*Journal of Thermal Analysis and Calorimetry, Vol. 91 (2008) 3, 715–722*

# THERMAL ANALYSIS OF CELLULOSE ACETATE MODIFIED WITH CAPROLACTONE

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Cellulose acetate (CA) was modified with caprolactone (CL) under various reaction conditions in an internal mixer. The thermal behavior and relaxation transitions of the samples were determined by dynamic mechanical analysis and differential scanning calorimetry. Various relaxation transitions were detected in externally and internally modified cellulose acetate by DMTA. These were assigned to the glass transition of the main chain, to the movement of single glucose units and to hydroxymethyl groups. The β′ transition must belong to structural units larger than a single glucose ring and their formation must depend on sample preparation conditions. No transition could be assigned to grafted polycaprolactone (PCL) chains by DMTA. Contrary to other groups, we could not detect even the transitions of modified CA by DSC. Only the crystallization of oligomeric PCL homopolymer was observed mostly when it diffused to the surface of the sample.

***Keywords:*** *calorimetry, caprolactone, cellulose acetate, dynamic mechanical analysis, grafting, relaxation transitions*

## Introduction

The interest in polymers from renewable resources increases continuously. These materials are available in large quantities and they possess numerous advantageous properties [1–3]. Biocompatibility and biodegradability makes them even more interesting in many application areas. However, natural polymers, mainly polysaccharides, consist of large, rigid molecules and they cannot be processed very easily with the usual processing technologies of thermoplastic polymers [4–6]. As a consequence, many attempts are made to modify them both to improve processability and to adjust their properties to the intended application. Natural polymers can be modified physically by plasticization, or chemically through the reaction of their active –OH groups [7–9]. The benzylation of wood [10], the plasticization of starch [11, 12], and the grafting of cellulose [13] or cellulose acetate with aliphatic polyesters are typical examples of such modifications [14–21].

The modified polymers are often characterized by thermal analysis. Dynamic mechanical analysis (DMTA) and/or differential scanning calorimetry (DSC) are frequently used for the analysis of their molecular structure or for the determination of structure-property correlations [16–24]. Usually several transitions can be detected on the traces recorded by these techniques, but the assignment of the transitions to various structural units is difficult and sometimes controversial. Besides the main chain of the polymer, the motion of a considerable number of smaller structural units may result in these transitions. The situation is further complicated by plasticization or chemical modification. The association of the active –OH groups with plasticizers or water may result in new structural units and transitions, while long grafted side chains might have their own relaxation transitions [10, 16, 23].

The relaxation transitions detected in wood, starch, cellulose acetate and its derivatives modified with aliphatic esters can be divided into four main groups. The α transition appearing at the highest temperature is assigned to glass transition, to the segmental movement of the main chain of the polymer. Practically, all sources agree on the assignment of this transition [10, 16, 23–25]. More controversy surrounds the identification of the other transitions, which are usually detected at around +50, –50 and between –80 and –120°C. These transitions are often related to the movement of smaller structural units, to glucose rings, to methyl and methylol groups, to associated water and to the glass transition or even to the melting of the grafted aliphatic polymer

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chains in chemically modified polymers [26, 27]. The assignment of transitions is made even more difficult by the fact that the detected traces are inconsistent, reproducibility is poor, and both the position and the intensity of the transitions vary in a wide range. Some peaks appear on the first heating or cooling run in DSC, but are not detected in subsequent heating cycles [21, 28]. The rigidity of the molecules results in relatively small changes in heat capacity what further complicates detection and identification. Most probably these difficulties in measurement and interpretation result in the controversy encountered sometimes in publications [16, 21, 28].

In this study, we modified cellulose acetate with caprolactone by reactive processing and characterized our materials, among other techniques, by thermal analysis. We made an attempt to assign the detected transitions to the structure of the modified polymer both in the recorded DMTA and DSC traces. We compared our results to those published previously and tried to resolve some of the contradictions which we encountered during analysis. Although considerable number of techniques and measurements were used for the complete characterization of the materials produced, we focus our attention on thermal analysis here and only these results will be reported as a consequence.

## Experimental

The cellulose acetate (CA) used in our experiments was supplied by Daicel Chemical Industries Ltd. and it had a degree of substitution (DS) of 1.7. ε-caprolactone (CL) was purchased from Sigma Aldrich. Its purity was >99% and it was used without further purification. Tin-bis(2-ethylhexanoate) of 95% purity obtained also from Aldrich was applied as catalyst. Toluene and acetone, products of Spektrum 3-D, Hungary, were used for the purification of the reaction products. Benzylated cellulose and starch plasticized with glycerol were used as reference materials in the assignment of relaxation transitions detected by DMTA in the spectra of modified cellulose acetate. Experimental details related to the preparation and structure of these materials can be found elsewhere [29–31].

The reactions were carried out in a Brabender W 50 EH internal mixer at 50 mL charge volume. The caprolactone content was 45 mass% in each reaction, and 0.1 mass% catalyst was added to the reaction mixture. Reaction temperature changed between 120 and 220°C, while reaction time varied between 5 and 45 min. The speed of the rotors in the internal mixer was kept constant at 50 rpm. Reference samples were also prepared without catalyst to investigate the effect of external plasticization on properties. The amount of caprolactone as external plasticizer varied between 15 and 55 mass%. Reaction products were purified by toluene extraction to remove unreacted caprolactone and the polycaprolactone homopolymer (PCL) possibly also forming in the reaction, as well as to determine the amount of grafted PCL (gPCL). The same purification procedure was used on samples prepared without catalyst in order to check the occurrence or absence of grafting reaction. 2 g sample was extracted with 160 mL solvent for 24 h. The extracted sample was dried in vacuum at 80°C for 3 days. Graft ratio was determined from changes in sample mass, i.e. 100 x (CA-g-PCL – CA)/CA, and from the relative intensity of aliphatic methylene groups ($CH_2/CH_3$) in the FTIR spectra of modified CA samples.

Various methods were used for the characterization of the products including gel permeation chromatography (GPC), $^1$H NMR and FTIR spectroscopy. The morphology of the samples was characterized by X-ray diffraction (XRD) using a Phillips PW 1830/PW 1050 equipment with $CuK_\alpha$ radiation at 40 kV and 35 mA anode excitation. Other details of the characterization techniques were described in detail previously [29, 32].

Dynamic mechanical analysis was carried out using a Polymer Labs MkII DMTA apparatus at 1 Hz frequency and 2°C min$^{-1}$ heating rate in the temperature range of –100 and +200°C. The dimensions of the samples were 35×10×1 mm and the measurements were done in single cantilever mode to determine the storage ($E'$) and loss ($E''$) moduli. Before the experiments the samples were stored in a vacuum oven at 80°C until constant mass was reached to remove unreacted caprolactone from them. DSC measurements were done using a Perkin Elmer Diamond DSC apparatus equipped with a cryofil cooling system. Two heating and a cooling runs were carried out on 5 mg samples with 10°C min$^{-1}$ heating and cooling rates, respectively. The temperature was calibrated by indium and zinc as reference materials.

## Results and discussion

The results are reported in several sections. Based on dynamic mechanical analysis, we try to identify the main relaxation transitions of the neat and the externally plasticized cellulose acetate first. We compare the spectra of various plasticized natural polymers to each other to be able to draw general conclusions about molecular motions in these materials. Subsequently we discuss the effect of

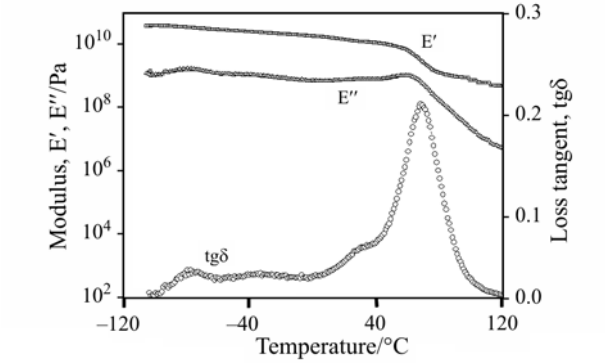


**Fig. 1** Dynamic mechanical spectrum of a cellulose acetate sample plasticized externally with 35 mass% caprolactone

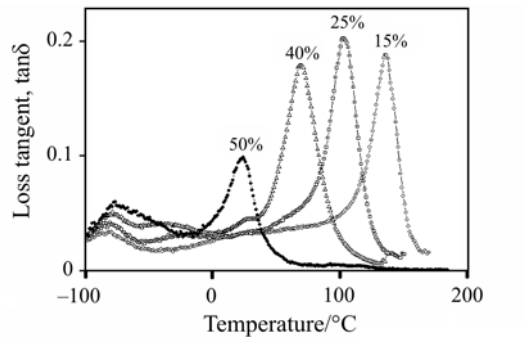


**Fig. 2** Effect of the amount of external plasticizer on the relaxation transitions of CA

grafting of caprolactone on the detected transitions. The melting and crystallization characteristics as well as the crystalline structure of polycaprolactone oligomers and homopolymers (PCL) are presented next, followed by the analysis of the DSC traces of internally plasticized cellulose acetate (CA-g-PCL).

*Relaxation transitions, structure*

The DMTA spectrum of cellulose acetate modified with 35 mass% caprolactone is presented in Fig. 1. The sample was prepared by the homogenization of the components at 180°C for 20 min without catalyst. We assume that under these conditions grafting does not take place, only external plasticization occurs. The temperature dependence of storage and loss moduli, as well as that of loss tangent is shown in the figure. The three correlations supply the same information thus for the sake of clarity we present only the loss tangent in subsequent figures. Four peaks can be detected in the spectrum. The glass transition temperature, or α transition, indicating the onset of segmental movement of large units of the stiff CA molecules appears at the highest temperature, which is about 70°C in the present case. Another transition, the β relaxation peak, appears at around –30°C. The identification of this peak is more contradictory, in the literature it is assigned to the movement of individual repeat units (glucose rings) [32, 33], or water associated with hydroxymethyl groups [26]. Other explanations are given in modified CA; the peak is assigned to the movement of grafted side groups or chains there [16]. According to literature references, the position of this transition covers a wide range from –50 to about 15°C [16, 23, 25, 26]. The β relaxation peak was more intensive and appeared at higher temperatures in cellulose acetate with a degree of substitution of 2.1 [31, 32]. Another relatively small peak or shoulder appears at around +30°C for this sample. The peak becomes very weak or even disappears from the spectrum of other samples. Its identification is difficult, sometimes it is related to groups associated to water or might result from the interaction of single repeat units and the main chain [34]. We refer to this peak as β′ transition in the further part of the paper. Finally a small peak is detected at around –85°C. This γ transition is usually related to weakly bonded water [25, 33] or methyl groups being present in various materials including, lignin or benzylated cellulose [3, 10].

Our cellulose acetate contains only a limited number of hydroxymethyl groups, but the groups of lignin and benzylated cellulose are not present. As a consequence, the γ relaxation peak cannot be assigned to those groups. We present four spectra in Fig. 2, which might help the identification of the structural unit assigned to the γ relaxation peak. The spectra of four CA samples containing varying amounts of caprolactone as external plasticizer are compared to each other in the figure. We can clearly see that the intensity of the γ relaxation peak increases with increasing CL content and it also shifts towards higher temperatures. We explain these changes by the interaction of caprolactone with the free –OH group of cellulose acetate [32]. Larger groups of associated molecules formed by secondary bonds between the plasticizer and the –OH groups of CA are less mobile than the latter alone. Water interacts with the –OH groups in the same way, which might explain that this peak is often assigned to associated water [25–27].

Figure 2 offers additional information about the effect of plasticization. The position of the α transition shifts considerably towards lower temperatures with increasing caprolactone content, which is expected. Besides decreasing $T_g$, also the intensity of the β transition varies, which was explained earlier by the breaking down of large segments to smaller structural units, probably to individual glucose rings [32]. We can also see that the β′ transition is extremely weak in all cases, basically it can be detected only on the spectrum of

CA containing 40 mass% caprolactone. Both the position and intensity of the β and β′ transitions change with composition, but it is difficult to detect any clear tendency as a function of caprolactone content.

In order to check the general validity of the assignment of the transitions presented above, we compared the dynamic mechanical spectrum of four natural polymers plasticized in different ways and in different extent. The chemical structure of cellulose and starch are very similar, both of them consists of D-glucose units. As a consequence, we expected to detect the same transitions in their DMTA spectra with slight differences caused by dissimilarities in configuration or in the type and extent of modification. Figure 3 presents the spectra recorded on externally plasticized cellulose acetate produced under conditions when grafting does not take place (180°C, 20 min, 35 mass% CL, no catalyst) (a), on internally plasticized CA prepared at 180°C, 20 min (b), on benzylated cellulose with an estimated degree of substitution of about 1.8 (c) and on starch plasticized with 30 mass% glycerol (d). The spectra are very similar to each other as expected, even the glass transition temperatures are in the same range. The β relaxation peak also appears in all spectra, but its intensity and position varies according to the nature of the polymer and the extent of plasticization. The β′ transition is very weak in most samples with the exception of the externally plasticized CA, while the γ peak can be detected unambiguously only in this latter polymer. The similarity of the spectra proves that the segments of these natural polymers are very similar. The movement of smaller units becomes possible upon plasticization. Their size and behavior

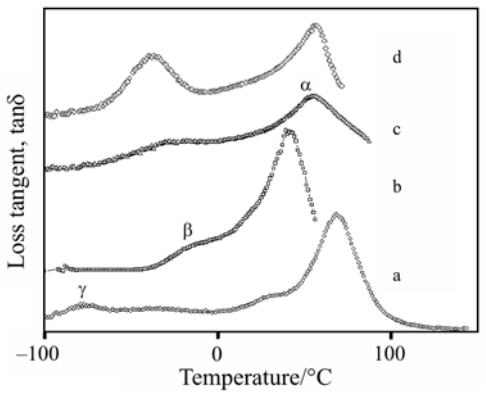


**Fig. 3** Comparison of the DMTA spectra of various plasticized natural polymers. a – CA, 180°C, 20 min, 35 mass% CL, no catalyst, b – CA, 220°C, 45 min, 45% CL, c – benzylated cellulose, degree of substitution 1.8, d – starch plasticized with 30 mass% glycerol. The traces have been shifted along the vertical axis to facilitate comparison

and thus also the position and intensity of the related transitions are more sensitive to the type and conditions of modification than those of the α transition. Segments consist of several repeat units, while the β relaxation can be assigned to much smaller entities. This structural unit might be a single glucose ring, which can rotate around the C–O bonds of plasticized CA, when strong hydrogen bonds do not act among the chains.

*Effect of grafting*

The DMTA spectra of three CA samples modified in different extent are compared to each other in Fig. 4. Two visible changes can be observed on the spectra. The position and intensity of the α relaxation transition decrease with increasing degree of grafting, while the γ relaxation completely disappears from the spectra. The disappearance of this peak cannot be explained with the loss of water, since the spectra of Fig. 2 were recorded on samples processed at 180°C, i.e. water cannot be present in large quantities in them either. On the other hand, grafting goes through hydroxyl groups, and more than possibly through hydroxymethyl groups. As a result of grafting these groups disappear, or at least their number decreases considerably, indicating that the peak is related to the movement of free –OH groups. This observation is in line with earlier results obtained on CA with a degree of substitution of 2.1 [32].

On the other hand, it is rather surprising that the intensity of the β relaxation peak remains practically the same with increasing degree of grafting. In the previous stage of this study done on cellulose acetate with DS=2.1, the changes in the position and intensity of the α relaxation peak were accompanied by a considerable increase in the intensity of the β peak [32]. We concluded from these changes that large segments break down to smaller structural units

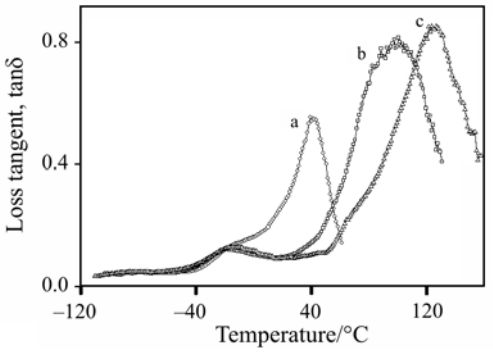


**Fig. 4** Effect of internal plasticization on the relaxation transitions of CA. a – 220°C, 45 min, PCL+gPCL=44.8 mass%, b – 180°C, 20 min, 40.1 mass%, c – 160°C, 20 min, 33.7 mass%

during plasticization. The lack of such changes in the case of CA with DS=1.7 needs further investigation.

In view of published information we find rather strange that new transitions did not appear in the spectra as an effect of grafting. Polycaprolactone has two transitions, its $T_g$ around –60°C and its melting peak around +60°C [16, 35–37]. Transitions in these regions were detected by DSC and DMTA in CA modified by polycaprolactone [16, 19]. As the spectra presented in Fig. 4 prove, we could not detect any transition in the temperature range mentioned above by DMTA. The β′ relaxation might be related to the melting of PCL, but this transition disappears from the spectrum of extracted samples. Obviously, grafted chains are not long enough for a separate $T_g$ to appear for PCL and apparently grafted molecules cannot crystallize in CA. The melting of such side chains is very difficult to detect by DMTA anyway; we may hope that DSC analysis gives us further information about the thermal behavior of grafted PCL chains. We might expect to observe a transition for glucose units grafted with PCL side chains, but the mobility of these grafted units obviously does not differ from that of the smaller entities which give rise to the β relaxation transition. Although several authors mention various transitions related to grafted PCL chains [38–42], we could not reproduce their observations and could not detect them in our DMTA experiments.

*PCL crystallization and structure*

Several groups characterized grafted CA by DSC. The glass transition of CA modified with various aliphatic polyesters was analyzed in detail by Teramoto *et al.* [19, 21]. They found that long alkyl chains are able to crystallize separately in the grafted polymer. They detected the melting of this crystalline phase by DSC and proved its presence also by XRD [21]. Our GPC and MALDI-TOF investigations proved that caprolactone chains of limited length are attached to CA under our conditions, the average length of PCL chains is maximum 9 repeat units. In order to find transitions by DSC, we must have information about the structure, as well as melting and crystallization behavior of oligomeric PCL.

The melting and crystallization of PCL with an average length of 7 repeat units is presented in Fig. 5. We can detect two peaks and a shoulder on the melting trace of the oligomer in the first heating run. The main peak appears at 43°C ($T_{m1}$). The material crystallizes at 15°C at 10°C min$^{-1}$ cooling rate ($T_c$) as the crystallization trace presented in the figure shows (cooling). The shape of the trace changes slightly in the second heating run, but its basic character remains

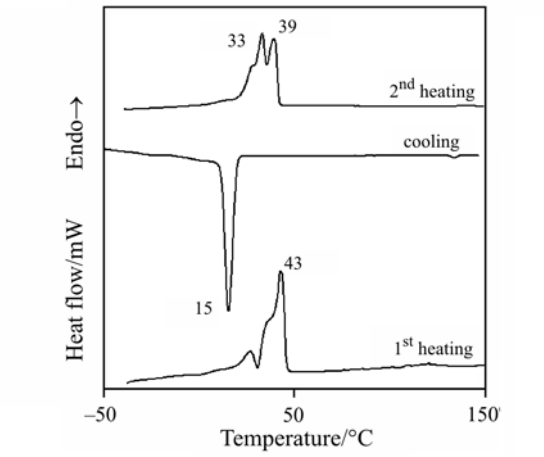


**Fig. 5** Melting and crystallization of oligomeric PCL with an average chain length of 7

unchanged; i.e. we detect a slight shoulder and two melting peaks at 33 ($T_{m2a}$) and 39°C ($T_{m2b}$). The relatively irregular melting behavior of the oligomer must be related to the well-known sluggish crystallization of aliphatic polyesters and recrystallization during melting, or to the formation of various crystal modifications. The melting and crystallization behavior of high molecular mass PCL is very similar, with the difference that both the melting and crystallization peaks appear at higher temperatures ($T_{m1}$=52, $T_c$=22, $T_{m2a}$=42 and $T_{m2b}$=48°C). These results clearly prove that even short PCL chains crystallize under appropriate conditions, thus we may detect their melting by DSC also in the graft polymer.

X-ray diffraction is another convenient method for the detection of the presence of PCL crystals. The XRD trace of the PCL oligomer (b) and a

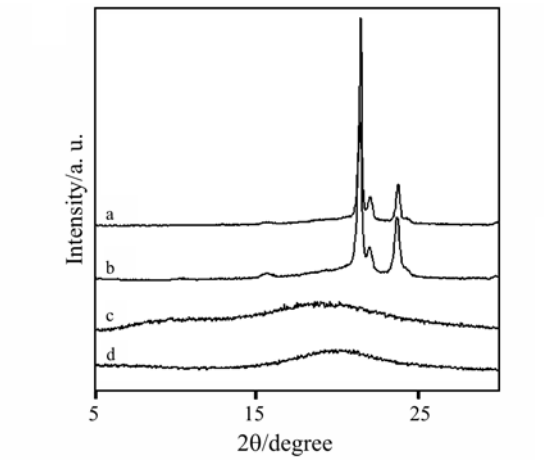


**Fig. 6** XRD spectra of CA and PCL. a – PCL homopolymer with large molecular mass, b – oligomeric PCL, c – cellulose acetate, d – CA-g-PCL, 200°C, 30 min

polymer with higher molecular mass (a) is presented in Fig. 6. Sharp, characteristic reflections are detected at 21.3, 22.0 and 23.8° and molecular mass does not seem to influence either the position or the relative intensity of the reflections. If the crystalline phase is present in the CA-g-PCL polymer, we must be able to detect it by XRD. The results of Teramoto *et al.* [21] proved, indeed, that if the chains are long enough and the aliphatic polyester is present in sufficient amounts, it crystallizes in the graft polymer and the crystals can be detected by XRD.

We included also the XRD trace of neat (c) and a modified (d) cellulose acetate in Fig. 6 for comparison. The trace of the first (c) does not exhibit sharp peaks, but two very diffuse reflections at around 10 and 19°. Similar XRD traces were published by Kamide and Saito [28] on CA with a degree of substitution of 2.92 and the reflections were assigned to the crystal II type structure of cellulose. Reactive processing modified the XRD trace of CA (d) somewhat, the peak detected at the lower angle of reflection disappeared completely, while the other changed shape and position slightly. Nevertheless, we can conclude from these results that the level of crystalline order is very low both in CA and in the modified polymer. Moreover, crystalline PCL could not be detected in the latter by X-ray diffraction.

*DSC study of modified CA*

Most of the groups studying CA by DSC could detect the glass transition temperature of the polymer. Hatakeyama *et al.* [16, 24] investigated the relaxation transition of CA chemically modified with caprolactone and besides the glass transition temperature of modified CA they identified also the $T_g$ and the melting temperature of the grafted chains. Because of the success of these groups, we made an attempt to study the thermal behavior of CA and modified CA also with DSC. Unfortunately this attempt remained unsuccessful, since we could not detect any transition on the DSC trace of neat CA (not shown). This did not surprise us very much since the heat capacity change of polymers at $T_g$ is related the increase in molecular mobility, which is not very large in rigid cellulose acetate. Nevertheless this result contradicts those published by various groups [16, 19–21, 24].

DSC measurements were done on all the modified polymers as well. We had serious difficulties to detect any changes in the traces of these samples too. We definitely could not identify the $T_g$ of grafted PCL chains or that of modified CA in the corresponding temperature ranges, at –60°C and 50–150°C, respectively. The only consistent deviation from the baseline was observed at around

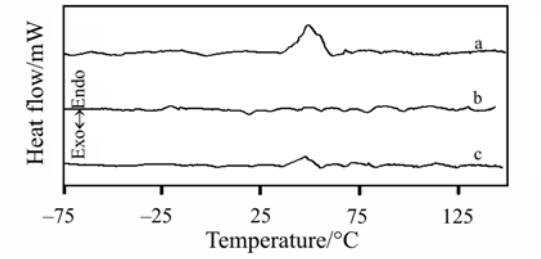


**Fig. 7** DSC traces of CA reacted with 45 mass% at 180°C for 45 min in the presence of 0.1 mass% catalyst. a – first heating, b – cooling, c – second heating

40–50°C, where crystalline PCL melts (Fig. 5). Even this peak could be detected only at a very large magnification of the DSC signal. To demonstrate the absence of secondary relaxation transitions, the DSC traces of CA reacted with caprolactone at 180°C for 45 min is presented in Fig. 7. A relatively small peak appears at around 50°C on the first heating run, the intensity of which further decreases in the second run. This phenomenon, i.e. the decrease of the intensity or even disappearance of transitions in the second run was observed by other groups as well [21]. No peak can be detected on the cooling run.

We observed that samples containing considerable amount of PCL homopolymer usually became opalescent after a certain storage time. We assumed that oligomeric PCL diffuses to the surface of compression molded plates and crystallized there. As a consequence, we wiped the plate and repeated the measurement. The trace obtained is compared to that of the original sample in Fig. 8. All traces shown in the figure were recorded in the first heating run. We can see that the simple wiping of the sample

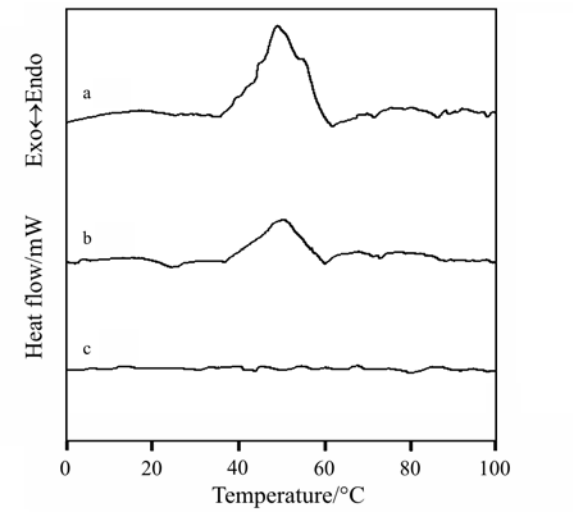


**Fig. 8** DSC traces recorded in the first heating run on the sample of Fig. 7. a – after storage, b – wiped before measurement, c – extracted (no PCL homopolymer)

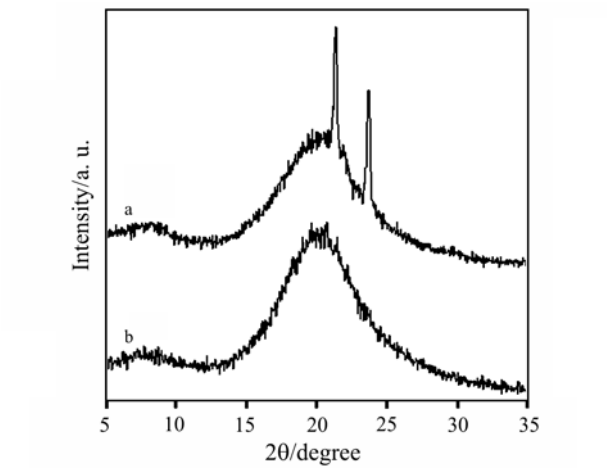


**Fig. 9** XRD traces of modified CA samples a – after storage, b – wiped before the measurement

resulted in a considerable decrease in the intensity of the melting peak of PCL, which completely disappeared after the extraction of the sample (Fig. 8c). These results clearly indicate that oligomeric PCL homopolymer crystallizes in modified CA, but especially on the surface of the samples, if sufficient time is allowed for diffusion. On the other hand, from trace c) we can also conclude that short grafted chains do not crystallize in the modified CA polymer.

In order to check the validity of these conclusions we investigated the same samples also by XRD analysis. The XRD traces of the original and the wiped sample are shown in Fig. 9. The sharp reflections characteristic for crystalline PCL (compare to Fig. 6) can be clearly seen on the trace of the sample yielding also a melting peak in DSC (see trace a) in Fig. 8). On the other hand, these reflections are completely absent from the trace measured after the wiping of the surface of the sample. The observed behavior is very consistent and could be repeated also with other samples. Accordingly, we can state that oligomeric PCL homopolymer diffuses to the surface of modified CA and crystallizes there. Crystallization is much slower even for the homopolymer in modified CA, while short grafted chains cannot crystallize at all. Other transitions could not be detected because of the limited length of grafted chains or because of the rigidity of large CA molecules. The contradiction with the results of Teramoto [19, 21] and others [16, 18, 24] might be explained by the fact that they had much longer PCL chains in larger amount in their modified CA than we did.

## Conclusions

Various relaxation transitions were detected in externally and internally modified cellulose acetate by DMTA. These were assigned to the glass transition of the main chain, to the movement of single glucose units and to hydroxymethyl groups. The β′ transition could not be identified unambiguously, since both its position and intensity varied from sample to sample. This transition must belong to structural units larger than a single glucose ring and their formation must depend on sample preparation conditions. No transition could be assigned to grafted PCL chains by DMTA. Contrary to other groups, we could not detect even the transitions of modified CA by DSC. Only the crystallization of oligomeric PCL homopolymer was observed mostly when it diffused to the surface of the sample.

## Acknowledgements

Daicel Chemical Industries Ltd. is acknowledged for the donation of the cellulose acetate sample. We would like to express our sincere gratitude to Kálmán Marossy (BorsodChem) for his competent assistance in maintaining our DMTA equipment and to Alfréd Menyhárd (Budapest U) for his help in the DSC measurements. The authors are indebted to the Hungarian Academy of Sciences for the scholarship of one of the authors. The project was partially financed by the National Scientific Research Fund of Hungary (OTKA Grant No. K68748).

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Received: August 13, 2007
Accepted: October 12, 2007

DOI: 10.1007/s10973-007-8684-5