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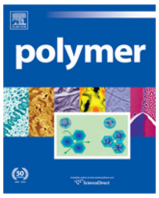

Physical gelation of cellulose acetate propionate solutions mediated by metal carbonyl complexes

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ABSTRACT

The weak physical gelation of cellulose acetate propionate–butyl butyrate solutions as a result of the in-situ decomposition of iron pentacarbonyl complexes was explored. Viscometry and infrared spectroscopy were used to monitor the iron pentacarbonyl decomposition reaction progress and its effect on viscosity. Changes in viscosity in of the cellulosic fluids in general and gelation in particular were found to be dependent upon the environment in which the $Fe(CO)_5$ decompositions occurred. Systems under inert atmospheres exhibited a marked increase in viscosity, while systems under oxidative atmospheres exhibited a general *decrease* in viscosity. We propose a hypothesis that explains the dependence of the viscosity of these cellulosic fluids as a function of the environmental conditions during the precursor decomposition. Under nitrogen atmospheres, zero-valent nanoparticles with highly reactive surfaces are synthesized, which form weak, transient bonds with the cellulosic polymer. The iron particles, under these circumstances, serve as weak bridges between adjacent polymer chains. Conversely, the primary particles synthesized under an oxidative atmosphere are metal oxides, which are less attractive to the polymer chain and, therefore, do not yield such bridges. This work demonstrates the capability to apply a simple method to control the viscosity of cellulose ester fluids.

1. Introduction

Metal carbonyl complexes have attracted much attention in the nanomaterials literature because of their ability to form metal or metal oxide nanoparticles of narrow size distribution in polymeric media [1–5]. However, despite the extensive use of these complexes as metallic precursors, their ability to increase the viscosity of some polymer systems has been largely overlooked. Rolker and Glasner [6,7] observed that the viscosity of ester-containing polymers was increased when they were treated with iron, cobalt, or nickel carbonyl complexes at elevated temperatures in nitrogen. In this process, the metal carbonyls were assumed to behave as catalysts for increasing the degree of polymerization. Rolker's work emphasized only the impact of this high-temperature treatment on the polymer system, and the mechanism of this phenomenon has not been elucidated. Hence, one of the goals of this work is to determine whether the metal complexes behave as catalysts for covalent polymer–polymer bonding, as Rolker asserts, or whether their reactive decomposition generates products that associate with the polymer chains.

We will show that the thermal decomposition of $Fe(CO)_5$ in a cellulose acetate propionate–butyl butyrate fluid leads to an increase in viscosity, even up to the point of thermoreversible weak physical gel formation. This increase in viscosity will be shown to be a result of the interactions of the metal carbonyl decomposition intermediates and products with the polymer.

Cellulose acetate propionate (CAP) is a particularly interesting polymer in which to examine the influence of metal carbonyl complex thermal decomposition. It is a cellulose ester of the general formula shown in Fig. 1 and a derivative of cellulose, a macromolecule that accounts for over half the carbon in the biosphere [8]. Rolker's work indicates that ester bonds are critical to the phenomenon described above [6,7]; therefore, CAP, with its abundance of ester bonds along the polymer chain, is an appropriate candidate for this study.

In this study, we examined the changes in the viscosity of cellulose acetate propionate–butyl butyrate–iron pentacarbonyl systems. We observed the occurrence of gelation under specific

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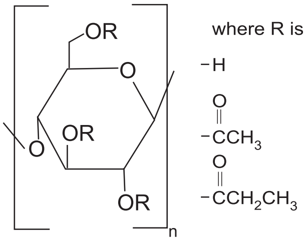

Fig. 1. The structure of cellulose acetate propionate. Not all of the original cellulose OH groups are converted in the esterification process, and esterification may occur at any of the three original OH positions.

conditions and developed a framework for the understanding of the underlying mechanism of this phenomenon.

2. Experimental

Unless otherwise noted, all polymers, reagents, and solvents were purchased and used as received from Sigma Aldrich. In a typical experiment, 4.0 g of cellulose acetate propionate (CAP) (75,000 g/mol M_W, $DS_{propionyl} = 2.5$, $DS_{acetyl} = 0.2$) was added to a 100 mL volumetric flask, which was filled with butyl butyrate (144.211 g/mol, 0.89 g/cm^3). This fluid, along with a magnetic stirring bar, was poured into a 100 mL three-neck flask, equipped with a magnetic stirrer, a thermometer, a condenser, and a septum stopper. Depending on the experiment, a specific gas (either oxygen or nitrogen) was bubbled through the fluid at 15 mL/min for at least 5 h before reaction at room temperature.

This sealed, purged flask was heated to 150 °C, and 7.6 mM filtered iron pentacarbonyl, $Fe(CO)_5$, 99.5% (195.895 g/mol, 1.49 g/cm^3) was added to it. This temperature was maintained until the $Fe(CO)_5$ carbonyl peaks in the infrared were no longer observed. The specifics of the above reaction procedure were modified as necessary to accommodate various experimental variables (*e.g.* the identity of the metal carbonyl). For example, triruthenium dodecacarbonyl, which is a solid at room temperature, was dissolved in butyl butyrate before its addition to the polymer solution.

Aliquots were removed via syringe through the septum stopper before, during, and after the reaction. The samples were analyzed via viscometry and Fourier transform infrared (FTIR) spectroscopy. The progress of the thermally-induced decomposition reaction was monitored by infrared spectroscopy. For liquid specimens, KBr windows surrounded a 250 μm liquid film, which was analyzed in a Thermo Nexus 670 infrared spectrometer. For each specimen, 128 scans were taken at a resolution of 2 cm^{-1}, and concentration was correlated to absorbance by Beer's Law. Viscosity was used to measure the resistance to flow of the fluids during $Fe(CO)_5$ thermolysis and was determined with a Haake model RV20 viscometer with an NVST-II spindle and cylinder at 22 °C.

For transmission electron microscopy (TEM) analysis, 20 µL of fluid were dropped, *via* micropipette, onto a carbon-coated copper grid (Ted Pella) resting on filter paper. A Hitachi HF-2000 transmission electron microsocpe with 200 kV accelerating voltage was used for imaging the formed particles.

3. Results and discussion

The viscosity of the fluid was strongly dependent upon the environment in which the metal carbonyl decompositions occurred. Fig. 2 shows the shear rate-dependent room-temperature viscosity of 7.6 mM $Fe(CO)_5$ in a 4.0% (w/v) CAP–butyl butyrate system bubbled with oxygen (a) and nitrogen (b) at 150 °C as a function of $Fe(CO)_5$ reaction time. The room-temperature viscosity of the former system decreased considerably as a function of time, while the viscosity of the latter system increased significantly. The latter system formed a gel at room-temperature after about 2 h of reaction of the $Fe(CO)_5$, and the viscosity of the former system approached that of pure solvent after the same amount of time at room temperature.

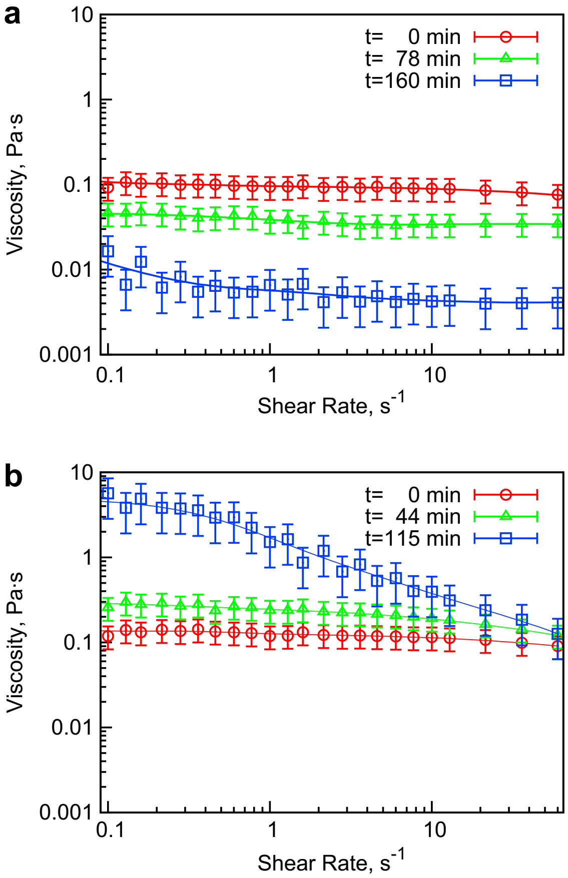

Fig. 2. a) Room-temperature viscosity of the oxygenated CAP–butyl butyrate-$Fe(CO)_5$ system. The viscosity decreased significantly over time. b) Room-temperature viscosity of the nitrogenated CAP–butyl butyrate–$Fe(CO)_5$ system. The viscosity increased significantly for 2 h of $Fe(CO)_5$ thermolysis, after which a room-temperature gel was observed.

The dependence of the viscosity of these systems on the environmental conditions under which the decomposition was conducted is shown in Fig. 3, which shows the room-temperature viscosity at a fixed shear rate, arbitrarily chosen as 10 s^{-1}, along with $Fe(CO)_5$ concentration as determined by the disappearance of the carbonyl absorption bands at 2021 and 1996 cm^{-1}, corresponding to the singly degenerate out-of-phase motion of the axial carbonyls with A2" symmetry (axial stretching mode) and to the doubly degenerate motion of the equatorial carbonyls with E′ symmetry (equatorial mode), respectively [9–14] as a function of decomposition reaction time, as shown in Fig. 4.

The $Fe(CO)_5$ concentration-viscosity-time plots for both the system under a nitrogen atmosphere (Fig. 3 a) and the system under an oxygen atmosphere (Fig. 3 b) reveal opposing correlations between decomposition reaction kinetics and the viscosities of these systems. The decomposition reaction of the metal carbonyl precursor occurred faster in oxygen. In oxygen, the reaction was 95% complete at approximately 60 min, while the reaction was 95% complete in nitrogen at about 90 min. This discrepancy in reaction rate is most likely due to additional reaction pathways that were not possible in inert atmosphere. Under these conditions, $Fe(CO)_5$

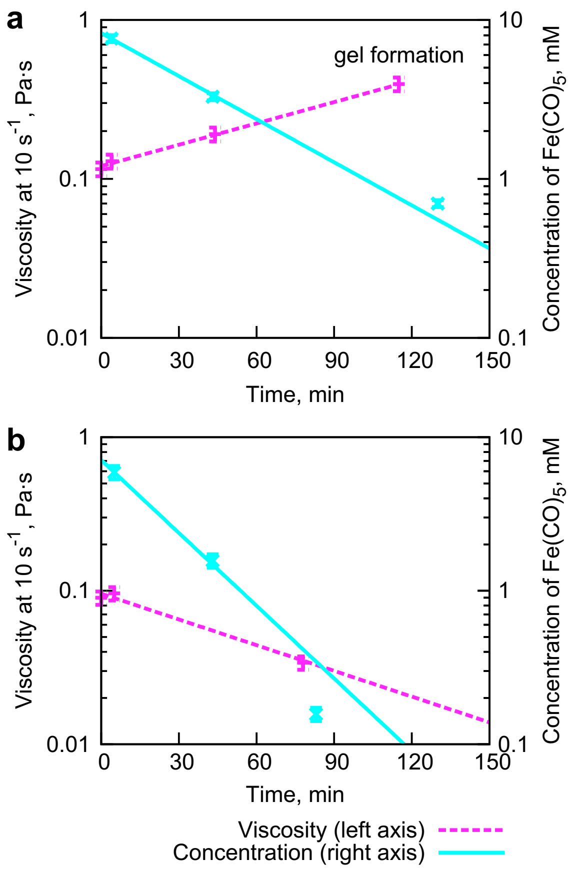

Fig. 3. Room-temperature viscosity and $Fe(CO)_5$ concentration of a) the nitrogenated CAP–butyl butyrate–$Fe(CO)_5$ system and b) the oxygenated CAP–butyl butyrate–$Fe(CO)_5$ system as a function of time. The lines represent best-fit first order kinetics.

(or, most likely, one of its highly reactive derivatives) was able to react directly with elemental oxygen to form an oxide [15,16].

Unlike the decomposition reaction rates that show the same general behavior for both the oxygen and inert environments (albeit the modestly different rates), the viscosities in both systems exhibit opposing behavior as a function of reaction time. The decrease in viscosity in the oxygenated system can be understood after performing a control experiment in the absence of $Fe(CO)_5$. A 4.0% CAP–butyl butyrate system showed a similar decrease in room-temperature viscosity when heated at 150 °C over the same time period, possibly due to the significant polymer scission that may occur under these conditions. This likely depolymerization is peripheral to this work; however, we shall speculate about its mechanism briefly. Glycosidic bonds are quite susceptible to oxidative cleavage under acidic and basic conditions [17], which could exist after ester hydrolysis along the polymer chain around 150 °C [18].

Hence, the decrease in polymer molecular weight that is responsible for the decrease in viscosity for both the $Fe(CO)_5$-containing polymer solution and the $Fe(CO)_5$-free polymer solution (Figs. 2a and 3b) is most likely caused by the thermal treatment. Conversely, the viscosity of a similar control solution placed under nitrogen remained unchanged. Moreover, the room-temperature viscosity of a $Fe(CO)_5$–CAP–butyl butyrate solution increased and eventually led to weak physical gelation.

While the decrease in the viscosity of the oxygenated system is easily explained, the reasons for the increase in viscosity and subsequent gelation of the Fe(CO)5–CAP–butyl butyrate solution that was placed under a nitrogen atmosphere are less obvious. In order to explain the increase in room-temperature viscosity and subsequent gelation of the nitrogenated $Fe(CO)_5$–CAP–butyl butyrate system, we first compared it to the control for which the viscosity remained unchanged. Therefore, it can be concluded that the increase in viscosity and subsequent onset of gelation was somehow related to the presence of the $Fe(CO)_5$ in the system.

The explanation that we propose (Fig. 5) is that the reactive, zero-valent species that are formed during the decomposition of $Fe(CO)_5$ (such as Fe^0) associate with the polymer chain. Because the reaction products are known to exist as clusters [1–5], shown here in Fig. 6, we can expect each cluster to associate with several different polymer chains, thereby promoting the formation of a weak physical gel.

Let us now justify and clarify our designation of the fully reacted, nitrogenated system as a weak physical gel. In this work, we invoke the broad definition of gelation described by Rubinstein [19] and Ferry [20], rather than the more rigid criterion described by Winter and Chambon [21]. Without perturbation or temperature elevation, the weak gel is not observed to flow over months of storage, which satisfies the broad criteria of Rubinstein and Ferry (namely that the material is substantially diluted and exhibits no steady state flow on specific time scales). Furthermore, experimental evidence indicates that the bonding between polymer and particle is weak and transient, as has been shown by three separate experiments. 1) The weak gel formed in the nitrogen atmosphere pathway shown

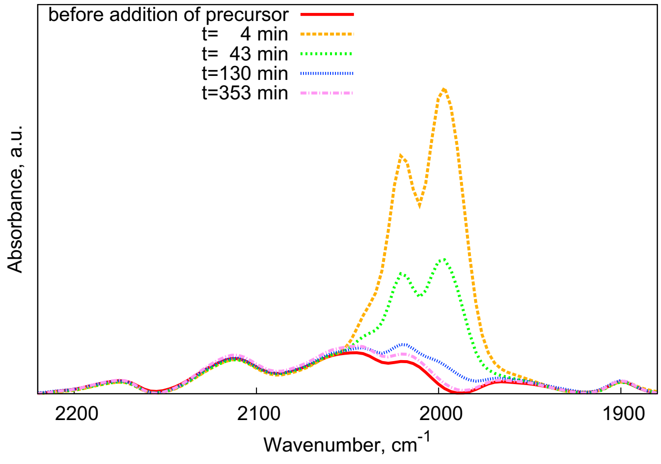

Fig. 4. Infrared spectra of the $Fe(CO)_5$–CAP–butyl butyrate system before and during reaction. $Fe(CO)_5$ concentrations in Fig. 3 were determined spectroscopically by the absorbance of the carbonyl peaks around 2000 cm^{-1} after normalization *via* Beer's Law.

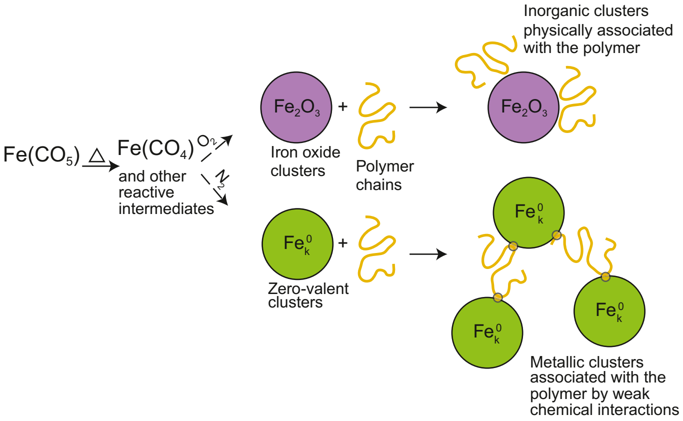

Fig. 5. The general explanation for the occurrence for the phenomenon reported in this work. In nitrogen, the zero-valent nanoparticles that result from the thermal decomposition of $Fe(CO)_5$ interact with the polymer. However, in oxygen, these nanoparticles are fully oxidized and cannot interact with the polymer.

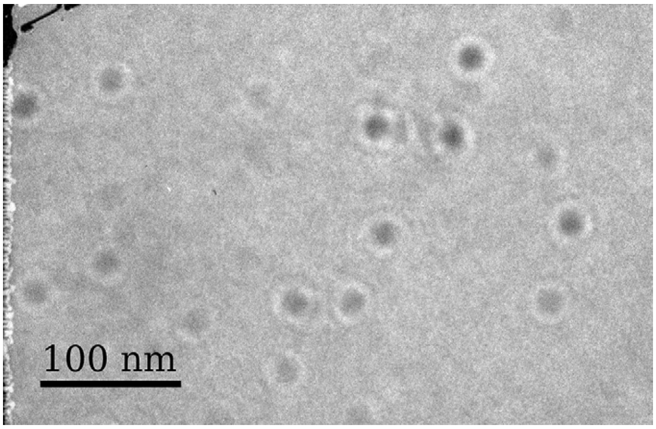

Fig. 6. Particles synthesized by the thermal decomposition of $Fe(CO)_5$ in the nitrogenated CAP–butyl butyrate system. The black scale bar represents 100 nm.

in Fig. 5 is a thermal (reversible) gel, rather than a chemical (covalent) gel. The increase of its temperature to approximately 90 °C will yield a transformation from a weak gel to a liquid; 2) The gel can be mostly dissolved in excess acetone, which is an excellent solvent for CAP. The centrifugation of this CAP/Fe gel–butyl butyrate–acetone system yields an off-white, opaque precipitate. However, this precipitate is a minor component and does not affect the gelation. After the acetone (but not residual butyl butyrate) is driven off from the supernatant and the supernatant is cooled, a weak gel is formed once again. The affinity of acetone to the polymer enhances polymer–solvent interaction and diminishes polymer–particle interaction. Conversely, butyl butyrate is a much poorer solvent, and hence, polymer-solvent interactions are inhibited; 3) The viscosity of the gel decreases dramatically at high shear rates, as seen in Fig. 2b. Such behavior indicates the breakdown of the weak gel with sufficient stress. Because the gel can be destroyed and re-formed by variation in temperature, solvent, and shear stress, we infer that the bonding between particle and polymer is weak and transient.

Let us now further develop and justify this hypothesis in relation to the literature published on the subject. $Fe(CO)_5$ is known to decompose via a cascade mechanism in which discrete CO ligands dissociate from the metal core, *i.e.* [22–26] as shown in Equation (1).

$$\mathrm{Fe(CO)_5} \rightarrow [\mathrm{Fe(CO)_4}] + \mathrm{CO} \rightarrow [\mathrm{Fe(CO)_3}] + 2\mathrm{CO} \rightarrow \ldots \mathrm{Fe} + 5\mathrm{CO} \qquad (1)$$

The intermediates and products shown in Equation (1) are both highly reactive and zero-valent. Hence, the specific intermediates shown in Equation (1) may be observed in the infrared only in the gas phase, at extremely low pressures, and at short time scales (in order to limit molecular collisions and, therefore, further reaction) [25]. It is not surprising, therefore, that these species react even more readily in the condensed phase, where such reactions can occur on the order of picoseconds, as reported by Welch *et al.* [27]. We can expect, therefore, that the metal cluster products of $Fe(CO)_5$ decomposition in nitrogen will associate with the polymer chains for the same reasons that iron readily forms oxides or hydroxides when exposed to air or water.

These accounts support our hypothesis, *i.e.* that these zero-valent species form weak bonds with the polymer chain. The specific chemical group of the polymer that bonds with the iron, however, is unclear. Infrared and Raman spectra showed no new peaks in this study. Literature reports [28–34] have determined that Fe^0 from $Fe(CO)_5$ decomposition interacts with OH groups, as shown in Equation (2). This explanation is further supported by Kurokawa *et al.*, who observed this type of bonding in cellulose ester–metal alkoxide systems [35,36]. Furthermore, other researchers report the presence of hydrogen bonding between metal carbonyl decomposition and alcohol groups in cellulose derivatives [37]. Recall that the chemical structure of the CAP polymer implies that there is an abundance of OH groups along the polymer chain.

$$\mathrm{Fe_x(CO)_y} + \rangle\mathrm{CAP\text{-}OH} \longrightarrow [(\mu\text{-H})\mathrm{Fe_x(CO)_{y-2}}\{\mu\text{-OCAP}\langle\}] + 2\mathrm{CO} \qquad (2)$$

In addition to the OH groups, there is also an abundance of COOR groups, and these can also associate with zero-valent iron particles [37]. Moreover, the observations of Rolker *et al.* [6,7] regarding the increase of the viscosity of ester-containing polymers in the presence of some transition metal carbonyls at elevated temperatures imply that ester group in the polymer is necessary for inducing the occurrence of such a process. This suggests the formation of a weak Fe–COOR bond, where the inorganic species serve as weakly bonded bridges between polymer chains thereby promoting a rise in viscosity. This is supported by Buser and Heidinger [38], who reported resin hardening by the mixture of metal ions (specifically, Pb^{2+} and Mn^{2+}) with polyesters. Of course, in the presence of oxygen during the decomposition reaction (as discussed in the previous section), the zero-valent metallic species are oxidized by

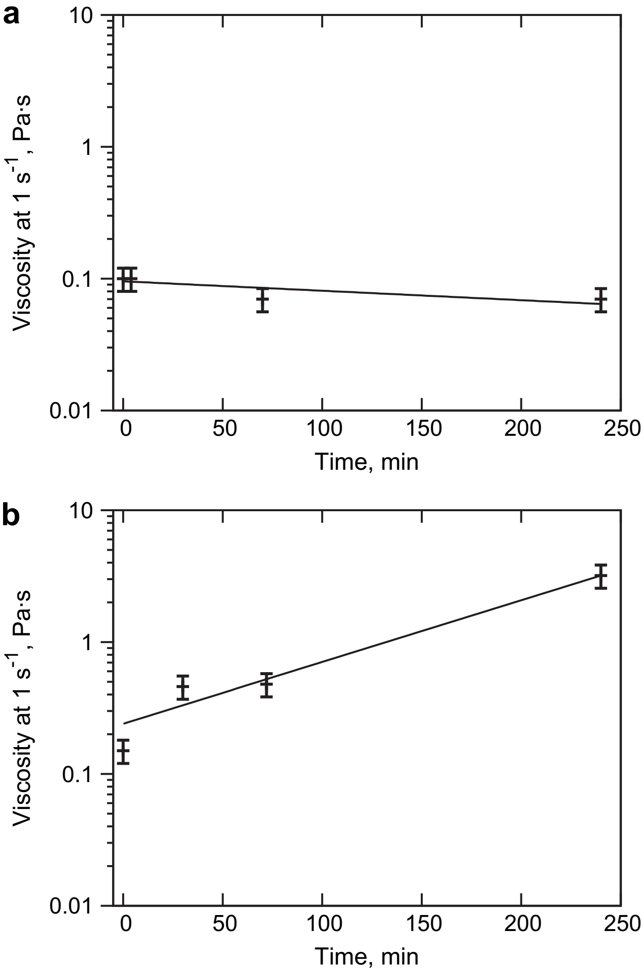

Fig. 7. Room-temperature viscosity of the nitrogenated $Ru_3(CO)_{12}$ system (a) and $Co_2(CO)_8$ (b) as a function of time. Our hypothesis predicts that decomposing a noble metal carbonyl will not significantly affect the viscosity of the system and that decomposing an oxide-forming metal carbonyl will lead to an increase in viscosity. These predictions are accurate. The solid black lines represent best-fit first order kinetics.

the available oxygen [15,16] and are therefore unable to associate with the polymer. This hypothesis explains the fact that weak physical gelation occurs only in nitrogenated systems.

To test whether our hypothesis is correct, we used different metal carbonyl precursors whose thermolysis products would exhibit different affinities toward the polymer. For example, we would expect the thermal decomposition of the carbonyl complex of a noble metal, such as $Ru_3(CO)_{12}$, to impart no significant changes to solution viscosity in this system under nitrogen because the reaction products of Ru would have a considerably lower attraction to the polymer. (The electrochemical half-reaction $Ru{=}Ru^{++} + 2e^-$ has a standard electrode potential of $+0.455$ V SHE [39].) Conversely, an oxide-forming metal carbonyl similar to $Fe(CO)_5$, such as $Co_2(CO)_8$, would be expected to exhibit similar behavior, leading to the onset of weak physical gelation in this system under nitrogen. (The half-reaction $Co{=}Co^{++} + 2e^-$ has a standard electrode potential of -0.277 V SHE (*cf.* $Fe{=}Fe^{++} + 2\ e^-$, -0.440 V SHE).) Indeed, the experimental data are in good agreement with our predictions, as can be seen in Fig. 7. The Ru-based system shows no significant changes in viscosity, while the Co-based system eventually forms a gel, as predicted.

This method of viscosity control is particularly relevant because a traditional limitation of cellulose esters is the severe molecular weight loss due to processing. The molecular weight of some native cellulose fibers may be greater than 10^6 g/mol. However, after processing and esterification, the resultant molecular weights may be less than one tenth of the original value [40]. Therefore, the method of using iron particles to control the viscosity of cellulose esters is valuable because it enables the discerning scientist to impart properties consistent with longer molecular weight polymers, such as increased viscosity, if such properties are desired.

4. Conclusions

In this work, we have shown that the decomposition of $Fe(CO)_5$ in the CAP–butyl butyrate system in nitrogen leads to an increase in viscosity, followed by the onset of gelation, while the viscosity of the same system in oxygen decreases significantly. The decrease in viscosity under oxygen was shown to be a result of the oxidative degradation of the polymer chain at elevated temperatures irrespective of the presence of $Fe(CO)_5$ in the system. However, the increase in viscosity of the system under nitrogen was determined to be a direct consequence of the presence of $Fe(CO)_5$ thermolysis products in the system. We propose that the intermediates and products generated by the thermal decomposition of reactive metal carbonyl precursors associate with the polymer, which leads to weak bonding between iron particles and the polymer chains. However, if the decomposition products are inactive (*e.g.*, if they are noble or metal oxides), these associations cannot occur, and no significant viscosity change is observed. We used ruthenium and cobalt carbonyl complexes, which differ in their reactivity (Co a base metal and Ru noble), in order to test this hypothesis. The results showed that the less reactive metallic species embedded in the CAP–butyl butyrate system (Ru) were in fact unreactive and did not associate with the polymer, while the more reactive metallic species (Co) gave rise to gelation, in good agreement with the predictions of our hypothesis. This work is significant because it shows a simple, economical way to control the viscosity of cellulose ester fluids.

Acknowledgments

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References

[1] Hess PH, Parker JP. Polymers for stabilization of colloidal cobalt particles. Journal of Applied Polymer Science 1966;10(12):1915–27.
[2] Smith TW, Wychick D. Colloidal iron dispersions prepared via the polymer-catalyzed decomposition of iron pentacarbonyl. The Journal of Physical Chemistry 1980;84(12):1621–9.
[3] Thomas J. Preparation and magnetic properties of colloidal cobalt particles. Journal of Applied Physics 1966;37(7):2914–5.
[4] Dan N, Zubris M, Tannenbaum R. Effect of polymeric media on the kinetics of nanocluster nucleation and growth. Macromolecules 2005;38(22):9243–50.
[5] David K, Tadd EH, Tannenbaum R, Tikku S, Dan N. Effect of polymer architecture on metal nanoclusters. Polymer 2006;47(25):8344–9.
[6] Rolker J, Glasner T. Modification of acrylate polymers by treatment with metal carbonyl, U.S. Patent, number 3,959,231, 1973.
[7] Rolker J, Glasner T. Method of modifying polymers and novel product, U.S. Patent, number 3,959,231, 1976.
[8] Voet D, Voet JG. Biochemistry. 3rd ed. John Wiley & Sons, Inc.; 2004.
[9] Fateley WG, Lippincott ER. Normal co-ordinate analysis of the vibrational spectrum of iron pentacarbonyl. Spectrochimica Acta 1957;10(1):8–16.
[10] O'Dwyer MF. Infrared spectra and normal coordinate analysis of iron pentacarbonyl. Journal of Molecular Spectroscopy 1958;2(1–6):144–51.
[11] Edgell WF, Wilson WE, Summitt R. The infrared spectrum and vibrational assignment for $Fe(CO)_5$. Bonding considerations. Spectrochimica Acta 1963;19(6):863–72.
[12] Edgell WF, Dunkle MP. Some aspects of the infrared spectrum of liquid iron pentacarbonyl and its *n*-heptane solutions. Journal of Physical Chemistry 1964;68(3):452–6.
[13] Sato S, Suzuki T. Infrared reflection absorption spectra of $Fe(CO)_5$ adsorbed on au surfaces. Journal of Electron Spectroscopy and Related Phenomena 1997;83(1):85–91.
[14] Hauchard C, Pépin C, Rowntree P. $Fe(CO)_5$ thin films adsorbed on au(111) and on self-assembled organic monolayers: I. Structure. Langmuir 2005;21(20):9154–65.
[15] Lee J-Y, Kang B-C, Jung D-Y, Boo J-H. Selective growth of iron oxide thin films using the combined method of metal-organic chemical vapor deposition and microcontact printing. The Journal of Vacuum Science and Technology B 2007;25(4):1516–9.
[16] Morjan I, Alexandrescu R, Soare I, Dumitrache F, Sandu I, Voicu I, et al. Nanoscale powders of different iron oxide phases prepared by continuous laser irradiation of iron pentacarbonyl-containing gas precursors. Materials Science and Engineering: C 2003;23(1–2):211–6.
[17] Hon DN-S, Shiraishi N, editors. Wood and cellulosic chemistry. Marcel Dekker; 1991.
[18] Ito H, Padias AB, Hall HK. Thermal deesterification and decarboxylation of alternating copolymers of styrene with β-substituted t-butyl α-cyanoacrylates. Journal of Polymer Science Part A: Polymer Chemistry 1989;27(9):2871–81.
[19] Rubinstein M, Colby RH. Polymer physics. Oxford University Press; 2003.
[20] Ferry JD. Viscoelastic properties of polymers. John Wiley & Sons, Inc.; 1961.
[21] Winter HH, Chambon F. Analysis of linear viscoelasticity of a crosslinking polymer at the gel point. Journal of Rheology 1986;30:367–82.
[22] Seder TA, Ouderkirk AJ, Weitz E. The wavelength dependence of excimer laser photolysis of $Fe(CO)_5$ in the gas phase. Transient infrared spectroscopy and kinetics of the $Fe(CO)_x$ (x=4,3,2) photofragments. The Journal of Chemical Physics 1986;85(4):1977–86.
[23] Engelking PC, Lineberger WC. Laser photoelectron spectrometry of the negative ions of iron and iron carbonyls. Electron affinity determination for the series $Fe(CO)_n$, n = 0,1,2,3,4. Journal of the American Chemical Society 1979;101(19):5569–73.
[24] Lewis KE, Golden DM, Smith GP. Organometallic bond dissociation energies: laser pyrolysis of iron pentacarbonyl, chromium hexacarbonyl, molybdenum hexacarbonyl, and tungsten hexacarbonyl. Journal of the American Chemical Society 1984;106(14):3905–12.
[25] Weitz E. Studies of coordinatively unsaturated metal carbonyls in the gas phase by transient infrared spectroscopy. The Journal of Physical Chemistry 1987;91(15):3945–53.
[26] Zubris M, King R, Tannenbaum R. Kinetics of Fe–Co nanoalloy formation via decomposition of their carbonyl precursors. Journal of Materials Chemistry 2005;15(12):1277–85.
[27] Welch JA, Peters KS, Vaida V. Medium effects on the photodissociation of hexacarbonylchromium ($Cr(CO)_6$). The Journal of Physical Chemistry 1982;86(11):1941–7.
[28] Khalil H, Mahajan D, Rafailovich M, Gelfer M, Pandya K. Synthesis of zerovalent nanophase metal particles stabilized with poly(ethylene glycol). Langmuir 2004;20(16):6896–903.
[29] Kataby G, Ulman A, Prozorov R, Gedanken A. Coating of amorphous iron nanoparticles by long-chain alcohols. Langmuir 1998;14(7):1512–5.
[30] Brenner A, Burwell R. The surface chemistry of molybdenum in states of lower oxidation on alumina. Journal of Catalysis 1978;52(3):353–63.

[31] Brenner A, Hucul D. Catalysts of supported iron derived from molecular complexes containing one, two, and three iron atoms. Inorganic Chemistry 1979;18(10)):2836–40.

[32] Bjorklund RB, Burwell RL. The reaction of nickel tetracarbonyl with γ-alumina. Journal of Colloid and Interface Science 1979;70(2):383–91.

[33] Brenner A, Hucul D. The synthesis and nature of heterogeneous catalysts of low-valent tungsten supported on alumina. Journal of Catalysis 1980;61(1):216–22.

[34] Psaro R, Recchia S. Supported metals derived from organometallics. Catalysis Today 1998;41(1–3):139–47.

[35] Kurokawa Y, Ohta H, Okubo M, Takahashi M. Formation and use in enzyme immobilization of cellulose acetate–metal alkoxide gels. Carbohydrate Polymers 1994;23(1):1–4.

[36] Nakane K, Ogata N, Kurokawa Y. Formation of inorganic (tac, tan) fibers by thermal decomposition of cellulose acetate–tantalum alkoxide precursor gel fibers. Journal of Applied Polymer Science 2006;100(6):4320–4.

[37] He F, Zhao D, Liu J, Roberts C. Stabilization of Fe–Pd nanoparticles with sodium carboxymethyl cellulose for enhanced transport and dechlorination of trichloroethylene in soil and groundwater. Industrial & Engineering Chemistry Research 2007;46(1):29–34.

[38] Buser K, Heidinger W. Hardening of epoxy resins, German patent, number 1054705 1959.

[39] Pourbaix M. Atlas of electrochemical equilibria in aqueous solutions. National Association of Corrosion Engineers; 1974.

[40] Rees DA. The shapes of molecules; carbohydrate polymers. Oliver & Boyd; 1967.