Polymer Bulletin

A New Value for the Heat of Fusion of a Perfect Crystal of Cellulose Acetate

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Summary

The enthalpy of fusion of a perfect crystal (ΔH_f^o) of cellulose acetate was determined in this work. In order to do so, cellulose samples from different sources were heterogeneously acetylated. The cellulose acetate samples were characterized by differential scanning calorimetry (DSC) and wide angle X-ray scattering (WAXS). The diffractograms were deconvoluted into halos and peaks using the Pseudo-Voigt peak function. From these deconvolutions, the hypothesis that best represented the two-phase model was the one in which the amorphous model was represented by the halos at 11° and 21°, considering an ordered amorphous model. The WAXS crystallinities of the samples were then calculated from these values and plotted against the enthalpy of fusion of the materials, and from this relationship the ΔH_f^o for the cellulose acetate was determined to be 58.8 J/g.

Keywords:

Cellulose Acetate / Crystallinity / DSC / WAXS

Introduction

Cellulose acetate is obtained from cellulose through the substitution of its cellulosic hydroxyl groups by acetyl groups, what leads to materials with distinct degrees of substitution (DS). The DS is the average number of acetyl groups in each glycosidic repeat unity, so that a completely substituted material will have a DS of 3 [1].

The chemical and physical properties of cellulose acetates, as for example their solubility and their degree of crystallinity, depend on their DS. The crystallinity, for instance, increases with the DS of the sample, since the more substituted the cellulose acetate, the more uniform it is, what leads to a better chain packing [2].

Cellulose acetates are produced according to two distinct methodologies, which are referred to as homogeneous and heterogeneous processes. In the homogeneous (commercial) process, cellulose is acetylated by a solution containing acetic acid, acetic anhydride and a catalyst, usually sulfuric acid, and the produced cellulose triacetate (CTA) is solubilized in the reaction medium. In the heterogeneous process,

a non swelling diluent is added to the system, which causes the produced CTA to remain insoluble. Then, there is a direct conversion of cellulose into solid CTA, what keeps the integrity of the fibers and produces a more crystalline product than that obtained through the homogeneous route [3].

Knowing about the crystallinity of polymers is important because it affects the mechanical and chemical properties of these materials. For example, since cellulose diacetate is more amorphous than CTA, it is also more biodegradable [4].

Polymer crystallinity has been studied mainly through Wide Angle X-Ray Scattering (WAXS) and Differential Scanning Calorimetry (DSC) [5]. Through WAXS [6], the crystallinity can be quantified by

$$\%C = \frac{A_c}{A_c + A_a} \times 100 \tag{1}$$

where A_c and A_a are the areas under the crystalline peaks and the amorphous halos, respectively [6].

Through DSC [6], crystallinity is conventionally calculated using the ratio between the heat of fusion of the material in study and the heat of fusion of a perfect crystal of the material, as shown in equation (2):

$$\%C = \frac{\Delta H_f}{\Delta H_f^o} \times 100 \tag{2}$$

where ΔH_f is the enthalpy of fusion of the sample and ΔH_f^o is the enthalpy of fusion of a totally crystalline material.

Several values have already been proposed regarding the enthalpy of fusion of a perfect crystal of cellulose acetate. The first of these, and most used one nowadays, was obtained by Takahashi et al. (1979), who determined the ΔH_f^o of CTA to be 34.4 J/g. This value was obtained from the melting point depression of a system composed by commercial CTA and dibuthyl phthalate [7], using Flory's equation [8] for the melting point depression of a polymer-diluent system:

$$\frac{1/T_m - 1/T_m^o}{\nu_1} = \frac{R}{\Delta H_f^o} \frac{V_u}{V_1} \left(1 - \frac{BV_1}{R} \frac{\nu_1}{T_m}\right) \tag{3}$$

where T_m and T_m^o are, respectively, the melting temperatures of the polymer-diluent system and pure polymer, ΔH_f^o is the heat of fusion of a perfect crystal of the polymer, ν_1 is the volume fraction of diluent, V_u and V_1 are the molar volumes of a monomer unit and diluent, respectively, and B is the cohesive energy density. The T_m^o value used by Takahashi et al. (306 ºC), according to those authors, was obtained by Malm et al. [9].

Later (1991), Sun and Cabasso [10], using DSC, obtained the value of 11.3 J/g for a perfect crystal of cellulose acetate using the relationship between ΔH_f and the change in the calorific capacity (ΔC_p) at the glass transition (T_g) of several cellulose acetate samples. According to those authors, this value, much lower than that found by Takahashi et al., was due to a defective structure of the commercial CTA used by them.

In 1999, at the Macromolecules' 99 meeting, in Bath-UK, Rodrigues Filho et al. [11] proposed the value of 48.8 J/g for the ΔH_f^o of CTA. In order to obtain such values the authors used the concept of accessibility [12], according to which, as water sorption occurs almost totally in the amorphous regions, the area of the endothermic peak due to loss of absorbed water is directly related to the amorphous fraction. Then, from the relationship between the enthalpy of fusion (ΔH_f) and the enthalpy of dehydration (ΔH_w) of several cellulose acetate samples, the authors found ΔH_f^o by extrapolating the ΔH_f to the value where ΔH_w was zero. This ΔH_f^o value, which has been recently used [13], has proved to be more accurate than the previous ones, since some of the values of ΔH_f for some of their samples were higher than the ΔH_f^o calculated by Takahashi et al. [7] and by Sun and Cabasso [10].

Recently, in 2005, the ΔH_f^o of cellulose acetate was brought back to discussion at the X International Macromolecular Colloquium, in which Cerqueira et al. [14] compared the ΔH_f of several cellulose acetate samples with their WAXS amorphous areas, and obtained the value of 56.3 J/g for the ΔH_f^o of cellulose acetate. This value may be considered, within the experimental error, very close to that presented by Rodrigues Filho et al. [11] (48.8 J/g) and points out the necessity of discussion about it, since it disagrees with those found by Takahashi et al. [7] and by Sun and Cabasso [10].

The aim of the present paper is to determine the most appropriate value for the ΔH_f^o of cellulose acetate using DSC and WAXS.

Experimental

Heterogeneous acetylation

Cellulose acetate samples were prepared using the following sources: purified sugar cane bagasse cellulose; filter paper Whatman 4; and two cellulose pulps furnished by Rhodia S.A. (Santo André – SP), IMP-FLORANIER-FDL (pine/sulfite/USA) and LW-ACET (eucalyptus/ Kraft/ Lençóis Paulista – SP).

These materials were acetylated according to the methodology developed by Rodrigues Filho et al. [12], which is described bellow:

A solution containing 16 mL of glacial acetic acid, 24 mL of toluene and 0.40 mL of perchloric acid was added to 1 g of ground cellulose and stirred for 10 minutes. After this period, the solution was separated from the cellulose, and 15 mL of acetic anhydride was added to it. Then, it was returned to the flask containing cellulose and stirred again for a few minutes, after which, the system was left to stand. The acetic anhydride was added to the solution and not directly into the mixture containing cellulose. This procedure dilutes the acetic anhydride, so that the cellulose won't be hyperacetylated. This procedure guarantees that the cellulose is more uniformly acetylated [15].

The cellulose acetates obtained by the acetylation of purified sugar cane bagasse cellulose were allowed to react for 24 hours (bag24) and 48 hours (bag48), respectively. The filter paper was acetylated for 24 hours (paper), and the cellulosic pulps were both acetylated for 48 hours (sulfite and kraft).

After these acetylation times the mixture was vacuum filtered, and the filtered product was washed with 50 mL of absolute ethanol, followed by three additional washes with 50 mL of distilled water, and once again with 50 mL of absolute ethanol. Finally, the material was oven dried at 105 ºC for 3 hours.

Fourier Transform Infrared (FTIR)

The FTIR spectra were recorded on a BOMEM MB103C3 using KBr pellets. Thirty scans were collected for each measurement over the spectral range of 400-4000 cm^{-1} with a resolution of 4 cm^{-1}.

Wide angle X-ray diffraction (WAXS)

The WAXS experiments were carried out in a Rigaku Rotaflex RU 200B, at a 4°/min rate, using Kα Cu radiation with 50 KV, 100 mA and Ni filter.

The difractograms were deconvoluted into peaks and halos referring to the amorphous and crystalline regions. These deconvolutions were obtained using the Pseudo-Voigt peak function from Origin® 7.0, which is shown bellow:

$$y = y_0 + A\left[m_u \frac{2}{\pi} \frac{w}{4(x - x_c)^2 + w^2} + (1 - m_u) \frac{\sqrt{4\ln 2}}{\sqrt{\pi}w} e^{\frac{-4\ln 2}{w^2}(x - x_c)^2} \right] \quad \textbf{(4)}$$

where w is the full width at half maximum, A is the area and m_u is a profile shape factor.

Differential scanning calorymetry (DSC)

The experiments were carried out in a Dupont 2100 equipment, using a scanning rate of 20 °C/min and nitrogen flow of 50 cm^3/min.

Results and Discussion

FTIR - Fourier Transform Infrared

According to the FTIR spectra, all the cellulose samples were converted into cellulose acetate since all of them presented a peak at 1750 cm^{-1}, the carbonyl stretching band, which does not occur at non substituted cellulose. Some of the FTIR spectra are shown in Figure 1.
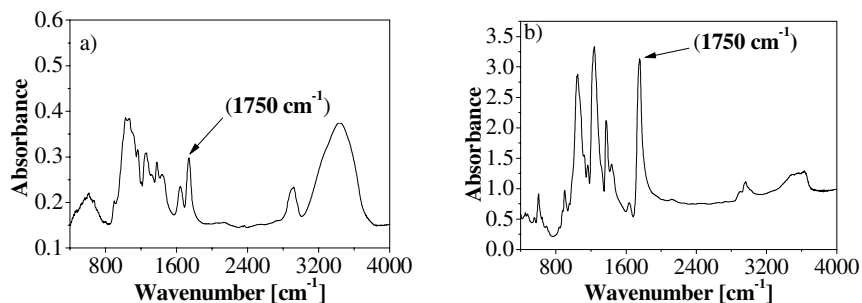

Figure 1. Infrared spectra of cellulose acetate samples. a) bag24; b) bag48.

WAXS – Wide angle X-ray scattering

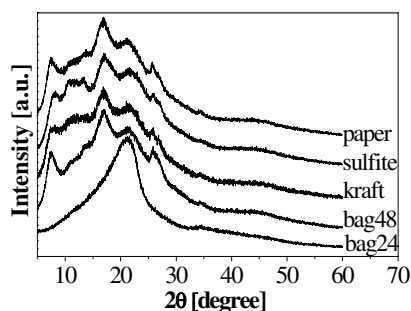Figure 2 presents the WAXS patterns of the cellulose acetates.

Figure 2. WAXS patterns of the cellulose acetates produced from: paper - Whatman 4 paper filter, 24 h; sulfite - IMP-FLORANIER-FDL (pine/sulfite/USA), 48 h; Kraft - LW-ACET (eucalyptus/Kraft/ Lençóis Paulista –SP), 48 h; bag24 e bag 48 – sugar cane bagasse cellulose, 24 h e 48 h respectively [14].

It may be observed that all the materials but bag24 present semicrystalline diffraction patterns. These diffractograms were deconvoluted into peaks and halos referring to the contributions of the amorphous and crystalline regions. Figure 3 presents the typical deconvolution pattern used in this paper.
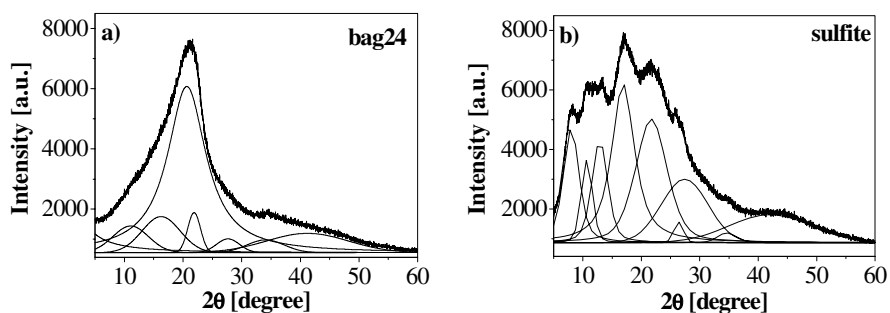

Figure 3. Typical deconvolution of the WAXS patterns a) bag24 b) sulfite.

Usually, when considering the two phase model (amorphous /crystalline), the diffractograms of semicrystalline materials are deconvolluted using a broad halo, which corresponds to the amorphous region of the material, known as van der Waals halo or amorphous halo, which is located around 20º and is present in all organic polymers [16]. Some amorphous polymers also present an halo around 10º, which is caused by the parallelism of polymer chains [17,18]. Narrower peaks corresponding to the crystalline diffraction are also used [19]. By considering that, the WAXS patterns were deconvoluted, and these deconvolutions were evaluated according to the two phase model, attributing an amorphous or crystalline character to the areas of the maxima that were obtained from the deconvolution process. According to the two

phase model, a plot of the crystalline areas versus the amorphous areas should produce a negative linear relationship. The following hypotheses were then proposed:

    a) Hypothesis I: the area of the halo at 21° was considered as the amorphous halo and the sum of the areas of the maxima at 8°, 11°, 13° and 16° was considered as the crystalline area.

    b) Hypothesis II: the sum of the areas of the maxima at 11° and 21° was considered as the amorphous area, and the sum of the areas of the maxima at 8°, 13°, and 16° was considered as the crystalline area.

The results may be observed in Figure 4.
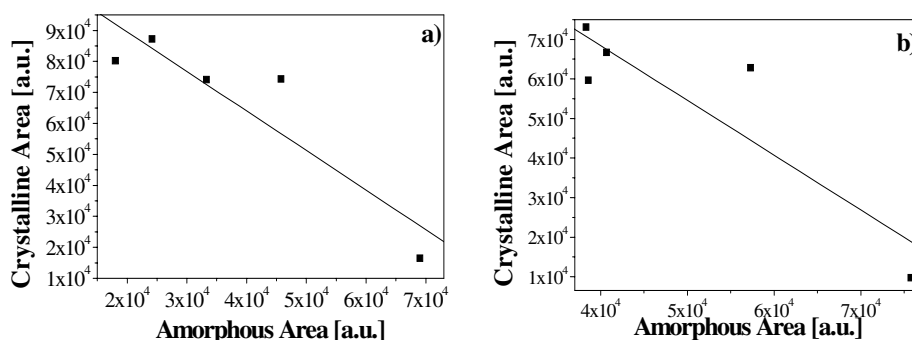
Figure 4. Crystalline area versus amorphous area. a) Hypothesis I, b) Hypothesis II.

In both hypotheses it is observed the expected negative a linear relationship between the crystalline and amorphous areas obtained from the proposed deconvolution of the WAXS diffractograms, indicating that these proposals are according to the two phase model. It must be pointed out that other deconvolution patterns were proposed, but failed in presenting the expected behavior, being discarded for this reason.

DSC – Differential Scanning Calorimetry

The DSC thermograms are presented in Figure 5.

The enthalpy of dehydration (ΔH_w), enthalpy of fusion (ΔH_f) and melting temperature (T_m) values of the materials are shown in table I.
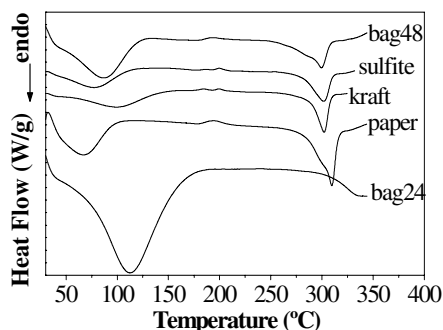

Figure 5. DSC thermograms of the cellulose acetates samples [14].

Table I. ΔH_w, ΔH_f and T_m values of the acetylated materials.

Materials	ΔH_w (J/g)	ΔH_f (J/g)	T_m (ºC)
Sulfite	54	36.7	302.16
Kraft	64	35.8	302.08
Paper	66	39.0	309.69
bag48	84	30.0	299.42
bag24	265	–	–

According to these data, except for bag24, all the materials present an endotherm of fusion located at approximately 300 ºC, confirming their semicrystalline character shown by WAXS. Instead of an endotherm of fusion, the thermogram of bag24 presents the beginning of a degradative process. This sample, differently from the others, is fundamentally amorphous as shown by its WAXS pattern.

It should be emphasized that most of the ΔH_f values of the acetylated samples in this work were higher than the $\Delta H_f°$ calculated by Takahashi et al. (34.3 J/g) [7] for a perfect crystal of cellulose acetate. This value, 34.3 J/g was obtained by Takahashi et al using Flory's equation for the melting point depression of a polymer diluent system [7] (Eq. 3). However, it was calculated considering the T_m value of samples obtained by Malm et al. (306ºC) [9] as being the $T_m°$. Malm et al. used CTA samples produced from the reacetylation of cellulose acetate samples [20], what according to those authors led to a completely substituted material. Yet, the T_m of this material can not be considered as its $T_m°$. Also, not only in Takahashi's paper [7], but also in ours the T_m of the samples are very close to Malm's "$T_m°$". For those reasons we may conclude that the use of Malm's $T_m°$ (306 ºC) by Takahashi et al. [7] to calculate the $\Delta H_f°$ of cellulose acetate was an inadequate approximation. Therefore, the value of Takahashi et al. (34.3 J/g) [7] is improper for calculating the degree of crystallinity of cellulose acetates.

Correlation between WAXS and DSC data

In this section, the proposed deconvolution for the WAXS data was correlated to the DSC data. This was made by plotting the crystalline areas of the diffractograms versus the ΔH_f of the cellulose acetates. If the proposed hypotheses are valid, the plot must present a positive linear relationship since the higher the enthalpy of fusion, the higher the crystallinity. This behavior can be observed in Figure 6 for both hypotheses.
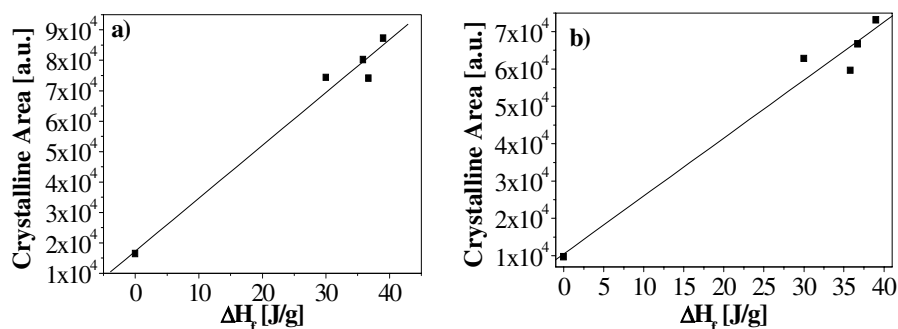
Figure 6. WAXS crystalline area versus the enthalpy of fusion of cellulose acetate samples. a) Hypothesis I; b) Hypothesis II.

Next, the enthalpy of dehydration was compared to the crystalline areas obtained from the WAXS deconvolution. The expected behavior is a negative linear relationship since the higher the crystallinity of the samples, the lower the water absorption by the material. This is shown in Figure 7.
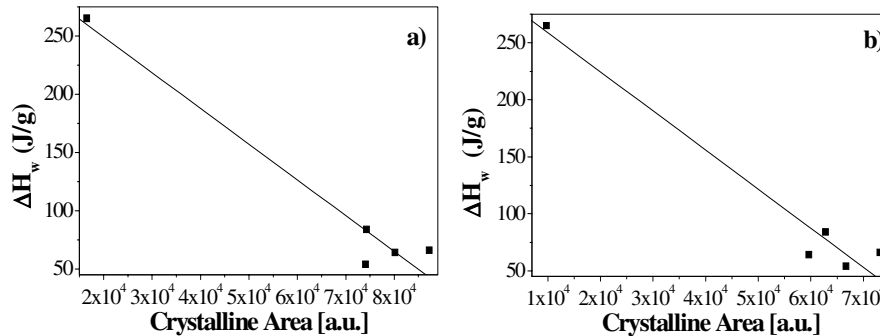

Figure 7. Enthalpy of dehydration versus WAXS crystalline areas of cellulose acetate samples. a) Hypothesis I; b) Hypothesis II.

As the expected behavior was verified for the relationships discussed above, it was established a new relationship between the enthalpy of fusion of the samples, obtained by DSC, and their crystallinities, obtained by WAXS. In this case, it is expected a positive linear relationship since the higher the crystallinity, the higher the ΔH_f of the sample. This is shown in Figure 8.
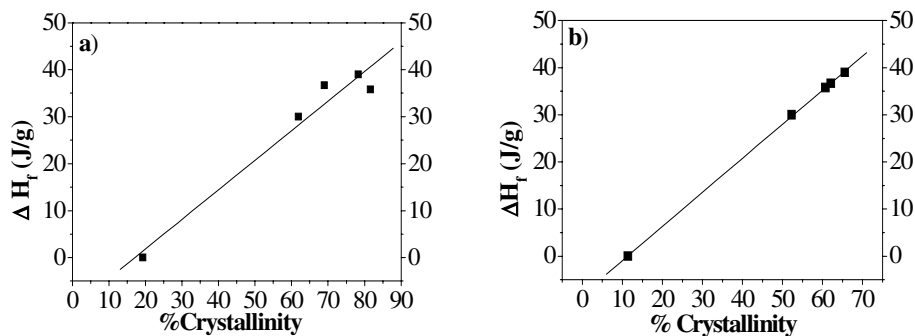

Figure 8. Relationship between the enthalpy of fusion and the % Crystallinity of several materials. a) Hypothesis I; b) Hypothesis II.

It is observed that even though bag24 does not exhibit an endotherm of fusion, it presents approximately 20 % and 10 % of crystallinity through WAXS in hypothesis I and II, respectively. This crystallinity could be interpreted as an amorphous ordering which isn't detected by DSC.

A 20 % value seems to be too high to be considered only as ordering, thus, hypothesis I was rejected. In hypothesis II, the sample bag24 presents approximately

10 % of crystallinity, which is a more acceptable value for ordering. In spite of this degree of ordering, bag 24 presents a WAXS pattern that is fundamentally amorphous, and for this reason, it does not have to be considered to determine the enthalpy of fusion of the perfect crystal, ΔH_f^o. Moreover, in theory the enthalpy of fusion should be zero for a sample that does not present crystallinity. Figure 9 presents the plot of the enthalpy of fusion versus the crystallinity of the samples.
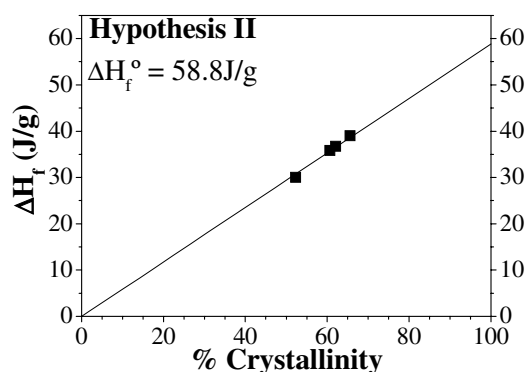

Figure 9. Relationship between the enthalpy of fusion and the %C of the samples (linear relationship forced through zero).

Through the relationship shown in Figure 9 it was possible to calculate the heat of fusion of a perfect crystal of cellulose acetate as 58.8 J/g.

Conclusion

Through the correlations between the DSC and WAXS results, we have proposed the value of 58.8 J/g for the enthalpy of fusion of a perfect crystal of cellulose acetate.

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