CELLULOSE CHEMISTRY AND TECHNOLOGY

SOLUBILITY OF SUPERCRITICAL CO_2 IN CELLULOSE NITRATE WITH AND WITHOUT ETHYL ACETATE

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In this paper, the gravimetric method and Fickian diffusion model were utilized to investigate the influence of ethyl acetate on the solubility of supercritical carbon dioxide ($scCO_2$) in cellulose nitrate at different saturation temperatures and pressures, and also the interactions in the $scCO_2$/ethyl acetate/cellulose nitrate system were researched by FTIR. The solubility increased a lot initially, but decreased subsequently with increasing the ethyl acetate content, which could be explained by the different interactions occurring in the $scCO_2$/ethyl acetate/cellulose nitrate system characterized by FTIR. The solubility reached the highest value (26.99 wt%) with 4 wt% ethyl acetate. It was also found that the solubility decreased with increasing the saturation temperature, but increased with increasing the saturation pressure. Meanwhile, the values of sorption and desorption diffusivity were proportional to the amount of CO_2 inside the cellulose nitrate matrix.

Keywords: $scCO_2$, cellulose nitrate, ethyl acetate, solubility, FTIR

INTRODUCTION

In polymer extrusion, increasing the processing temperature and introducing organic solvents and plasticizers are the general methods to reduce melt viscosity. However, some polymers, such as poly(lactic acid), poly (lactide-co-glycolide), polymide and wood plastic composite, are prone to degrade when increasing the processing temperature, which leads to reducing their service lives and application scope.[1-4] What is worse, most of the organic solvents are toxic, harmful and environmentally unfriendly. It has been found that supercritical carbon dioxide ($scCO_2$) dissolved in polymer melts can decrease the viscosity and lower the processing temperature resulting from the enhancement in the free volume of polymers and the lubrication in molecular chains. Meanwhile, the use of $scCO_2$ improves the processing efficiency and mechanical performances of polymer.[5-8]

As we know, a supercritical fluid (SCF) is defined as the substance whose both saturation temperature and pressure are higher than their critical values. Compared with traditional solvents, SCF has the properties of liquid-like density and gas-like viscosity, which make it a potential solvent for various applications.[9-11] It has been found that $scCO_2$ has been widely used in polymer processing due to its non-toxicity, non-flammability, chemical inertia and low cost.[12-14] These outstanding properties of $scCO_2$ make it ideally suited for replacing organic solvents in polymer processing. The amount of $scCO_2$ dissolved in polymers is a vital parameter for the selection of the solvent in the polymer extrusion process.[15,16] The more $scCO_2$ dissolved in polymers, the higher is the reduction in the processing viscosity. Generally, the solubility is influenced by various factors, such as saturation temperature, saturation pressure and, sometimes, the intermolecular interactions between $scCO_2$ and polymers. Fourier transform infrared spectroscopy (FTIR) is an outstanding and practical tool to investigate the specific interactions.[17-22] Many results suggest that the interactions between $scCO_2$ and polymers, containing Lewis base sites, should most likely be the Lewis acid-base reaction. Fried and Li[18] recorded the FTIR spectra of cellulose acetate (CA) and poly(methyl methacrylate)(PMMA) in the presence and absence of CO_2, and they found that the carbonyl stretching vibrations for CA and PMMA were shifted to higher wavenumber in the presence of CO_2. Kazarian[19-21] studied the effects of the carbonyl group of polymers on the interactions between CO_2 and polymers. There was a splitting of the bending mode when CO_2 appeared in polymers containing a carbonyl group, e.g. PMMA, where the carbonyl group acted as an electron donor and CO_2 acted as an electron acceptor. Besides, there was no such splitting reported in PS or PE. Nalawade[17,22] used FTIR to study the interactions between CO_2 and different polymers. The infrared spectra variations of high pressure CO_2 in polyesters (P120 and P130), poly(ethylene glycol) (PEG) and polyphenylene oxide (PPO) indicated that the characteristic vibration shifted to a higher wavenumber with the increasing CO_2 pressures.

Cellulose nitrate plays an important role in the society.[23-26] It is widely applied in a variety of industries, such as coating, weapon energy, automobile industry, pharmaceuticals, varnishes, artificial leather and image materials. The traditional forming process of cellulose nitrate introduces adequate organic solvents and plasticizers to decrease the glass transition temperature of cellulose nitrate, which is close to its melting and ignition temperatures. However, the harmful and environmentally unfriendly solvents are opposite to the sustainable development of human beings. Despite the huge potential of $scCO_2$ as a solvent and plasticizer in polymer extrusion, the investigation of $scCO_2$ solubility in cellulose nitrate is quite scarce.

Ethyl acetate, a common solvent used in the molding process of cellulose nitrate, was selected as a solvent in this work. Firstly, we explored variations in the solubility of $scCO_2$ in cellulose nitrate by changing the ethyl acetate contents, and FTIR was employed to study the interactions in the $scCO_2$/ethyl acetate/cellulose nitrate system. Secondly, the solubility of $scCO_2$ in cellulose nitrate was studied with the change of the saturation temperature and pressure when the ethyl acetate content was 2 wt%. Lastly, the influence of solubility on the desorption of CO_2 was researched. The results in this paper would provide the theoretical and experimental data for further studying a safe cellulose nitrate forming process assisted by $scCO_2$.

EXPERIMENTAL

Materials

Carbon dioxide with a purity of 99% was purchased from Nanjing Fifty-Five (China). Ethyl acetate (>99.7%) was supplied by Beijing Chemical Agent Corporation. The diameter and height of the cylinder cellulose nitrate samples were 3.50 mm and 1.50 mm, respectively.

Experimental process

In a typical experiment, the samples were weighed firstly by an analytical scale (Sartorius AG ALC-110.4, with sensitivity of 0.01 mg) to record the initial weight, and were subsequently put into a high-pressure vessel. After CO_2 was injected into the vessel to remove the air in the high-pressure vessel, ethyl acetate was added into the vessel, and the vessel was then closed. CO_2 was charged into the vessel to reach the feasible saturation pressure. After a dissolution period for a certain temperature and pressure, the vessel was rapidly depressurized and the samples were immediately transferred to the microbalance for desorption measurements. The mass of the samples was recorded every 10 seconds. From the experimental data, we can obtain the solubility of $scCO_2$ dissolved in cellulose nitrate.

The samples taken out from the vessel were immediately transferred into the FTIR spectrometer (Shimadzu IR Prestige-21) at room temperature and atmospheric pressure to investigate the interactions in the $scCO_2$/ethyl acetate/cellulose nitrate system.

Data analysis

The analysis of solubility is similar with that of Berens and co-workers.[27] The methods in analyzing the sorption and desorption data can be described according to Crank and Park[28] as equation (1):

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(- \frac{(2n+1)^2 \pi^2 D t}{L^2} \right) \qquad (1)$$

where M_t, L, D represent the amount of CO_2 absorbed into the polymer samples at time t, the sample thickness and the diffusion coefficient, respectively. For a long sorption process, equation (1) can be simplified as equation (2):

$$\frac{M_s}{M_\infty} = 1 - \frac{8}{\pi^2} \exp\left(-\frac{\pi^2 D_s t_s}{L^2} \right) \quad (2)$$

where M_s and D_s are the sorption amount after a certain period sorption time t_s and the sorption diffusivity.

Equation (2) was also applied to determine the sorption diffusivity by plotting $\ln(1-M_s/M_\infty)$ against (t_s/L^2). The short-time approximation of equation (1) can be directly introduced to analyze the desorption process following equation (3):

$$\frac{M_d}{M_\infty} = 1 - \frac{4}{L}\sqrt{\frac{D_d t_d}{\pi}} \quad (3)$$

where M_d and D_d represent the sorption amount at desorption time t_d and the desorption diffusivity. D_d was determined by plotting (M_d/M_∞) against $(t_d^{1/2}/L)$.

RESULTS AND DISCUSSION

Influence of ethyl acetate on solubility

The samples were saturated for 6 hours in the mixture of CO_2 and ethyl acetate (2 wt% of the samples) at 40 ^oC and 25 MPa. The desorption curves of cellulose nitrate, measured by the gravimetric method, are illustrated in Figure 1. The amount of CO_2 dissolved into cellulose nitrate (M_d) decreases with the desorption time (t_d). In spite of the fast desorption processing initially, it takes a long time for CO_2 to escape from the cellulose nitrate matrix. The linear relationship between M_d and the square root of t_d indicates that the Fickian diffusion law is suitable for describing the diffusion of CO_2 in cellulose nitrate, as shown in the inserted figure. According to the Fickian diffusion law,[29] the solubility of $scCO_2$ in cellulose nitrate is obtained by extrapolating M_d to $t_d^{1/2}=0$ linearly. The solubility in this condition is about 17.13 wt% calculated from the Fickian diffusion law.

In accord with the aforementioned method, the effects of ethyl acetate contents (0-5 wt%) on solubility were studied as shown in Figure 2. The presence of ethyl acetate actually accelerates the equilibrium rate of CO_2 dissolving into cellulose nitrate. Moreover, compared with the absence of ethyl acetate, it takes less time to achieve the dissolution equilibrium. The solubility is obviously facilitated by the means of introducing a small amount of ethyl acetate into the $scCO_2$/cellulose nitrate system. As shown in Table 1, the equilibrium solubility increases with increasing the content of ethyl acetate when the ethyl acetate content is no more than 4 wt%. However, the solubility decreases with a higher solvent content (5 wt%) instead. Simon[30] thought that the variation of solubility resulting from the addition of solvents was due to the additional interactions between the solute and the solvent. Hence, we utilized an FTIR spectrometer to investigate the interactions in the $scCO_2$/ethyl acetate/cellulose nitrate system.

Infrared spectroscopy was employed to study the changes in the band shift of the nitrate ester group of cellulose nitrate, as shown in Figure 3. The center of the IR absorption band of the nitrate ester groups in the $scCO_2$/cellulose nitrate system shifts from 1636.1 cm^{-1} (Figure 3 line a) to 1635.7 cm^{-1} (Figure 3 b). The tiny red shift by 0.4 cm^{-1} after the $scCO_2$ treatment implies weak interactions between CO_2 and the nitrate ester group of cellulose nitrate. When the contents of ethyl acetate in the $scCO_2$/ethyl acetate/cellulose nitrate system are 2 wt%, 3 wt% and 4 wt%, respectively, the centers of the FTIR absorption band shift toward a higher frequency by 5 cm^{-1} (Figure 3 c), 6 cm^{-1} (Figure 3 d), 7 cm^{-1} (Figure 3 e), respectively. When the ethyl acetate content is 5 wt%, the band shifts toward a higher frequency, 5 cm^{-1} (Figure 3 f), which is lower than those of 3 wt% and 4 wt%. The decrease in the shift with 5 wt% ethyl acetate may be the contribution of the solvent-solvent interactions rather than the solvent-polymer interactions. Domingo[31] reported a similar phenomenon in the study of the solubility of $scCO_2$ and acetone in polymethylmethacrylate (PMMA). The sorption amount, as a function of acetone contents (ranging from 7.0 to 32.0 wt%), reached the maximum value when the acetone content was 15 wt%. Domingo thought that the decrease in solubility with higher acetone content resulted from the solvent-solvent interactions, which were greater than the solvent-polymer interactions.

Figure 4 shows the band variation of the antisymmetric stretching mode of CO_2. Compared with 2 wt%, 3 wt% or 4 wt% ethyl acetate, the band of the antisymmetric stretching mode of CO_2 seems to have no changes basically when the ethyl acetate content is 5 wt%. It suggests that the CO_2-ethyl acetate interactions do not increase with increasing the ethyl acetate content. The decrease in solubility at a high ethyl acetate content (5 wt%) may be attributed to an increase in the interactions between ethyl acetate itself.

Table 1
Comparison of M_∞, D_d and D_s of SC-CO_2 in cellulose nitrate

SC-CO_2+ethyl acetate	M_∞ (wt%)	D_d ($10^{-10}m^2/s$)	D_s ($10^{-10}m^2/s$)
SC-CO_2+0wt%ethyl acetate	15.7419	1.1503	0.3449
SC-CO_2+2wt%ethyl acetate	17.1287	2.7908	0.4969
SC-CO_2+3wt%ethyl acetate	23.9493	10.8369	0.5151
SC-CO_2+4wt%ethyl acetate	26.9882	13.2571	0.5426
SC-CO_2+5wt%ethyl acetate	22.0778	4.8886	0.5051

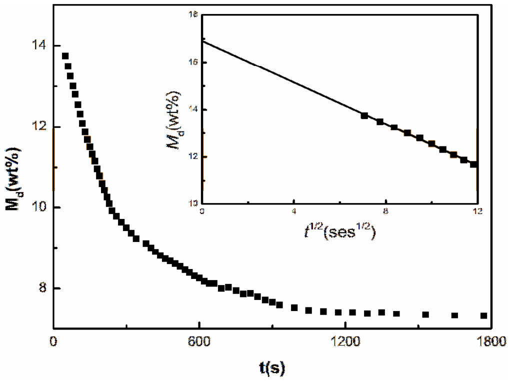

Figure 1: Desorption curve of $scCO_2$ in cellulose nitrate (Inset plot of M_d as a function of $t^{1/2}$ for an initially short desorption time)

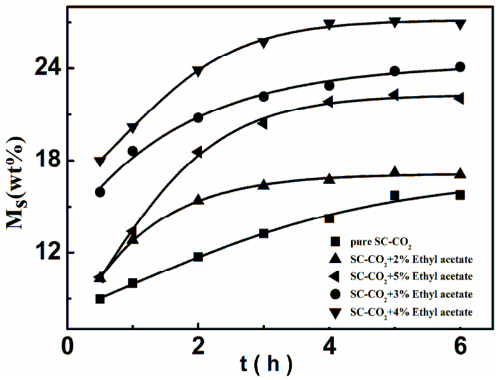

Figure 2: Effects of ethyl acetate content on the solubility of $scCO_2$ in cellulose nitrate

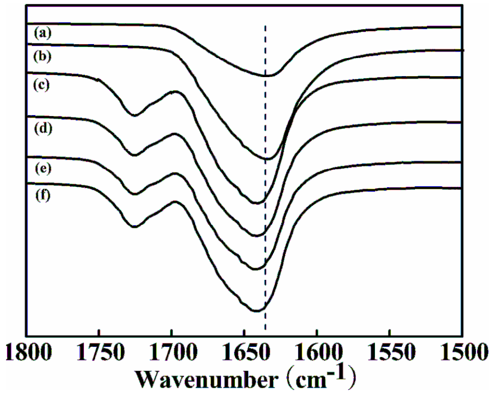

Figure 3: FTIR spectra of the nitrate ester group of cellulose nitrate for: (a) before; and immediately after $scCO_2$ treatment containing ethyl acetate (b) none; (c) 2 wt%; (c) 3 wt%; (d) 4 wt%; (f) 5 wt%

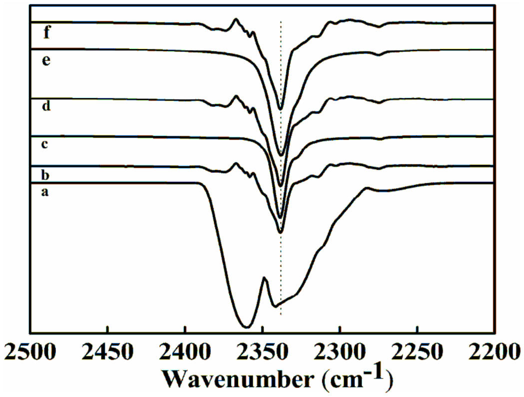

Figure 4: Comparison of FTIR spectra for the antisymmetric stretching mode of CO_2 for (a) scCO2; $scCO_2$ containing ethyl acetate; (b) 2 wt%; (c) 3 wt%; (d) 4 wt%; (f) 5 wt%

Therefore, the enhancement of solubility with the addition of ethyl acetate is presented as following. As ethyl acetate is carried into the cellulose nitrate matrix by CO_2, its plasticization performance on cellulose nitrate causes a reduction in the entanglement among the molecular chains of cellulose nitrate, and it results in increasing the free volume of the samples. Consequently, the presence of ethyl acetate accelerates the mass transfer of CO_2 into cellulose nitrate. That is, it is easy for CO_2 to dissolve into cellulose nitrate, which enhances the solubility. When the content is 5 wt%, greater interactions between ethyl acetate itself lead to a decrease in the plasticization of ethyl acetate. Thus, the solubility drops off subsequently.

Influence of saturation temperature and pressure on solubility

For a given content of ethyl acetate (2 wt%), the effects on solubility and diffusion are studied when the saturation temperature ranges from 40 °C to 60 °C and the saturation pressure ranges from 15 MPa to 25 MPa.

Figure 5 shows the curves of solubility with the changing pressure at the different saturation temperatures. The solubility of $scCO_2$ in cellulose nitrate containing ethyl acetate (represented by the upper three solid lines) is higher than those without ethyl acetate (represented by the lower three dotted lines). It demonstrates that the addition of ethyl acetate not only leads to a dramatic increase in solubility, but also shortens the period of equilibrium time. The growth in saturation pressure at the same saturation temperature leads to an increase in solubility. However, the pressure does not make a distinct difference in equilibrium time. The increase of saturation pressure leads to the increase of the molecular potential energy of CO_2, and CO_2 can be compressed into the cellulose nitrate matrix more easily. Therefore, the solubility increases with the increasing saturation pressure.

Figure 6 shows the solubility curves at different saturation temperatures under 25 MPa. The solubility decreases with increasing the saturation temperature, which is corresponding with the Arrhenius diffusion law. Because of the increasing saturation temperature, the attraction between CO_2 and cellulose nitrate decreases, and CO_2 trends to escape from the cellulose nitrate matrix resulting from the higher saturated vapor pressure. Furthermore, the saturation temperature seems to be more significant than the saturation pressure in affecting the equilibrium time, and it comes faster at a higher saturation temperature.

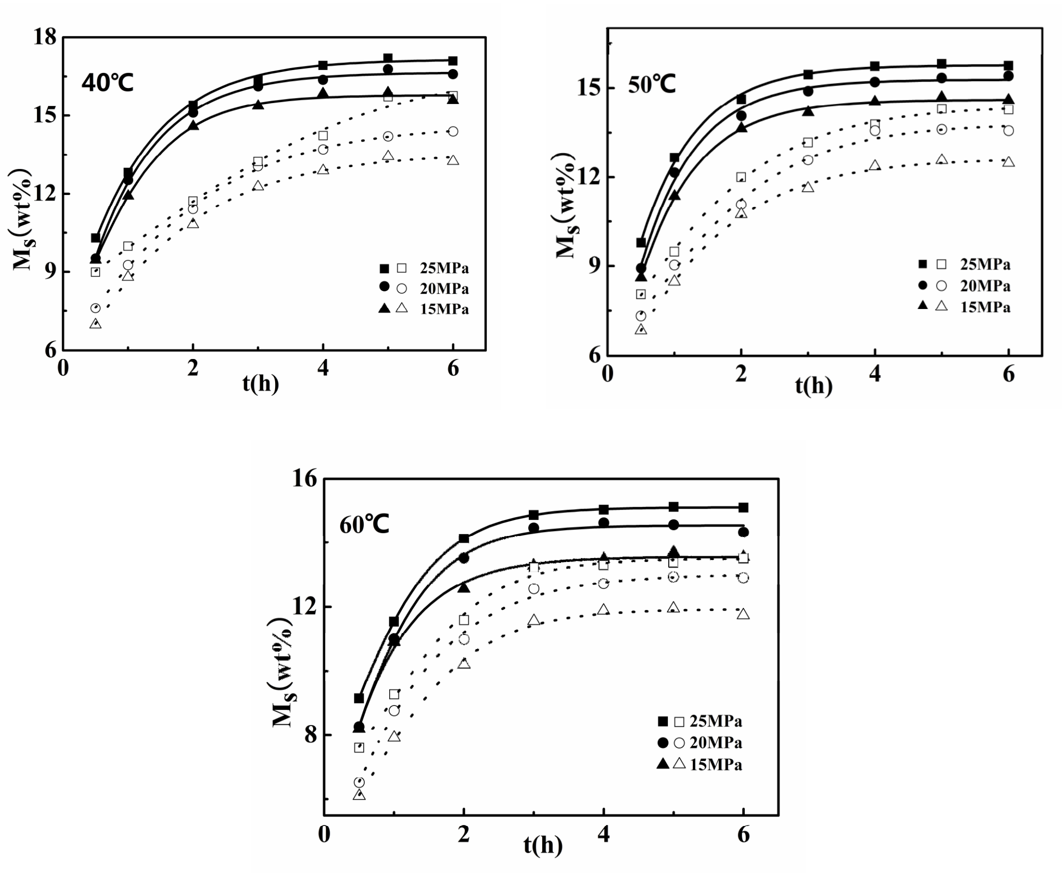

Figure 5: Solubility curves at different saturation pressures (15 MPa, 20 MPa, 25 MPa) and temperatures (40 °C, 50 °C, 60 °C) (Dotted line: $scCO_2$; solid line: $scCO_2$ containing ethyl acetate)

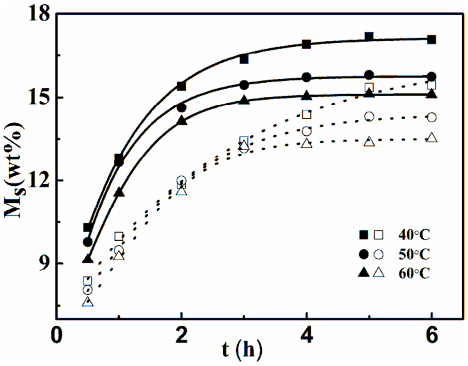

Figure 6: Solubility curves at different saturation temperatures under 25 MPa (Dotted line: $scCO_2$; solid line: $scCO_2$ containing ethyl acetate)

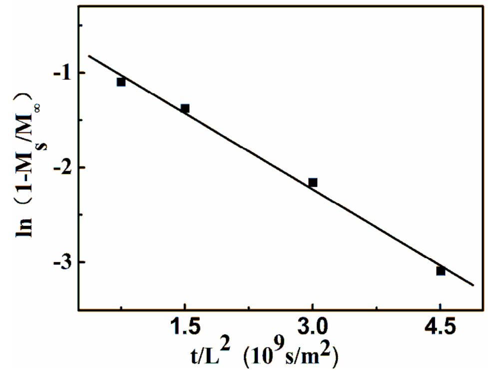

Figure 7: Plot of $\ln(1-M_S/M_\infty)$ against (t_s/L^2) after different saturation time

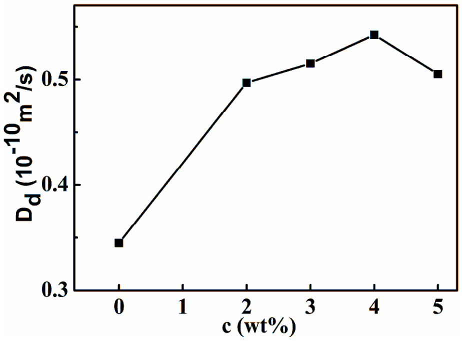

Figure 8: Plot of the sorption diffusivity against ethyl acetate content

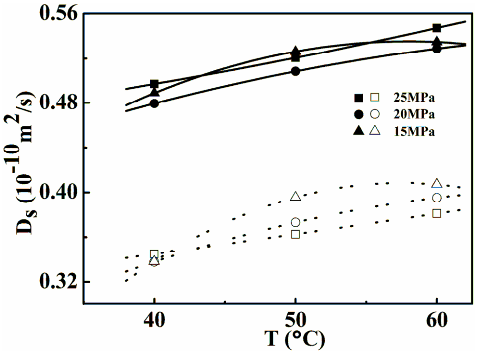

Figure 9: Influence of saturation pressure and temperature on the sorption diffusivity (Dotted line: SC-CO_2; solid line: SC-CO_2 containing ethyl acetate)

Sorption diffusivity of CO_2 in cellulose nitrate

Figure 7 shows the plot of $\ln(1-M_s/M_\infty)$ against (t_s/L^2). The sorption diffusivity (D_s) during different saturation time in the mixture of CO_2 and 2 wt% ethyl acetate at 40 °C and 25 MPa could be evaluated from the slope of the graph and calculated by equation (2). The D_s values for other experimental conditions are then obtained with the same method.

As Figure 8 shows, it can be concluded that D_s at 40 °C and 25 MPa, as a function of ethyl acetate contents (ranging from 0 to 5 wt%), firstly increases and then decreases, and it reaches the maximum value (5.426×10^{-11} m^2/s) when the ethyl acetate content is 4 wt%. The variation tendency of D_s is in accordance with the CO_2 solubility in cellulose nitrate, which is related to the interactions in the $scCO_2$/ethyl acetate/cellulose nitrate-acetate system.

In Figure 9, it can be seen that D_s increases with increasing the saturation temperature and shows no distinct trend with the variation in the saturation pressure. Compared with the dotted lines, there is a remarkable enhancement in D_s in the presence of ethyl acetate (2 wt%) as the solid lines, which could be contributed to the plasticization performance of ethyl acetate.

Desorption diffusivity of CO_2 in cellulose nitrate

After the samples were saturated for 6 h in the mixture of CO_2 and 2 wt% ethyl acetate at 40 °C and 25 MPa, the desorption diffusivity (D_d) could be obtained by the slope of (M_d/M_∞) against ($t_d^{1/2}/L$) and calculated by equation (3), as shown in Figure 10.

In Figure 11, D_d increases with increasing the ethyl acetate content till 4 wt%. At 5 wt%, D_d decreases instead, and the variation is similar to that of the solubility, as observed above. It is obvious that the desorption process occurs when the samples are under conditions of ambient temperature and atmospheric pressure. Therefore, D_d values are just related with the mount of CO_2 in the cellulose nitrate specimens.

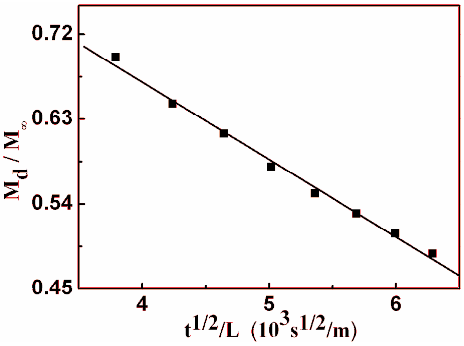

Figure 10: Plot of (M_d/M_∞) against ($t_d^{1/2}/L$)

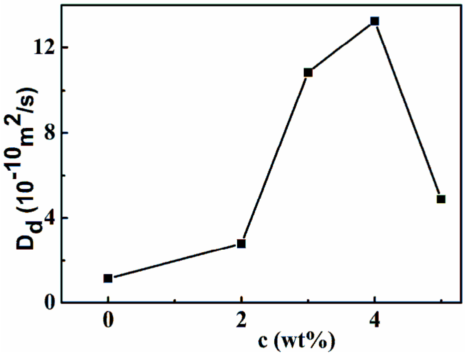

Figure 11: Plot of desorption diffusivity against ethyl acetate content

CONCLUSION

The gravimetric method was applied to study the influence of ethyl acetate on the solubility of $scCO_2$ in cellulose nitrate, and the interactions between $scCO_2$ and cellulose nitrate were explored by FTIR with and without ethyl acetate. A remarkable enhancement in solubility, as well as an obvious decrease in the saturation time, is performed by the introduction of ethyl acetate into the $scCO_2$/cellulose nitrate matrix, and are both ascribed to the interactions in the $scCO_2$/ethyl acetate/cellulose nitrate system. The interactions were characterized by FTIR. When the ethyl acetate content is not more than 4 wt%, the equilibrium solubility of $scCO_2$ in cellulose nitrate increases with increasing the content, while their values decrease at a higher solvent percentage (5 wt%) instead. FTIR proves that the interactions between ethyl acetate itself produce unfavorable effects on the ethyl acetate-cellulose nitrate interactions. Meanwhile, the results indicate that the higher saturation pressure favors the solubility, while the solubility decreases with increasing the saturation temperature. The equilibrium solubility (2 wt% ethyl acetate) reaches a maximum value, while the saturation temperature is 40 °C and the saturation pressure is 25 MPa, and the minimum value appears at 60 °C and 15 MPa. The sorption diffusivity values increase with increasing the saturation temperature, which is similar to the change rule of solubility. The values of desorption diffusivity are proportional to the amount of CO_2 dissolved into the cellulose nitrate matrix.

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