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Association behaviors between carboxymethyl cellulose and polylactic acid revealed by resonance light scattering spectra

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Abstract   Resonance light scattering (RLS) spectra were used to study the formation of complexes of carboxymethyl cellulose (CMC) and polylactic acid (PLA) in a mixed solvent of 10% DMSO/90% H_2O(V/V). The RLS results showed that the CMC and PLA could form a steady homogeneous complex due to the interaction of hydrogen bonding. With the increasing of CMC mass fraction in the complex, the observed durative enhancement RLS signal with two inflexion points indicated the forming of complexes and aggregation of complexes. The aggregation equilibrium and thermo stability of the complexes were also investigated based on RLS values.

Keywords   Carboxymethyl cellulose · Polylactic acid · Association ·
Complex · Resonance light scattering

Introduction

It is well known to us that when polymer-polymer interactions are stronger than the interactions inside of polymer-solvent, the two polymers can form interpolymer complexes (IPCs) upon mixing the two constituent polymer solutions in solvent [1]. IPCs have received much considerable research interest during the past decade mainly because of their important role in foods and related soft solid materials, and there is a continuing need to modify the properties of these materials for the

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enhanced and novel applications [2–4]. The IPCs can be formed by intermolecular secondary binding forces, such as coulombic interaction and hydrogen bonding, etc., and the properties of these complexes or blends strongly depend on the components and parameters of preparation process [5, 6].

The search for material-specific applications for natural polymers is currently a topic of great interest due to the increasing environmental concerns. Convenient blends of natural and biodegradable synthetic polymers with a reactive group capable of reacting with the natural polymer may be wide used ideally because the (IPCs) based on polysaccharides would be anticipated to give rise to a diversity of degradation phenomena according to the degree of graft substitution onto the carbohydrate backbone and the total composition [7, 8].

In the family of biodegradable synthetic polymers, poly(lactic acid) (PLA) appears to be the most attractive because of their facile availability, variable biodegradability, and good mechanical properties, which make it have the potential applications such as the drug delivery systems, sutures, and surgical implants [9–12]. Cellulose derivatives have attracted great interest in the past as they are used in food, cosmetics, pharmaceuticals, etc. [13]. But PLA is easy to be degraded and has high hydrophobic property, which limits its application to a certain extent. As for carboxymethyl cellulose (CMC), it is one important polymer based on the renewable resource and has been widely used in various applications due to the fact that the individual chains are highly stabilized by a well-organized system of hydrogen bonds present at intra or inter macromolecular chains [14, 15]. But the rigidity of molecule chains also brings some limitation in its application. Therefore, to investigate the association behaviors of CMC and PLA is important for understanding their performance in solution and expected to expand their usage for further wide-ranging application.

Up to now, some techniques have been used to investigate the interaction between different macromolecules such as small-angle neutron scattering or small-angle X-ray scattering, gel permeation chromatography, capillary electrophoresis, fluorescence spectra and so on [16–21]. In recent years, as a newly developed technique, resonance light scattering (RLS) has received much attention to determination of biological macromolecules, trace amounts of inorganic ions, molecular structure and investigating interaction mechanism for its simplicity, rapidity and sensitivity [22–25]. RLS is special elastic scattering which might emerge when the wavelength of light scattering is located at or close to the molecular absorption band. In this case, the frequency of the electromagnetic wave absorbed by the electron is approach to its scattering frequency which leads to intensively absorb and re-scattering. In particular, RLS can be easily obtained by simultaneously scanning of the excitation and emission monochromators of ordinary fluorometer and maintains some advantages of the conventional light scattering and fluorescent spectroscopy synchronously.

For the moment, the complexes formed from CMC and PLA have been scarcely reported. In this paper, the main objective focuses on interaction mechanism between CMC and PLA in mixing solvent through the RLS method. From the simple theory based on RLS values, the association abilities and the thermal stability of the complex have been revealed. In particular, RLS is employed to "see" the formation and aggregation of complexes in mixing solvent directly.

Experimental

Materials and preparation of samples

All chemicals are of analytical-reagent grade or the highest available purity. All aqueous solutions are prepared with distilled, deionized water. CMC is purchased from Guangzhou Chemical Reagent Co. and PLA from Shanghai Chemical Reagent Co. CMC(0.1 g, dry basis) is dispersed in 50 ml de-ionized water and heated above 90 °C until gelatinize the CMC molecules, then 10 ml DMSO is added and the sample is kept stirring for 15 min. Finally, the CMC solution is transferred into a 100 ml volumetric flask with the final concentration 1.0 g/l. The PLA solution (0.1 g/l) is prepared by melting in mixed solvent of 10% DMSO/90% H_2O (V/V) following the above procedure. Blends of different mass ratios (10:90, 20:80, 30:70, 40:60, 50:50, 70:30, 90:10, w/w, dry basis) of CMC to PLA are prepared by pipetting the calculated volume of CMC and PLA solution obtained above, respectively, mixing them by churn up to form homogeneous solutions before determination in spectrofluorometer.

Apparatus and general procedure

The samples obtained are added into series of 10-ml calibrated flask, then incubates at room temperature for 0.5 h subsequently. The RLS measurements are performed by scanning simultaneously the excitation and emission monochromators of the RF-5301PC spectrofluorometer (Kyoto, Japan). When fixed the wavelength interval ($\Delta\lambda = 0$ nm) and keep the slits 1.5 nm wide, the RLS spectra is obtained. The fluorescence spectrum is obtained when excited at 380 nm with the emission slit 3.0 nm. These above measurements carried out at room temperature. The thermal properties of these samples are performed by VARIAN Cary Eclipse (Australian) spectrofluorometer equipped with a thermostated cell compartment at a certain heating rate and keep the slit 3.0 nm wide.

Results and discussion

Character of RLS spectra

The RLS spectra of the CMC and CMC/PLA blend are shown in Fig. 1. In this case, a specific interaction is observed by the distinct change of RLS signal. As can be seen from the Fig. 1, the RLS character peaks of PLA are locked at 381 and 440 nm and the RLS character peaks of CMC are locked at 381 and 479 nm, respectively. For CMC/PLA blend, there are three RLS character peaks locked at 381, 436 and 465 nm, respectively. Obviously, the RLS intensity of CMC/PLA blend is much higher than the sum of RLS intensity of the individual component. This phenomenon strongly implies the interaction between CMC and PLA due to the presence of hydrophilic groups in CMC and carbonyl group in PLA (shown in Scheme 1), which leads to the formation of hydrogen bond and consequently results
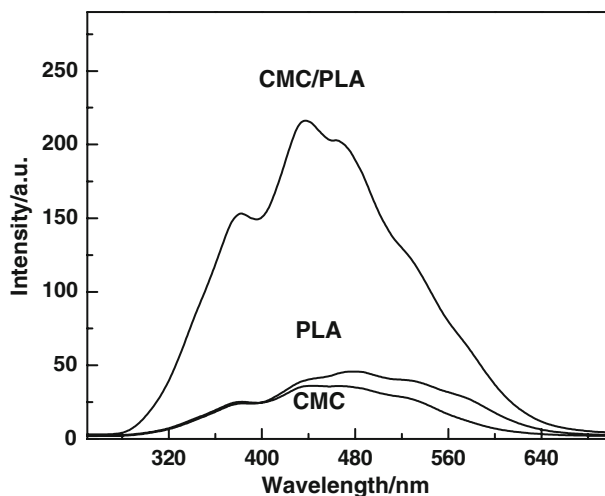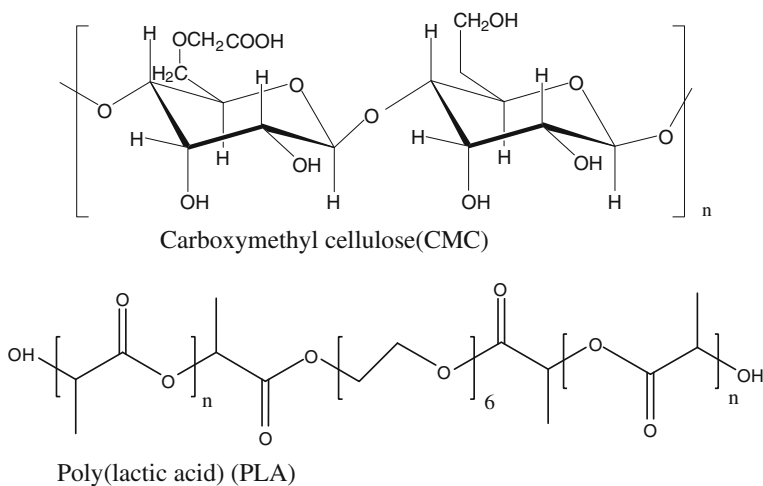
Fig. 1 RLS profile of CMC (0.1 mg/ml), PLA (0.1 mg/ml) and CMC/PLA = 1/1 blend

in the more swelled associates of PLA/CMC complex in comparative with the single polymer [26, 27].

Fluorescence emission evidence of association process of CMC and PLA

Another argument in favor of the association of CMC with PLA comes from the appearance of the weak fluorescence of PLA by addition of CMC. The fluorescence spectra of PLA, CMC and CMC/PLA blends are shows in Fig. 2 (excited at 390 nm). The characteristic fluorescence peak of PLA occurs at 448 nm with

Scheme 1 Schematic of the chemical structures of CMC and PLA molecules. Carboxymethyl cellulose (*CMC*) Poly(lactic acid) (*PLA*)
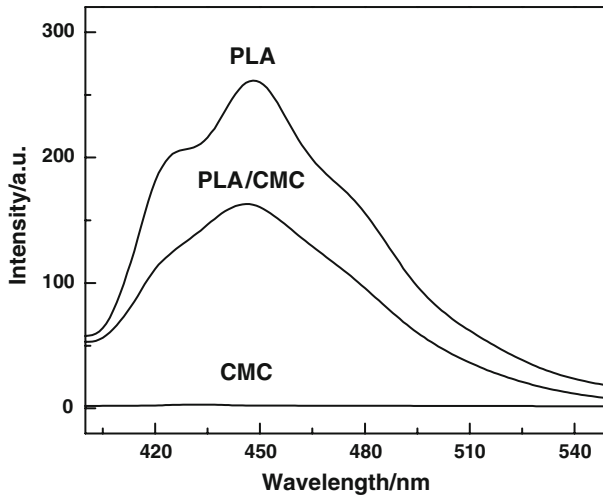
Fig. 2 Fluorescence spectra of CMC (0.1 mg/ml), PLA (0.1 mg/ml) and CMC/PLA = 1/1 blend

several shoulder peaks in the region from 390 to 560 nm, while CMC has no fluorescence emission. The blend of CMC to PLA not only results in the decrease of fluorescence intensity of PLA, but also leads to the blue shift of maximum emission wavelength from approximately 448–440 nm. It effectively suggests that there is association process between CMC and PLA. Probably the presence of hydrophilic groups along the CMC chains is likely to be responsible for formation of the stable CMC/PLA complex by hydrogen bonding which inhibiting the fluorescence emission of PLA [28].

Association process of CMC and PLA

Since the component ratio of two kinds of macromolecules can influence their association process in solution, to further understand the aforementioned results, the influence of the component ratio on the formation of CMC/PLA complexes has been considered. Figure 3a displays the RLS profiles of CMC/PLA complexes as a function of the mass ratio (MR) (MR = m_{CMC}/m_{PLA}) at room temperature. It can be seen that the RLS intensities of the blends increase as the MR increases. Because both the RLS intensity of single CMC and PLA are weak, this persistent increase of RLS intensity is due to the association process between CMC and PLA in solutions. Furthermore, in Fig. 3b, the plot of RLS intensity versus MR shows two obvious inflexion points at 5/5 and 7/3, suggesting some important characteristic of the interaction between these two polymers.

Figure 4 shows the schematic representation of the association process between PLA and CMC at various mass ratios. There are three regions with the change of the mass ratio as follows: (1) Formation of complexes, MR < 5/5. (2) Association equilibrium, 5/5 < MR < 7/3. (3) Turning into aggregate, MR > 7/3. When MR < 5/5, the RLS intensity of the complexes enhances dramatically, which can
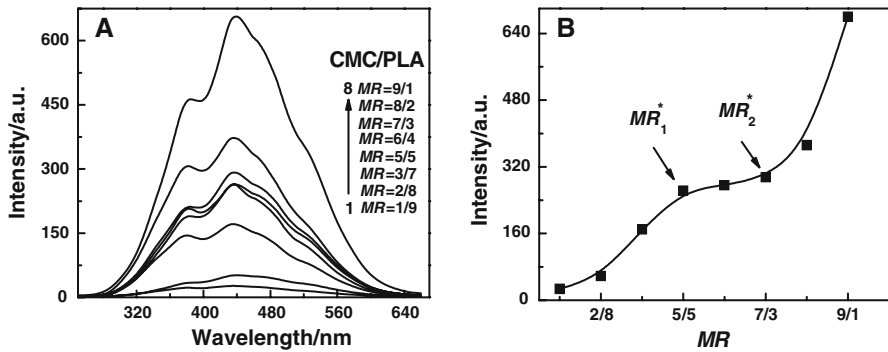
Fig. 3 RLS profile of CMC/PLA blends in different of mass ratio: **a** RLS profile as a function of wavelength; **b** RLS profiles as a function of mass ratios
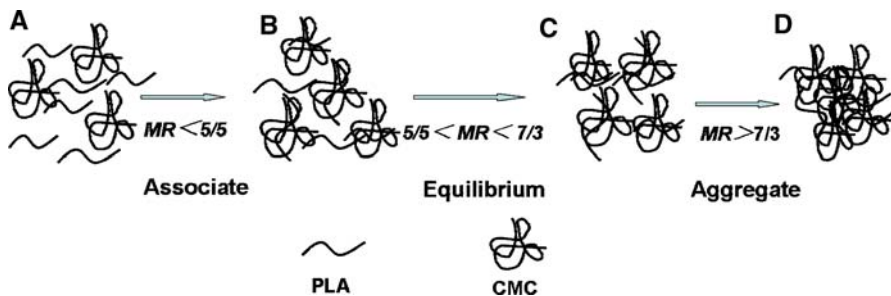

Fig. 4 Schematic representation of the association process between PLA and CMC

be attributed to the association process of these two polymers. The RLS intensities sharply grow up mainly because of the great change in shape of complex. Maybe PAA molecule chains are coiling for interaction with CMC by formation of hydrogen bonding. But with increasing the amount of CMC molecules, a plateau region appears in the range of 5/5 < MR < 7/3, this indicates the formation process of complexes reaches a temporary association equilibrium. Interestingly, in the range of MR from 7/3 to 9/1, the RLS intensity increases remarkably again, which implies at the MR 7/3, the aggregation of CMC/PLA complex might occur. This is because that the high concentration of CMC results in the aggregation of CMC/PLA complex by the interaction of hydrogen bonds between CMC and the complexes [29].

As can be seen from Fig. 3b, the presence of the aggregation for CMC/PLA complexes occurs when MR > 7/3. The aggregation process in solution can be explained on the basis of the simplistic association model [30]. The model assumes a dynamic equilibrium between aggregates of CMC/PLA complex.
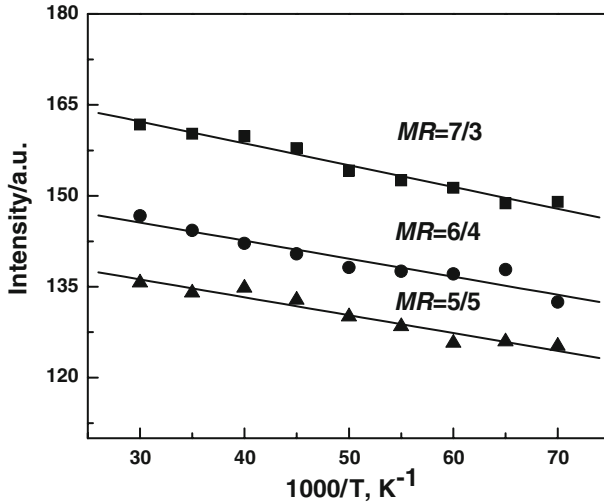
$$M_i + M = M_{i+1} \tag{1}$$

Fig. 5 Relationship of RLS intensity and temperatures for CMC/PLA complex with various mass ratios

where $i = 1, 2, \ldots$

Here M_i is the aggregate consisting of i particles. When gaining another particle, M_i is to become M_{i+1}. Then the equilibrium constant $K_{eq} = [M_{i+1}]/[M_i][M]$ can be obtained. So we can assume the aggregation equilibrium in different temperatures.

As shown in Fig. 5, the RLS intensity of CMC/PLA complexes at MR 7/3 does not change significantly as temperature increases, which means that K_{eq} is independent of temperature T. From the expression $K_{eq} \propto \exp[-\Delta H/RT + \Delta S/R]$, where R is the gas constant, ΔH and ΔS are the molar enthalpy change and the molar entropy change in aggregate process, temperature independence of K_{eq} can be leads to $\Delta H \approx 0$. This suggests that the aggregation formation is governed mainly by the entropy increase.

Thermal stability of CMC/PLA complexes revealed by RLS

For multicomponent polymer solutions, the total scattered intensity, I_{total}, is given by [31]:

$$I_{total} = I_{complex} + I_{CMC} + I_{PLA} \tag{2}$$

where I_{CMC}, I_{PLA} and $I_{complex}$ are the scattering light intensity from free CMC molecules, free PLA molecules and the formed complex between CMC and PLA, respectively. From Fig. 1, it can be seen that the scattering light intensity of free PLA and CMC is very low compared with the complex. In addition, in these polymer solution systems, there are few free CMC or PLA free molecules to exist due to their interaction, so the contribution of free CMC and PLA to the RLS intensity of the polymer solution system can be neglected, so the intensity of RLS produces mainly based on the aggregation of particles in solution [32].

In this case, to investigate thermal stability of CMC/PLA complexes not only can further confirm the formation of the complexes but also obtain some useful information of the complex structure. Here, we investigated the thermal stability of the CMC/PLA complex by calculating the apparent decomposition activation energy.

The apparent decomposition activation energy for the thermal stability of CMC/PLA was determined from the RLS curves could be expressed as a function of the relative extent of change for RLS intensity, α, using the general formulation [33]:

$$\frac{d(\alpha)}{dt} = kf(1 - \alpha) \tag{3}$$

α is the extent of change of RLS intensity and is given by

$$\alpha = (I_0 - I)/I_0$$

$$k = Ae^{-E/RT} \tag{4}$$

$$f(1 - \alpha) = (1 - \alpha)^n \tag{5}$$

where k is described as a rate constant, I_0 is the RLS intensity at the initial temperature and I is the RLS intensity of polymer at certain temperature, R is the gas constant, and the Eq. 3 can be transformed by

$$\frac{d(\alpha)}{dt} = Ae^{-E/RT}(1 - \alpha)^n \tag{6}$$

If we suppose the decomposition process to be the first order reaction, $n = 1, \Phi = \frac{dT}{dt}$ then Eq. 6 can be rewritten in the form:

$$\frac{d(\alpha)}{dT} = \frac{A}{\Phi} e^{-E/RT}(1 - \alpha) \tag{7}$$

where Φ is the heating rate, here keep a fixed constant in this case, E_a is the apparent activation energy, A is the exponential factor, and therefore the follow simplified formulary can be obtained

$$\ln[\ln[1/(1 - \alpha)]] = -E_a/RT + \ln[(R/E_a)(A/\Phi)T^2] \tag{8}$$

Plots of $\ln[\ln[1/(1 - \alpha)]]$ versus $1/T$ for the temperature range from 25 to 70 °C, then the values of the apparent activation energies, E_a can be determined from the slopes of these plots.

Figure 5 shows the representative plots for RLS intensity of CMC/PLA samples as a function of temperature with various mass ratios. It can be seen that the durative decrease of RLS intensity of CMC/PLA is found and these plots posses the good linear relation with increasing temperature. The slope of these plots augments with increasing MR, which reflects the association information of different samples at various temperatures. Obviously, from the mutative slopes of these plots of CMC/PLA samples with different MR, the most stable association of CMC and PLA probable occurs at MR = 5/5, because the change of RLS intensity of the complex is the least with changing the temperature. It implies that PLA molecules wrapped by CMC molecules in appropriate proportion are prone to form the steady complex.
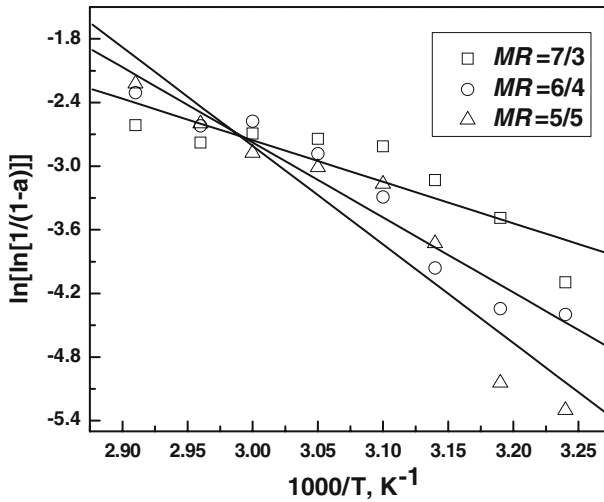
Fig. 6 Plots of $\ln[\ln[1/(1-\alpha)]]$ versus $10^3 T^{-1}(K^{-1})$ during the thermal degradation

Table 1 Activation energies and slope during the thermal treatment measured by RLS method

Sample	E_a (kJ/mol)	r
CMC/PLA = 7/3	19.05	0.876
CMC/PLA = 6/4	21.67	0.971
CMC/PLA = 5/5	22.43	0.946

To further make sure above conclusion, we estimate the apparent decomposition activation energy based on Eq. 8. As shown in Fig. 6, the fitting lines of $\ln[\ln[1/(1-\alpha)]]$ versus 1/T of CMC/PLA complexes with various MR are obtained by using Eq. 8. The slope and calculated apparent decomposition activation energies E_a of samples are listed in the Table 1. As seen from the Table 1, the E_a values for the samples with mass ratio 7/3, 6/4 and 5/5 are found to 19.05, 21.67, and 22.43 kJ/mol, respectively. This suggests that the sample with mass ratio 5/5 embodies a stronger association interaction between CMC and PLA and the relatively strong thermal stability of the complex, which leads to the increase of apparent activation energies of the decomposition process [34].

Conclusions

In this study, we report the possibility of association of CMC with PLA in solution without chemical modifications. The intermolecular hydrogen bonding between the oxygen atom of the carbonyl group of PLA and the hydrogen of the hydroxyl group of CMC is a mainly mode of action which leads to the forming of CMC/PLA complex. The thermal stability experimental results investigated by RLS indicate the complex of CMC/PLA formed with appropriate mass ratio has better thermal

stability property and the aggregation formation is governed mainly by entropy increase. As a simple, sensitive method, RLS is a useful tool to study the macromolecular interaction process and mechanism.

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