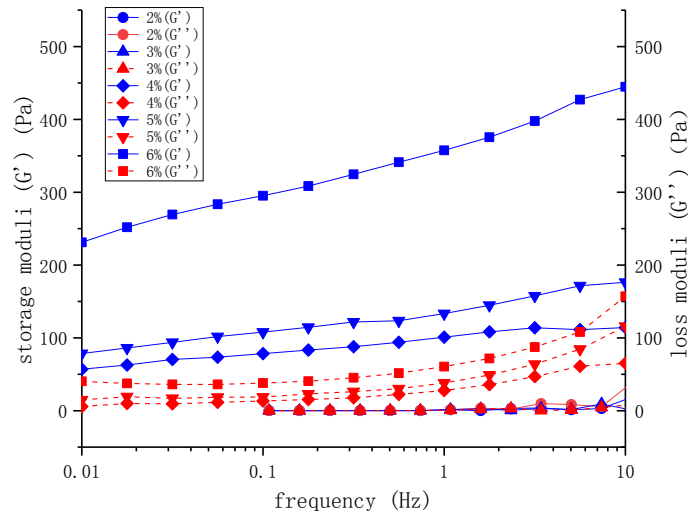
Figure 2. Frequency sweep curves of CMC/Eu-Tb at various concentration.

The results show that in the frequency sweep range, for CMC/Eu-Tb at concentrations of 2% to 3%, the viscous modulus G" is slightly higher than the elastic modulus G'; for CMC/Eu-Tb at concentrations of 4% to 6%, the elastic modulus G' is significantly higher than the viscous modulus G". It means that at the lower solution concentrations, the solutions tend to be less elastic and easier to flow. Most of the energies are lost through the viscous flow. As the solution concentrations increase, the solutions tend to be more elastic, and the system tends to form a gel.

3.3. Comparison of rheological properties of 3% CMC and 3% CMC/Eu-Tb
As can be seen in figure 3, the viscosity of CMC/Eu-Tb is lower than that of CMC, at the same concentrations; In addition, CMC has a lower elastic modulus G' than CMC/Eu-Tb and a higher viscous modulus G" than CMC/Eu-Tb. It is speculated that the degree of polymerization of CMC decreases after reacting with Eu^{3+} and Tb^{3+}, which leads to the phenomenon.
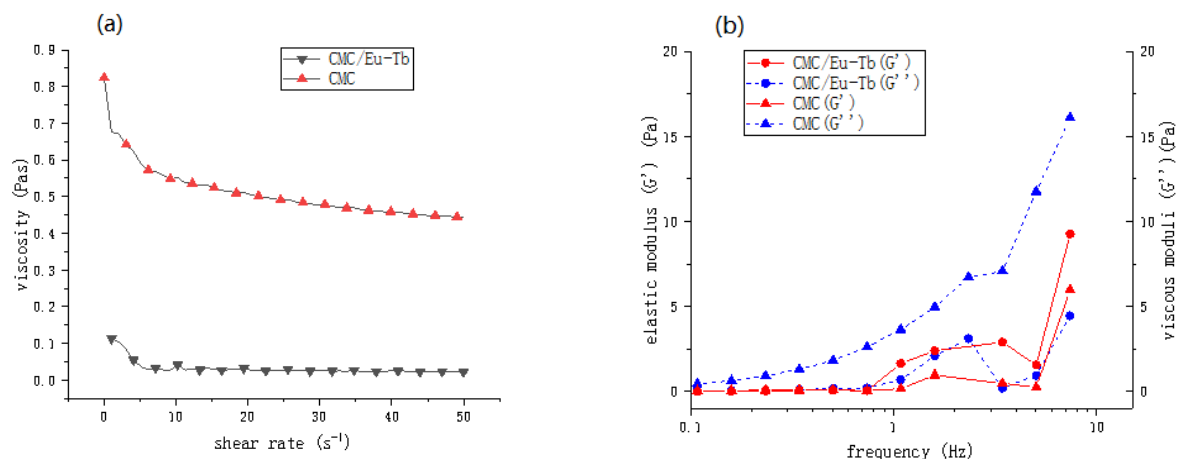

Figure 3. (a) The steady-state flow curves of 3%CMC/Eu-Tb and 3%CMC at 30℃ and (b) Frequency sweep curves of 3% CMC/Eu-Tb and 3% CMC.

4. Conclusions
The viscosity of CMC/Eu-Tb solution decreases with the increase of shear rate. The products solutions present the nearly Newtonian behavior at the low concentrations (2% - 3%); at the higher concentrations (4% - 6%), the products solutions present the pseudoplastic behavior; at the same temperature, flow behavior index decreases with increasing concentration, and consistency index increases with increasing concentration. In the experimental temperature range, the flow activation energy of CMC/Eu-Tb at various concentrations decreases with the increase of shear rate. Compared to CMC, the viscosity of CMC/Eu-Tb decreases.

Acknowledgments

References
[1]   Biswal D R and Singh R P 2004 Characterisation of carboxymethyl cellulose and polyacrylamide graft copolymer *Carbohydrate Polymers* **57** 379-87
[2]   McCoy S, Zuritz C and Sastry S 1987 *ASAE Paper* No. 87-6536 *ASAE International Winter Meeting* (Chicago, Illinois)
[3]   Abdelrahim K, *et al* 1994 Effects of concentration and temperature on carboxymethyl cellulose rheology *Food Science and Technology* **29** 243-53
[4]   Mohamed, *et al* 2000 Rheological properties of high concentrations of carboxymethyl Cellulose solutions *Applied Polymer* **79** 1787-801
[5]   Mamdouh, *et al* 1997 Rheological properties of carboxymethyl cellulose *Applied Polymer* **64** 289-301
[6]   Benchabane A and Bekkour K 2008 Rheological properties of carboxymethyl cellulose (CMC) solutions *Colloid and Polymer Science* **286** 1173-80
[7]   Li Q-Y, *et al* 2017 Structures and high fluorescence of novel nanocomposites of sodium carboxymethyl cellulose/Tb(III) prepared at different pHs *Polymer Composites* **38** E498-507
[8]   Liu Z L, *et al* 2011 Effect of Eu, Tb codoping on the luminescent properties of Y_2O_3 nanorods *Journal of Luminescence* **131** 12-6
[9]   Ye J, Wang B, *et al* 2016 Enhanced fluorescence and structural characteristics of carboxymethyl cellulose/Eu(III) nano-complex: Influence of reaction time *Carbohydrate Polymers* **135** 57-63
[10]   Michalis, *et al* 2009 On power-law relationships of the internet topology *ACM SIGCOMM Computer Communication Review* **29** 251-62