Insight to Cellulose - Polycarboxylic Acid Intermolecular Interactions Using TG and DSC Thermal Analysis Tools

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Abstract

Interactions between polycarboxylic acids and cellulose was evaluated by using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) profiles of their mixtures. TGA, DSC of cellulose and acids were recorded as baseline data and peak shifts were calculated by subtracting the peak maximum values of cellulose from that of cellulose-polycarboxylic acid mixtures. In TGA, DL-tartaric and citric acid with cellulose mixtures showed the largest positive shifts of +58 and +23 °C in the derivative-TGA second peak. In addition, DL-tartaric and citric acid showed the smallest cellulose DTGA peak 1 area/peak 2 area ratios of 0.50 and 1.58 respectively. In DSC the largest cellulose dehydration peak shifts of +39 and +21 °C were recorded for DL-tartaric and citric acids. In acids studied, polycarboxylic acids with one or more hydroxyl groups are more strongly interacting with cellulose in the solid state. The strong interactions of these acids are probably due to their ability to wrap round the polysaccharide chains forming multiple hydrogen bonding between -COOH and -OH of acid with -OH groups of cellulose.

Introduction

Cellulose is the most abundant biopolymer and the degradation and further processing of this polysaccharide can be the carbon source for renewable fuels and platform chemicals such as ethylene glycol, glycerol, levulinic acid and lactic acid. At present biochemical, chemocatalytic as well as pyrolysis methods are under study in cellulose processing and all these methods have limitations like poor product profiles and yields as well as enzyme, catalysts and energy costs resulting meager economic viabilities (Amarasekara 2013), (Wilson 2012). The extensively studied chemical catalytic approaches include the use of dilute mineral acids (Fan et al. 2012), concentrated acids (Camacho et al. 1996), solid acids (Hu et al. 2015), (Huang and Fu 2013), (Liu et al. 2015) mineral acid in neutral ionic liquids (Li et al. 2008), acidic ionic liquids (Amarasekara and Owereh 2009), (Da Costa Lopes and Bogel-Lukasik 2015), metal salts in aqueous acid and ionic liquid solutions (Amarasekara and Wiredu 2016a), (Amarasekara and Shanbhag 2013), as well as immobilized ionic liquids (Wiredu and Amarasekara 2014).

The use of organic acids as cellulose depolymerization or degradation catalysts is also known, but surprisingly only a limited number of researchers have studied the application of organic acids as homogeneous or heterogeneous catalysts in depolymerization or degradation of cellulose (Amarasekara 2013), (Sun and Cheng 2002), (Mosier et al. 2002), (Mosier et al. 2001). In one of the pioneering studies in this area, Mosier and co-workers have evaluated the catalytic activities of three common carboxylic acids: acetic, maleic and succinic in hydrolysis of cellulose in aqueous medium. In addition, they have compared these organic acids to mineral acid catalysts as well. The rigid dicarboxylic acid, maleic acid was identified as the most active of the three carboxylic acids studied (Mosier et al. 2001). Interestingly, they have further reported that the hydrolysis rates of Avicel cellulose are similar in both 5×10^{-2} M sulfuric and maleic acid mediums.

Heterogeneous catalysts with better recycling possibilities can also be used in cellulose depolymerization. In particular solid acid catalysts with high density of carboxylic acid and hydroxyl groups covalently connected to the solid surface have shown certain promise in this area (Su et al. 2018), (Kobayashi and Fukuoka 2018), (To et al. 2015), (Vilcocq et al. 2014). For example, Kobayashi and co-workers have recently reported that graphene bearing -COOH and -OH groups on the surface as catalysts could produce glucose yields as high as 88% in aqueous mediums and under gentle conditions (Kobayashi and Fukuoka 2018), (Shrotri et al. 2018). The enhanced catalytic effect of these heterogeneous catalysts with carboxylic acid and hydroxyl groups in close proximity to the active site was explained as a synergistic effect of multiple hydrogen bonding or interactions with the polysaccharide hydroxyl groups (Kobayashi and Fukuoka 2018), (Shrotri et al. 2018), (Amarasekara et al. 2019). In another recent example, Gross and co-workers have shown the exceptional cellulose depolymerization ability of a catalyst prepared by modification of the surface of cellulose nanocrystals by covalently attaching dicarboxylic acids as well as tricarboxylic acids (Spinella et al. 2016). While the carboxylic acid catalyzed cellulose degradation experiments signals the importance of synergistic effects of multiple -OH and -COOH groups for interactions between catalysts and cellulose, methodical studies on intermolecular interactions between cellulose and carboxylic acids is an elusive research area.

The studies on interactions of small molecules with polymeric materials is a challenging area due to the limited number of currently available tools. The most widely used techniques in this area are UV-Vis, IR and NMR spectroscopy; however certain limitations like solubility can lessen their applications in cellulose. The use of thermal properties as a tool for studying interactions between cellulosic materials and small molecules is rare. In one study Singhal et al. studied the interactions between benzoic acid and ethyl cellulose by differential scanning calorimetry to get an insight into controlled drug release (Singhal et al. 1999). During this work, they have noted that glass transition temperature (T_g) of ethyl cellulose was reduced up to 27.7% due to benzoic acid in solid solution. Furthermore, the melting enthalpy of benzoic acid, when plotted as a function of its concentration yielded a straight line suggesting the presence of hydrogen bonding interactions between benzoic acid and ethyl cellulose (Singhal et al. 1999). In another study, DSC was used as the primary tool in identifying the exothermal polymerization reactions between lignin fraction in cellulosic biomass in the presence of maleic acid (Philippou and Zavarin 1984). Inspired by these examples and as a continuation of our studies on interactions between polysaccharides and small molecules as well as metal ions (Fernando and Amarasekara 2021a), (Fernando and Amarasekara 2021b), (Amarasekara and Wiredu 2016b) we have explored the possibility of using thermal properties as a tool in evaluating the interactions between cellulose and carboxylic acids. In this publication we present our studies on interactions between cellulose and a selected set of polycarboxylic acids using thermogravimetry and differential scanning calorimetry. Nine common dicarboxylic acids, and a tricarboxylic citric acid were included in the study. In addition, hydroxy-acid lactic acid was also included for comparison.

Experimental

Instrumentation and materials

Sigmacell cellulose - type 101 (DP ~ 450, from cotton linters), carboxylic acids (> 99%) and Drierite (8 mesh) were purchased from Sigma - Aldrich Chemical Co, USA. Thermogravimetric analysis in 25–800°C temperature range was carried out in air using TA instruments TGA 2050 system. Approximately 5 mg of sample and Pt crucibles were used. The TG curves were recorded at a heating rate of 10°C / min. A Mettler Toledo DSC 3 STAR system was used to carry out DSC analysis. STARE-E software was incorporated to evaluate the transition temperature peaks and areas under the peaks in mJ. The difference between the power applied to the investigated sample was measured as a function of temperature. The mass of the samples placed in aluminum pan was approximately 5 mg and all experiments were carried out in air at a heating/cooling rate of 10°C/min.

General experimental procedures for TGA

A mixture of Sigmacell cellulose - type 101 (16.2 mg, 0.100 mmol of glucose equivalent) and carboxylic acid (0.100 mmol) was prepared and thoroughly ground together for 2.0 min. in an agate mortar and pestle to give a homogeneous sample. The mixture was dried in a Drierite (8 mesh) desiccator for 3 days at room temperature (23°C), then approximately a 5 mg portion was transferred to the platinum crucible and the TG curve was recorded in 25 - 800°C, in air using a heating rate of 10°C /min. Pure cellulose and carboxylic acid samples were also similarly dried and TGA curves were recorded under identical conditions.

$$\Delta P_A = [\text{carboxylic acid DTG peak in the cellulose carboxylic acid mixture (}^\circ\text{C)}] - [\text{carboxylic acid DTG peak (}^\circ\text{C)}]$$

$$\Delta P_{c1} = [\text{cellulose DTG peak 1 in the cellulose carboxylic acid mixture (}^\circ\text{C)}] - [\text{cellulose DTG peak 1 (}^\circ\text{C)}]$$

$$\Delta P_{c2} = [\text{cellulose DTG peak 2 in the cellulose carboxylic acid mixture (}^\circ\text{C)}] - [\text{cellulose DTG peak 2 (}^\circ\text{C)}]$$

The thermogravimetric analysis (TGA) data of cellulose, carboxylic acids and cellulose - carboxylic acid mixtures are shown in Table 1.

General experimental procedures for DSC

Approximately a 5 mg of the dried mixture prepared for the previous experiment was transferred to a 40µL aluminum crucible (Metler-Toledo ID: 26763), sealed and the DSC curve was recorded in 25 - 350°C, in air, using a scanning rate of 10°C / min. Pure cellulose and carboxylic acid samples were also similarly dried and DSC curves were recorded under identical conditions.

The first endothermic transition of cellulose with DSC peak (P_{c1}) was used as the probe in gauging the effect of acid groups and hydroxy groups on cellulose since other peaks are often masked by thermal transitions of carboxylic acids.

$$\Delta P_{C1} = [\text{cellulose DSC peak 1 in the cellulose carboxylic acid mixture (}^{\circ}\text{C)}] - [\text{cellulose DSC peak 1 (}^{\circ}\text{C)}]$$

The differential scanning calorimetry (DSC) data of cellulose, carboxylic acids and cellulose - carboxylic acid mixtures are shown in Table 2.

Comparison of cellulose-carboxylic acid mixing methods: effect of aqueous slurry mixing

An aqueous slurry of Sigmacell cellulose - type 101 (16.2 mg, 0.100 mmol of glucose equivalent), carboxylic acid (0.100 mmol) and 5.00 mL of deionized water was prepared in a wide neck 20 mL glass vial and open vial was heated in an oven at 60°C for 24 h to evaporate the water, then the vial was transferred to a desiccator and kept in the desiccator for 3 days to dry the sample. Thermogravimetric analysis of the mixtures were performed as in general TGA procedure. The DTGA peak positions of mixtures and peak areas are comparable to results in experiment 2.2 within $\pm 2^{\circ}\text{C}$ and $\pm 2\%$ respectively.

Results And Discussion

Thermogravimetric analysis of cellulose-polycarboxylic acid mixtures

Initially we have recorded the TGAs of pure cellulose and all carboxylic acids as baseline data. Then the cellulose-carboxylic acid mixtures were analyzed under identical conditions and this data are shown in Table 1. Pure cellulose was found to decompose in two steps as indicated by two peak maximums P_{C1} and P_{C2} at 352 and 472°C in DTG curve; shown as the first entry in the 3rd column of Table 1, as well as in figure 1a. The ratio of mass losses in two steps could be calculated from the area ratio of the two DTG peaks; area P_{C1} /area P_{C2} = 8.09, this result is shown in the first entry in the 6th column of Table 1. The cellulose - carboxylic acid mixtures showed decompositions in three steps and three peaks in each DTGA curve (P_A , P_{C1} , P_{C2}). The peak positions and percent areas of these peaks are shown in parenthesis under the 4th column in Table 1. The interactions of carboxylic acid groups as well as hydroxyl groups in acids with cellulose resulted shifts in carboxylic acid decomposition temperature reflected in DTG peak P_A and this shift (ΔP_A) is in the 5th column. In mixtures, cellulose composition DTGA peaks also showed significant shifts and these shifts (ΔP_{C1} , ΔP_{C2}) are too shown in the 5th column of Table 1. The relative weight losses at the two steps measured in cellulose carboxylic acid mixtures (area P_{C1} /area P_{C2}) are shown in parenthesis under entries 2-12 in column 6 of Table 1.

Previous studies on thermal decomposition of cellulose using TGA under inert atmospheres and in air have shown a strong bearing on the type of cellulose and the natural source of the biopolymer (Miranda et al. 2013), (Szcześniak et al. 2008), (Paes et al. 2010). However, all TGA curves showed a major mass loss event in the region of 300-360°C, which can be attributed to the cellulose decomposition, commonly referred to as the volatilization step. In this main event, depolymerization into monosaccharide and oligosaccharide is usually followed by the loss of volatile fragments. This thermal event is normally

observed in both oxidative and inert atmospheres and can be affected by crystallinity and crystal size of cellulose as well as the presence of substances bonded to surface microfibrils of cellulose (Kim et al. 2010), (Cabrales and Abidi 2010), (Barneto et al. 2011). The second drop in TGA curve is a minor weight loss and generally occurs after 400°C, and related to complete degradation and combustion of charred residue (Mamleev et al. 2007). In oxidative atmospheres this second step with charring process has been identified as the exothermic transition observed during cellulose pyrolysis (Morán et al. 2008).

The representative TGA results from our experiments using (a) Sigmacell cellulose (b). succinic acid (c). cellulose and succinic acid 1: 1 mole mixture are shown in Fig. 1. According to the TGA curve in Fig. 1 (a), cellulose appears to be stable in air up to about 300°C, and then rapidly decomposes in the first step up to about 360°C. Then the remaining charred residue completely decomposes in a second step. The derivative thermogravimetry analysis (DTGA) trace shows two peaks at 352 and 472°C. The representative pure carboxylic acid, succinic acid and its mixture with cellulose are shown as Fig. 1 (b) and 1(c) respectively. In the mixture, succinic acid DTGA peak is shifted from 216 to 206°C. Likewise, the cellulose DTGA peaks at 352 and 472°C are shifted to 320 and 463°C respectively.

In the series of mixtures studied, carboxylic acid - cellulose decomposition steps are shifted due to the interactions of -COOH and -OH groups. The shift in first DTGA peak (ΔP_{C1}) ranges from -35 to -18°C. All carboxylic acids except *m*- and *p*-phthalic acids caused negative shifts in P_{C1} , indicating that mixing with these carboxylic acids promotes the volatilization of cellulose to a lower temperature. Nevertheless, *m*- and *p*-phthalic acid - cellulose failed to show these lower temperature DTGA peaks. The shift in second DTGA peak (ΔP_{C2}) varied from -47 to +58°C. The addition of all carboxylic acids except DL-tartaric and citric acid caused a negative shifts in the second peak. This is most likely due to a general acid catalyzed pyrolysis of char formed in the first step. However, in the second weight loss step DL-tartaric acid and citric acid with four chelating groups in each (counting both -OH and -COOH) showed high positive shifts of +23 and +58°C respectively. These shifts towards higher temperatures imply a retardation in the char decomposition due to the chelation with these tetra - coordinating hydroxy polyacids. This remarkable effect is further evident in the P_{C1}/P_{C2} area ratio as well; where the tartaric acid and citric acid shows the lowest P_{C1}/P_{C2} values of 0.50 and 1.58 respectively. Therefore, the addition of DL-tartaric acid and citric acid with multiple -COOH and -OH groups have shown more pronounced effects on the cellulose decomposition process seen in the shifts and the weight losses at volatilization and char pyrolysis steps.

Differential scanning calorimetry analysis of cellulose-polycarboxylic acid mixtures

The DSC data of pure carboxylic acids and cellulose - carboxylic acid mixtures are shown in Table 2. The DSC peak maximums as well as area percentages of pure carboxylic acids and cellulose - carboxylic acid mixtures in parenthesis are shown in columns 3 and 4 of Table 1. In addition, we have calculated the shifts in first peak; which corresponds to dehydration of cellulose due to the interactions with the added carboxylic acid, and these values are listed as ΔP_{C1} , in the fifth column of Table 2. The representative

DSC plots from experiments using (a). Sigmacell cellulose (b). succinic acid (c). cellulose and succinic acid 1: 1 mole mixture are shown in Fig. 2. The DSC of pure cellulose showed two peaks at 118 and 331°C indicating two endothermic transitions of -137 and -140 Jg⁻¹ respectively (Fig. 2a). Several research groups have studied DSC of cellulose samples and have found that exact positions and the energy absorptions during these two transitions can significantly vary on the type, moisture content and crystallinity of the cellulose (Szczęśniak et al. 2008), (Picker and Hoag 2002). The first endothermic peak generally occurs in the 50-150°C region for native cellulose and is believed to be due to the dehydration process (Ciolacu et al. 2011). Then the second transition corresponds to the scission of glycosidic bonds, with laevoglucose formation. This phenomena is clarified by the fact that thermal degradation reaction starts in the amorphous region of the cellulosic materials (Ciolacu et al. 2011).

The second cellulose degradation is generally masked by the carboxylic acid thermal transitions and difficult to identify in most mixtures in this study. The shift of the first endothermic peak (ΔP_{C1}) can change in a wide range from -18 to +35°C for the series of mixtures studied. The highest ΔP_{C1} values are recorded for tartaric and citric acids, +39 and +21°C respectively. These two polycarboxylic acids with hydroxyl groups are the same acids showing the highest changes in area P_{C1} /area P_{C2} ratio in cellulose DTGA peaks during the thermogravimetric analysis experiments as well. Therefore, polycarboxylic acids with hydroxyl groups are the most strongly interacting group among the set of carboxylic acids studied. Interestingly, this result is different from our previous observations on interactions of the same series of polycarboxylic acids with cellulose model compound D-cellobiose in aqueous environment (Amarasekara et al. 2019). In that case the two 1,2-dicarboxylic acids, maleic and o-phthalic with two carboxyl groups rigidly held in a fixed geometry were found to be the ones most strongly binding to polysaccharide in water. Furthermore, this thermal analysis experiments suggests that, rigidly held in a fixed geometry feature of dicarboxylic acid is not an important requirement for interaction in solid state. However, the number of -COOH and -OH groups in polycarboxylic acid can significantly influence the thermal decomposition of the polysaccharide in the solid state.

Comparison of cellulose-carboxylic acid mixing methods

In order to study the effectiveness of cellulose carboxylic acid mixing by grinding the solid mixture we have prepared the cellulose - carboxylic acid mixture by using an aqueous slurry as described in the experimental section. These samples were also subjected to thermogravimetric analysis after drying to remove the water added and results were compared with data from grinding solid mixture experiments. The DTGA peak positions and peak areas from aqueous slurry method are comparable to results from grinding solid mixture experiments within $\pm 2^\circ\text{C}$ and $\pm 2\%$ respectively; suggesting that solid state grinding is equally effective as aqueous mixing, resulting intermolecular interactions between cellulose and carboxylic acids.

Conclusion

Thermal analysis techniques thermogravimetry and differential scanning calorimetry are shown as new tools for studying the interactions between polycarboxylic acids and cellulose in the solid state. Ten polycarboxylic acids and one monocarboxylic acid with a hydroxyl group was studied by measuring TGA and DSC profiles of their thoroughly blended equimolar mixtures. Polycarboxylic acids with one or more hydroxyl groups were identified as the group most strongly interacting with cellulose in the solid state. The geometry and rigidly held architecture of the carboxyl groups in polycarboxylic acid is not an important factor in the solid state, as we have observed in our previous solution phase studies. The strong interactions of DL-tartaric and citric acids are probably due to the presence of hydroxyl groups in addition to carboxylic acid groups. In addition, flexible molecular architecture with the ability to wrap round the polysaccharide chains with multiple hydrogen bonding between carboxylic acid and hydroxyl groups of acid with hydroxyl groups of polysaccharide is probably a vital factor in the solid state. In addition, thorough grinding of a cellulose and carboxylic acid mixture using the pestle and mortar is equally effective in producing intermolecular interactions as mixing in an aqueous slurry.

A number of diverse chemical reactions are possible while heating a cellulose - carboxylic acid mixture in an oxidative atmosphere and we have studied all thermal processes in air to stimulate more practical circumstances. The most probable reactions are: anhydride formation from di-acids, carboxylic acid decomposition, esterification of cellulose-OH groups, esterification of -OH groups in hydroxy acids, organic redox reactions, acid catalyzed cellulose depolymerizations and dehydrations. As pointed out in the introduction section, cellulose-polycarboxylic acid interaction is an unexplored research area, and the only related report in this field is a computational study on insight into the mechanism of secondary reactions in cellulose pyrolysis, where Lu *et al.* have studied the interactions between cellulose derived levoglucosan and acetic acid using density functional theory (DFT) methods (Lu et al. 2019). During this work they have noted that carboxylic acids produced by primary pyrolysis have significant influences on the secondary reactions; furthermore, levoglucosan and acetic acid were selected as intermediates interacting with each other determining further reactions. Lu and co-workers DFT study indicated that acid catalyzed dehydration reaction as the dominant interaction reaction among other possible reactions like esterification, organic redox reactions and acetic acid decomposition (Lu et al. 2019). Similarly, polycarboxylic acids used in our study may also promote dehydration of cellulose among other possible reactions. However, our experiments using 1,2-dicarboxylic acids like maleic and *o*-phthalic with preferences to form anhydrides have not shown early weight loss or any other evidence for anhydride formation. This newly developed TGA and DSC thermal analysis tools may be applied for studying intermolecular interactions between cellulose and other classes of small molecules such as amino acids, pharmaceuticals, dyes and inks as well.

Declarations

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Conflict of interest

The authors declare that they have no conflict of interest

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Tables

Tables 1 & 2 are available in the Supplementary Files section.

Figures

(a). Cellulose

(b). Succinic acid

(c). Cellulose and succinic acid 1: 1 mole mixture

Figure 1

Thermogravimetry (TG) and derivative thermogravimetry (DTG) curves of (a). cellulose (b). succinic acid (c). cellulose and succinic acid 1: 1 mole mixture

(a). Cellulose

(b). Succinic acid

(c). Cellulose and Succinic acid 1: 1 mole mixture

Figure 2

differential scanning calorimetry (DSC) of (a). cellulose (b). succinic acid (c). cellulose and succinic acid
1: 1 mole mixture

Supplementary Files

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