Modification of Cellulose Acetate with Oligomeric Polycaprolactone by Reactive Processing: Efficiency, Compatibility, and Properties

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ABSTRACT: Oligomeric polycaprolactone (oPCL) was used for the modification of cellulose acetate by reactive processing in an internal mixer at 180°C, 50 rpm, 60 min reaction time, and 45 wt % caprolactone (CL) content. The product of the reaction was characterized by several analytical techniques and its mechanical properties were determined by dynamic mechanical thermal analysis and tensile testing. The synthesized oPCL contained small and large molecular weight components. The small molecular weight fraction plasticized cellulose acetate externally and helped fusion. Although composition and structure did not differ considerably from each other when CL monomer or polycaprolactone oligomer was used for modification, the grafting of a few long chains had considerable effect on some properties of the product. The large molecular weight chains attached to CA increased the viscosity of the melt considerably and resulted in larger deformability. oPCL homopolymer is not miscible with cellulose acetate and migrates to the surface of the polymer. Exuded polycaprolactone oligomers crystallize on the surface but can be removed very easily. More intense conditions may favor the grafting of long chains leading to polymers with advantageous properties. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 3255–3263, 2009

Key words: cellulose acetate; grafting; oligomeric caprolactone; molecular structure; miscibility; mechanical properties

INTRODUCTION

The ever-increasing interest for new materials is driven by the continuously increasing technical and economical pressure put on the producer by the consumers. Increasing environmental awareness also initiated research and development on materials from renewable resources and on biologically degradable polymers.[1–5] Intensive research is done to use starch, cellulose and its derivatives, wood, and other natural polymers in various application areas including packaging, agriculture, and health care.[6–11] Aliphatic polyesters are produced by various methods to prepare biologically degradable products for such applications.[12–15] Various combinations of the two kinds of materials are also explored to improve processability and properties.[16–21] Unfortunately, both natural polymers and aliphatic polyesters have several drawbacks. The first class consists of large stiff molecules that cannot be processed with the high efficiency and productivity of thermoplastic polymers.[22–27] Natural polymers are also sensitive to heat as well as to moisture; their structure is complicated and depends on origin. Aliphatic polyesters often do not have the right glass transition or melting temperature; their processing is difficult, and their properties change with time.[28]

To overcome the inherent drawbacks of natural polymers, they are often modified in various ways. Because cellulose and wood is difficult to handle and modify, often cellulose acetate (CA) is used as a starting material for further modification. CA can be plasticized externally by various aliphatic and aromatic esters.[23–25,29–31] Unfortunately external plasticizers often migrate to the surface of the product, creating environmental and health hazards and leading to the continuous deterioration of properties. As a consequence, CA is frequently plasticized internally by the grafting of various compounds to the active —OH groups of the glucose ring. To combine the advantages of natural polymers and aliphatic

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polyesters, internal plasticization is often done with polyhydroxyalkanoates. Modification is often carried out in a beaker with large excess of reagents like lactic acid, caprolactone, valerolactone, or butyrolactone.[32] Reaction temperatures and times cover a wide range from 50 to 150°C and from 5 min to 48 h. These conditions usually result in grafting with a high efficiency and long grafted chains. Modification can be done also by reactive processing at higher temperatures and shorter times, but much less information is available about the efficiency of the grafting reaction and the resulting structure of the polymer.[30]

Both the cited Refs. 30 and 32 and our earlier study[33] indicate that homopolymerization occurs under relatively mild conditions, while grafting requires higher temperatures and longer times. The length of grafted chains increases with increasing reaction time and temperature, but it is always much shorter than that obtained in solution polymerization. Changes in the degree of substitution during grafting are small, which, together with other evidence, indicate that homopolymerization proceeds easier than grafting.

Taking into account these observations, we decided to modify CA with prepolymerized, oligomeric polycaprolactone to facilitate grafting and to accelerate the reaction. Caprolactone was polymerized for various times in the presence of alkyl tin catalyst to produce the oligomers and two products with slightly different molecular weights were used for the modification of CA by reactive processing. The structure of the products and their properties were characterized by various methods. The advantages and problems of the approach are analyzed in this report.

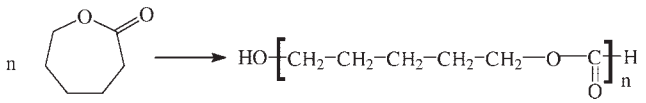
MATERIALS AND METHODS

The CA used in our experiments was supplied by Daicel Chemical Industries (Japan), 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.

oPCL was prepared at 150°C in inert atmosphere (Ar) in a three-necked flask equipped with a condenser and a gas inlet. The temperature of the reaction mixture was kept constant by an oil bath. The monomer and 0.1 wt% tin catalyst was introduced into the flask and the reaction was carried out with constant stirring for 15 and 30 min. The reaction product was characterized by GPC, matrix-assisted laser desorption ionization–time-of-flight (MALDI-TOF), and FTIR spectroscopy.

Grafting reactions were carried out in a Brabender W 50 EH internal mixer (Duisberg, Germany) at 180°C, 50 rpm, and 50 mL charge volume for 60 min. The caprolactone content was 45 and 0.1 wt % and catalyst was added to the reaction mixture. A reference sample was also prepared with monomeric caprolactone. Reaction products were purified by toluene extraction to remove unreacted caprolactone and the PCL possibly also forming in the reaction, as well as to determine the amount of grafted PCL (gPCL). A 2-g sample was extracted with 160 mL solvent for 24 h. The extracted sample was dried in a vacuum at 80°C for 3 days.

The composition and molecular weight of the product was determined by MALDI-TOF mass spectroscopy (MS). The MALDI MS measurements were performed with a Bruker BIFLEX III mass spectrometer (Bremen, Germany) equipped with a TOF analyzer. In all cases, 19-kV total acceleration voltage was used with a 3-kV pulse (extraction) voltage and with a delay time of 300 ns. The ions were detected in the reflectron mode. An LSI-type nitrogen laser (337 nm, 3-ns pulse width) operating at 2 Hz was used to produce laser desorption and 500 shots were summed. The matrix was dissolved in methanol in 20 mg/mL, while the samples were dissolved in 5 mg/mL concentrations. The ions were detected with a multichannel plate detector at a voltage of 1.65 kV. The spectra were externally calibrated with poly(ethylene glycol) (M_n = 1450 g/mol, M_w/M_n = 1.02). A volume of 0.5 μL of these solutions was deposited onto the sample plate (stainless steel) and allowed to air-dry. ^{1}H-NMR spectroscopy was carried out by using a Varian Unity Inova 400 MHz apparatus in deuterated DMSO at 40°C. The concentration of the samples was 10 mg/mL. Ten-micron-thick films were cast from the samples for FTIR analysis. Spectra were recorded by using a Mattson Galaxy 3020 apparatus in the wavelength range of 4000 and 400 cm^{-1} by 2 cm^{-1} resolution in 16 scans. The amount of gPCL was found to be proportional to the relative intensity of —CH_2— and —CH_3 groups appearing at 2943 and 1370 cm^{-1} wavelengths, respectively.[34] The color of the samples was determined with a Hunterlab Colorquest 45/0 apparatus on 1-mm-thick compression-molded plates. Standard yellowness index was calculated from color coordinates. Mechanical properties were characterized by tensile measurements according to the ISO 527 standard. Dog-bone-type specimens were cut from 1-mm-thick plates compression molded at 160°C by using a Fontijne SRA 100 machine. Five parallel measurements were done on all samples. Young's modulus was determined at 0.5 mm/min cross-head speed, while tensile strength and elongation-at-break values were



Scheme 1

derived from stress vs. strain curves recorded at 5 mm/min cross-head speed at a gauge length of 60 mm. Dynamic mechanical spectra of the samples were recorded by using a Polymer Labs MkII dynamic mechanical thermal analysis apparatus at 1-Hz frequency and 2°C heating rate in the temperature range of −100 and +200°C. Before all mechanical measurements, the samples were stored in a vacuum oven at 80°C until constant weight was reached to remove unreacted caprolactone from them.

RESULTS AND DISCUSSION

The results are presented in several sections. First we discuss the effect of oligomerization on the kinetics of the grafting reaction based on the time dependence of torque measured in the internal mixer. Subsequently, we present the composition, structure, and properties of the grafted polymers. Miscibility issues and the migration of nongrafted oligomeric species are considered in the last section of the article.

Polymerization and grafting

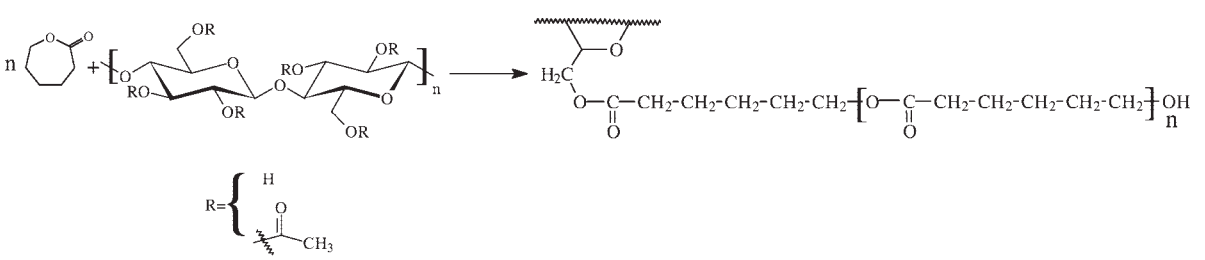
Oligomeric caprolactone is a solid waxy material, which crystallizes between 40 and 60°C, depending on the molecular weight of the polymer.[33,35,36] Such material was obtained during oligomerization when the reaction was carried out in the presence of traces of water. The oligomerization reaction is presented in Scheme 1.

The grafting of caprolactone to cellulose acetate is shown by Scheme 2.

Modification with the oligomer proceeds through esterification through the product obtained in the reaction described by Scheme 1. The average degree of polymerization of the oligomer obtained in the presence of water was 7–8. Reactive modification of cellulose acetate was very difficult with this material; melting and homogeneous mixing of the reaction mixture was practically impossible. Cellulose acetate with a degree of substitution of 1.7 contains a large number of free hydroxyl groups, which associate by hydrogen bonding and make the polymer insoluble in most solvents. The polymer alone cannot be melted and processed either; it needs an external plasticizer to help fusion.

When oligomerization was carried out in the absence of water, a liquid product was obtained, which contained a considerable amount of monomer and some high molecular weight components as well. The composition of the high molecular weight fraction of the reaction mixture of the oPCL2 sample polymerized for 30 min is presented in Figure 1. We can see that the most frequent chain length is 26 in this case. The time of oligomerization and the most frequent chain length of the oligomers used for modification are presented in lines 2 and 3 of Table I. Such composition was thought to be advantageous for reactive modification, because small molecular weight components were expected to plasticize CA externally and help fusion, while large molecules were expected to facilitate grafting.

These expectations were more or less verified by the reactive processing experiments carried out in the internal mixer. Changes in torque during the reaction are shown in Figure 2 as a function of time, when the reaction was carried out with oPCL2 and with monomer caprolactone for comparison. Torque is proportional to melt viscosity, which on the other hand, is determined by the molecular weight of the polymer. The grafting of even only a few long aliphatic chains to CA should lead to a considerable increase in molecular weight and viscosity. As trace (a) indicates, the reaction is very slow and only a small increase of torque can be observed at the end of the reaction when CL monomer is used as reactant. This observation is in complete agreement with earlier experience, which showed that grafting proceeds slower than homopolymerization and only relatively short chains are attached to CA as a result.[33,34]



Scheme 2

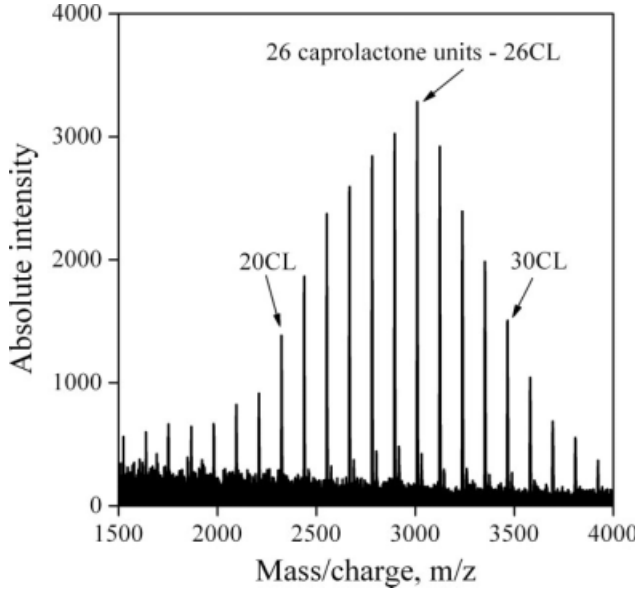


Figure 1 MALDI-TOF spectrum recorded on the high molecular weight fraction of the oPCL2 oligomer.

When CA is modified with oligomeric caprolactone torque starts to increase after about 35–40 min reaction time and with a considerably higher rate than in the previous case (Fig. 2, trace b). We assume that long aliphatic chains coupled to CA molecules result in the increase of molecular weight and viscosity. We recorded similar torque vs. time functions in all cases when oligomeric caprolactone was used for modification; the extent and rate of torque increase depended on the composition and average molecular weight of the oPCL used. Homopolymerization must proceed simultaneously and the final product should contain the monomer, PCL homopolymer, and PCL chains grafted to CA molecules. The main question is the relative amount of these components, their miscibility with the grafted polymer, and effect on properties.

TABLE I
Quantities Characterizing the Oligomeric PCL Used for Modification, the Efficiency of Grafting, the Composition, and the Structure of Modified Cellulose Acetate

Characteristic quantity	CL	oPCL1	oPCL2
Time of condensation (min)	0	15	30
Most frequent oligomer (nCL)	1	12	26
CL content (wt %)	5.4	3.3	2.1
PCL content (wt %)	14.6	16.7	14.9
gPCL content (wt %)	25.0	25.0	28.0
CH_2/CH_3 (gPCL content)	0.62	0.74	0.80
No of CL units/glucose ring	1.04	1.04	1.07
Degree of substitution	1.93	1.94	1.94
Average chain length (CL units)	4.13	4.00	4.10
Yellowness index	55.9	52.4	43.9

Composition and chemical structure

The composition and structure of the modified CA polymers obtained were analyzed by various methods. The results of the measurements are summarized in Table I. Caprolactone content was determined by drying the samples in a vacuum oven, which removes the monomer quite efficiently according to our previous experience.[3,34] The results showed that caprolactone content was the largest in the cellulose acetate modified with the monomer and its amount decreased with increasing degree of oligomerization, which agrees well with expectations. However, the differences were relatively small. PCL and gPCL content were deduced from the weight of the sample measured after extraction. Rather surprisingly, the composition of the three samples does not differ very much from each other irrespective of the initial composition of the modifying component. These conclusions are strongly corroborated by all results obtained by the various analytical techniques including ^{1}H-NMR and FTIR spectroscopy.

Earlier the extent of grafting was successfully quantified by the ratio of the number of —CH_2— and —CH_3 groups in the molecule as determined by FTIR analysis.[34] We estimated grafting efficiency from changes in the absorption intensity of aliphatic

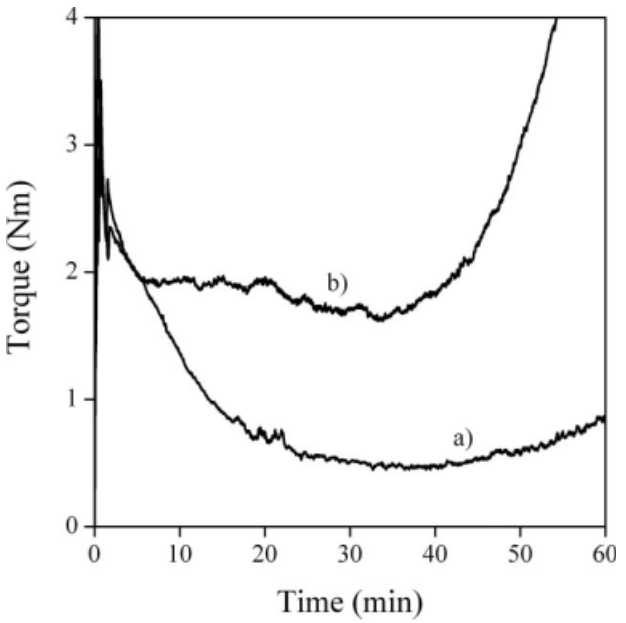


Figure 2 Changes in torque (viscosity) recorded during the reactive processing of cellulose acetate with CL monomer (a) and oPCL2 (b).

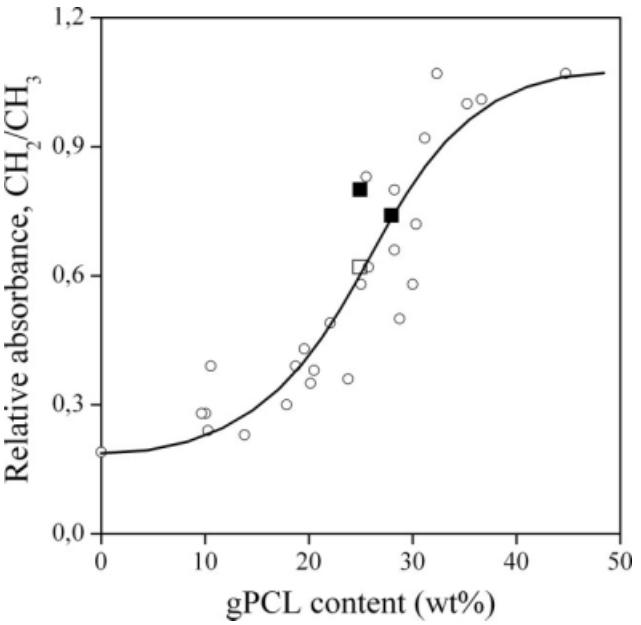


Figure 3 Correlation between the relative intensity of —CH_2— and —CH_3 vibrations appearing at 2943 and 1370 cm^{-1} in the FTIR spectrum of cellulose acetate modified with caprolactone and the gPCL content of the samples. Symbols: (■) oPCL, (□) CL, (○) CL under various conditions (see Ref. 33).

—CH_2— groups. The number of these groups changes only through the grafting of caprolactone or polycaprolactone to cellulose acetate. We assumed that the number of acetyl groups remained constant during the reaction, which was confirmed by the analysis of reaction products by MALDI-TOF and ^{1}H-NMR spectroscopy. Accordingly, the extent of grafting could be determined from the relative intensity of —CH_2— and —CH_3 groups appearing in the IR spectra at 2943 and 1370 cm^{-1}, respectively. The ratio of the absorbance of the two groups is plotted in Figure 3 as a function of the gPCL content of the modified polymers. Data obtained for a series of polymers prepared by the reaction of CA and CL monomer under various conditions in a previous study[33] are also plotted as reference. The correlation is surprisingly close (the solid line is drawn by hand only to guide the eye). CH_3/CH_2 ratios determined for the three polymers of this series fit the correlation perfectly, and this statement equally applies to the polymer modified with the monomer (□) and with the two oligomers (■). These results suggest that the composition of the initial reaction mixture has less influence on the composition of the product than reaction conditions. Open circles belong to polymers reacted chemically with CA in the presence of catalyst at various combinations of temperature and time in a previous study.[33]

Not only the composition but also the structure of the final CA-*g*-PCL polymers is very similar and leads to the same conclusion. We calculated the average number of CL units attached to CA, the degree of substitution, and the average length of PCL chains from ^{1}H-NMR spectra (see lines 8–10 in Table I). Similar to earlier experience, relatively small numbers of free —OH groups are grafted with PCL; the average degree of substitution increased from 1.7 to 1.94. The short average length of the PCL chains attached to CA, as well as the small number of CL units/glucose ring, is the consequence of the small number of grafting reactions.

In view of the results presented in this section (Table I), the considerable differences observed in Figure 2 in the time dependence of viscosity are difficult to understand. The only reasonable explanation is that a small number of relatively long chains are grafted to CA from oligomeric PCL, which significantly change its flow properties but do not modify considerably in the average values determined by ^{1}H-NMR spectroscopy. This assumption is supported by MALDI-TOF analysis, which shows that long PCL chains cannot be detected among compounds extracted from the reaction products (not shown). The length of the most frequent chain is around 7–9. Moreover, such dramatic effect of a few long chains on the rheologic properties of polymers was observed also for PE. A few branching reactions occurring during the processing of the polymer increased the melt viscosity considerably and led also to the deterioration of the mechanical properties of films produced from it.[37]

Properties

The hypothesis about the effect of long grafted aliphatic chains might be confirmed by the study of the mechanical properties of the polymers produced. Dynamic mechanical spectra were recorded on all samples, but hardly any differences were observed in them. Moreover, the exact interpretation of these differences is rather difficult due to the effect of small changes in composition and structure, which lead to considerable modification in both the position and the intensity of secondary (β, β′, γ) transitions (see Refs. 34 and 35). Similarity in structure and properties is further confirmed by Figure 4, in which the Young's modulus of the three samples is plotted against their total PCL (homopolymer and gPCL) content. Results obtained earlier are used as reference values again. Triangles indicate samples prepared without catalyst, in which caprolactone acts solely as external plasticizer. Naturally, not PCL, but CL content was plotted in the graph in this case. The correlation is very close, showing the dominating effect of CL content in the determination of stiffness. However, a more detailed analysis showed

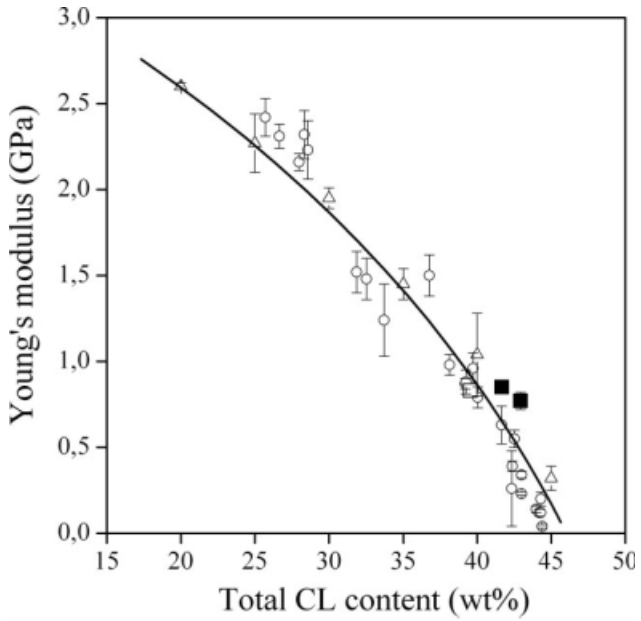


Figure 4 Dependence of the Young's modulus of CA modified with caprolactone by reactive processing on the CL content of the polymer. (Δ) CL as external plasticizer; other symbols are the same as in Figure 3.

earlier the beneficiary effect of grafted chains on the properties of CA-*g*-PCL.[38]

Unlike in stiffness, more significant differences can be observed in the tensile behavior of the polymers modified with CL monomer and different oPCL oligomers. In Figure 5 the stress vs. strain correlations of two polymers are compared immediately after the reaction (i.e., the samples a1) and b1) also contain various amounts of unreacted CL monomer). Both the strength and especially the deformability of the sample produced with the CL monomer are much smaller than the same properties of the materials prepared with oPCL1. Earlier studies proved that the high strength of cellulose polymers is the result of the hydrogen bonds among the chains. External plasticization (i.e., the replacement of secondary bonds between adjacent chains with bonds between the plasticizer and the polymer) leads to a considerable decrease of strength. The rigid chains of cellulose and cellulose acetate cannot form many entanglements; thus, deformability is usually small. Smaller CL content (see Table I) and the presence of long grafted chains result in larger yield stress and tensile strength and especially in larger deformability. The long flexible chains of PCL can easily form entanglements leading to larger ultimate deformations.

These results are further confirmed by the second set of data plotted in Figure 5 showing the stress vs. strain traces of the same samples after the removal of the caprolactone monomer in a vacuum oven. Both yield stress and tensile strength increases as a result of decreased external plasticization. The strong effect of the CL monomer is clearly seen. However, the deformability of CA modified with oligomeric PCL remains relatively large even after drying, which confirms both the presence and the effect of long aliphatic chains. Unfortunately the number of such chains is very small, as shown by the results of Table I.

Miscibility and diffusion

During the project, we observed that the transparency of the compression-molded plates changes with time. The plates are transparent immediately after preparation, but they become opaque during storage. The extent and rate in the change of transparency depends very much on the initial composition of the reaction mixture and on the degree of polymerization of the compound used for modification. These relations are demonstrated well by Figure 6, in which the decrease of light transmission is shown for two samples, for the one prepared with the CL monomer and the one produced with oPCL2. The transparency of the latter decreases very rapidly; it becomes opaque within a day or two, while light transmission through the other sample decreases much slower.

We observed that the decrease of transparency is the consequence of the migration of a compound or compounds, which cover the surface of the sample

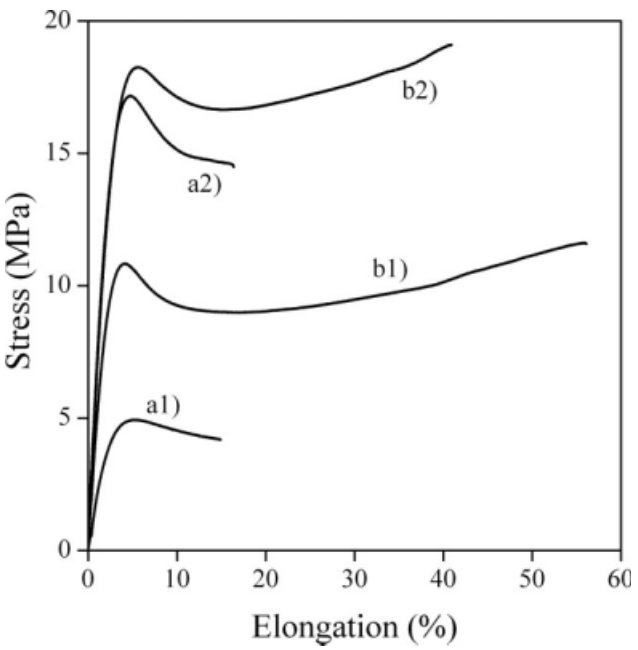


Figure 5 Stress versus strain traces of cellulose acetate modified with CL monomer (a1) and the oPCL1 oligomer (b1) recorded immediately after the reaction and after the removal of unreacted CL monomer in a vacuum oven (a2, b2).

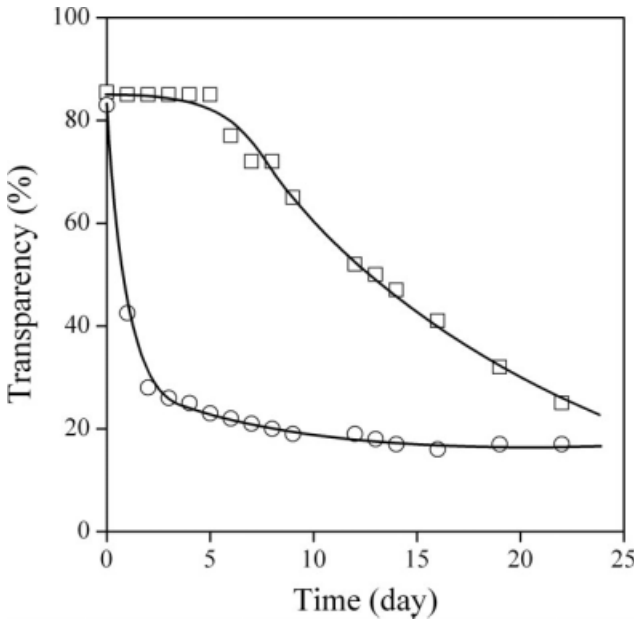


Figure 6 Changes in the transparency of compression-molded plates during storage under ambient conditions. Modification: (□) CL monomer, (○) oPCL2 oligomer.

after some time. We removed this substance from the surface and analyzed it. The MALDI-TOF spectrum recorded on this material is presented in Figure 7 and proves that it contains PCL oligomers of various chain lengths. The oligomer found in the largest quantity among the compounds has the chain length of 9. Figure 7 also confirms our earlier conclusion that most of the longest chains are attached to CA, because we did not find such compounds either among those extracted from the modified polymer

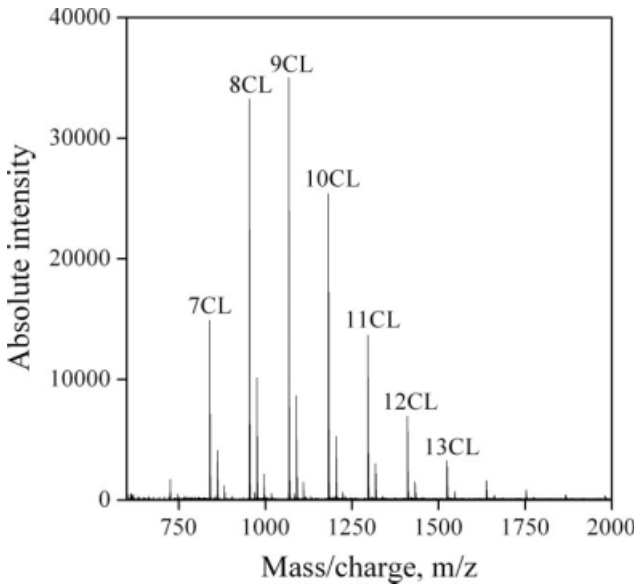


Figure 7 MALDI-TOF spectrum recorded on the material removed from a compression molded plate. Modification: oPCL2 oligomer.

or among the migrating oligomers. Naturally, the last fact alone does not prove our hypothesis about the grafting of long chains, because very long molecules might not be able to migrate to the surface in such a relatively short time. On the other hand, the difference between the two correlations shown in Figure 6 indicates that CA and PCL are not miscible with each other[31,39] and the solubility of oPCL in CA decreases rapidly with increasing molecular weight.

Earlier results proved that oligomeric PCL with relatively small molecular weight does not crystallize in CA-*g*-PCL, but it does relatively easily on the surface of compression-molded plates.[35] The melting and crystallization behavior of a PCL sample with a number-average molecular weight of 50,000 g/mol and that of the material removed from the surface of an opaque sample prepared with oPCL2 is shown in Figure 8. The melting trace of samples recorded in the second heating run is plotted in the figure in both cases. The high molecular weight polymer exhibits relatively sharp melting and crystallization peaks at 62.2°C and 27.7°C, respectively. The behavior of the material removed from the surface of the plate is undoubtedly very similar, but the corresponding transitions appear at smaller temperatures and their intensity is weaker as well, but this is at least partially due to the smaller sample size.

The presence of crystalline PCL was further confirmed by X-ray diffraction measurements. XRD traces recorded on compression-molded plates are

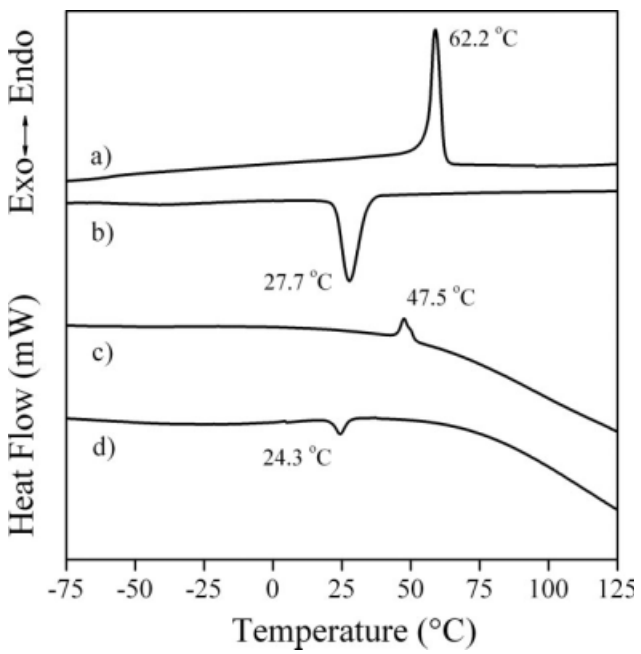


Figure 8 Melting and crystallization traces of a high molecular weight PCL polymer (a and b) and those of the material removed from the surface of the compression-molded plate of Figure 7(c, d).

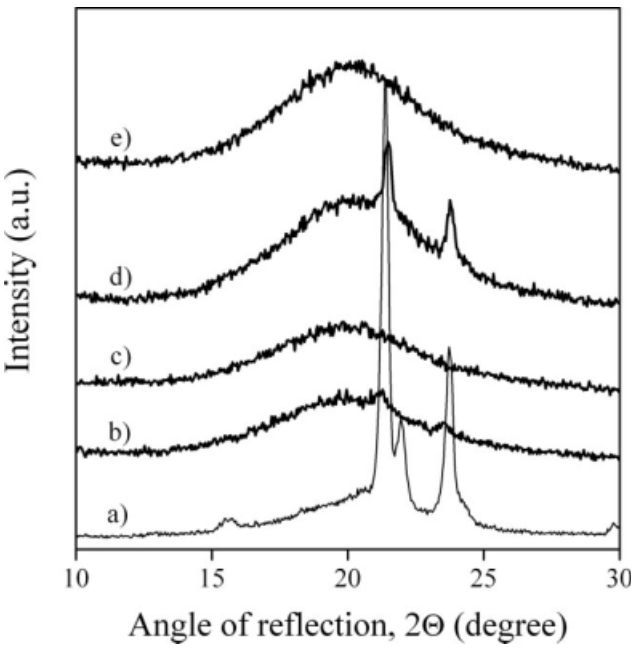


Figure 9 XRD spectra recorded on crystalline PCL oligomer and on compression-molded plates prepared from CA modified with caprolactone: (a) PCL oligomer, (b) plate, CL monomer, after storage, (c) plate, CL monomer, wiped, (d) plate, oPCL1 oligomer, after storage, (e) plate, oPCL1 oligomer, wiped.

presented in Figure 9. The trace of a crystalline oligomeric PCL prepared separately is shown as reference (trace a). The characteristic reflections of crystalline PCL appear at 21.3, 22.0, and 23.8 2θ angles. Trace (b) was recorded on the sample prepared with the CL monomer and stored under ambient conditions for 3 weeks. The characteristic reflections of crystalline PCL are hardly visible on the spectrum and they completely disappeared after the surface was wiped with a tissue (trace c). The intensity of the peaks related to crystalline PCL is quite strong in the XRD trace recorded on the sample produced with oPCL1 (trace d), but the peaks completely disappear after the cleaning of the specimen (trace e) in this case too. The results presented in this section clearly prove that oligomeric PCL is not miscible with CA, migrates fast to the surface, and crystallizes there.

CONCLUSIONS

The oligomeric PCL used for the modification of cellulose acetate contained small and large molecular weight components. The small molecular weight fraction plasticized cellulose acetate externally and helped the fusion of the polymer. Although composition and the quantities characterizing structure did not differ considerably from each other when CL monomer or PCL oligomer was used for modification, the grafting of a few long chains had considerable effect on some properties of the product. The large molecular weight chains attached to CA increased the viscosity of the melt significantly and also resulted in larger deformability, which might be beneficial in some applications. On the other hand, oligomeric PCL homopolymer is not miscible with cellulose acetate and migrates to the surface of the polymer. Exuded PCL oligomers crystallize on the surface of samples but can be removed very easily. More intense conditions, like higher temperatures and longer times, may favor the grafting of long chains and lead to polymers with advantageous properties.

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