

Thermoplastic Cellulose Acetate and Cellulose Acetate Compounds Prepared by Reactive Processing

HOLGER WARTH,¹ ROLF MÜLHAUPT,¹ JOACHIM SCHÄTZLE²

¹Freiburger Materialforschungszentrum und Institut für Makromolekulare Chemie der Albert-Ludwigs-Universität, Stefan-Meier-Strasse 21, D-79104 Freiburg, Germany

²Rhone Poulenc Rhodia AG, Hermann-Mitsch-Strasse 36a, D-79013 Freiburg, Germany

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ABSTRACT: Novel families of thermoplastic polysaccharides such as cellulose-2,5-acetate were produced by means of reactive processing technology that grafted cyclic lactones simultaneously onto polysaccharide, hydroxyfunctional plasticizer, and optionally also onto hydroxyfunctional fillers. Organosolv lignin, cellulose, starch, and chitin were added to effect reinforcement of the polymer matrix. Mechanical and thermal properties depended upon molecular architecture of the components and process parameters such as temperature, feed ratios, and screw speed. Such blends and composites utilize renewable resources and are of interest in waste disposal via biodegradation. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 231–242, 1997

Key words: renewable resources; blends; carbohydrate; cellulose; starch; lignin; composite

INTRODUCTION

The development of thermoplastics based on cellulose and its derivatives dates back to the 19th century. After pioneering work by Braconnot¹ and Schönbein² in the preparation of cellulose nitrates, it was Hyatt who discovered that camphor was effective as a plasticizer in obtaining thermoplastic cellulose nitrate, which is useful for producing moldings and films.³ Thermoplastic cellulose acetate became commercially attractive when injection molding was introduced. There are three main strategies leading to thermoplastic cellulose acetate: addition of low molecular weight plasticizers, formation of polymer blends, and chemical modification or grafting of the saccharide backbone. Due to the low cost and easy processability of the plasticized cellulose acetate, low molecular weight plasticizers^{4–9} like phthalates,^{10,11} gly-

erol,^{12,13} triacetate,^{14–16} or cyclic lactones¹⁷ are preferred. Their main disadvantage, however, is related to plasticizer migration that can account for loss of mechanical properties. Therefore, higher molecular plasticizers have been used. For example, Koleske et al. developed blends based on polycaprolactone.¹⁸ According to Vásquez-Torres et al., however, cellulose acetate and poly(caprolactone) appear to be incompatible.¹⁹ Daicel Ltd. filed several patents claiming grafting of cellulose acetate with caprolactone.^{20–27} The resulting products were transparent, highly flexible, and had good mechanical properties. However, the grafting process was carried out in solution, thus accounting for solvent emission during solvent recovery and recycling.

Today thermoplastic cellulose acetates are regaining interest as potentially biodegradable plastics for composting of plastic waste without encountering the water-solubility problems typical for starch based materials. The purpose of our research was the development of reactive pro-

Correspondence to: R. Mülhaupt.

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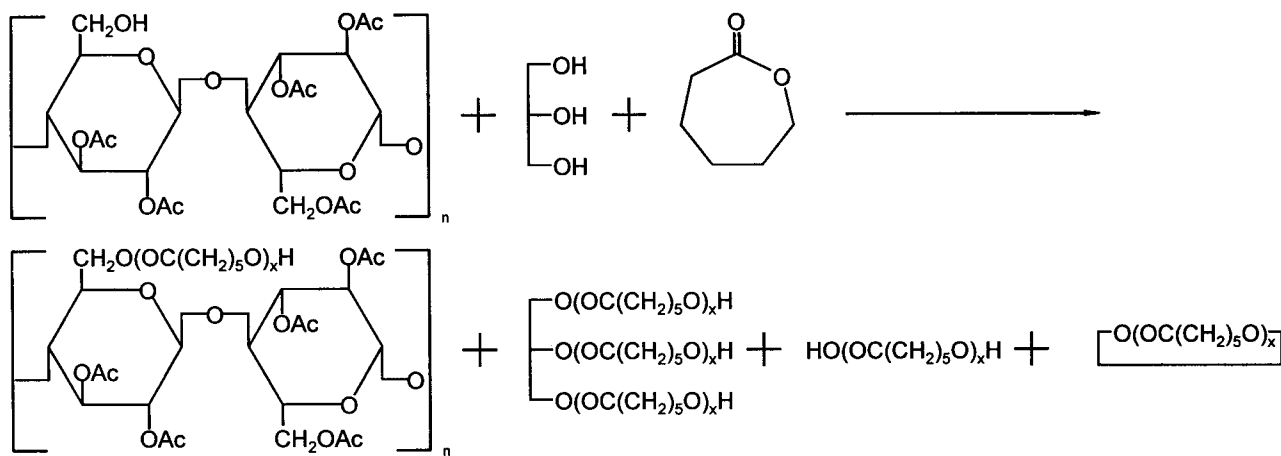


Figure 1 *In situ* grafting of cellulose-2,5-acetate plasticized with glycerol.

cessing technology, where both cellulose acetate and polyol plasticizers are grafted simultaneously via ring-opening polymerization of ϵ -caprolactone onto hydroxy groups of the polysaccharide and the polyol. This scheme is presented in Figure 1. Key advantages of this process are *in situ* formation of oligo- and poly(ϵ -caprolactone) as nonmigrating plasticizers combined with *in situ* compatibilization by simultaneously grafting oligo(ϵ -caprolactones) onto cellulose acetate and polyol plasticizer. The influence of process conditions, various polyol plasticizers, and cyclic lactones such as ϵ -caprolactone, glycolide (1,4-dioxane-2,5-dione), and lactide (3,6-dimethyl-1,4-dioxane-2,5-dione) on polymer properties were investigated. Moreover, in addition to mono- and polyfunctional alcohols such as methoxyethanol, diethylene glycol, glycerol, and sorbitol, epoxidized soybean oil (ESO) and polyethylene glycol (PEG) were used as plasticizers. Starch, cellulose, organosolv lignin, and chitin were added as fillers to produce thermoplastic compounds with improved stiffness.

EXPERIMENTAL

Materials

The commercial cellulose-2,5-acetate used in our experiments was supplied by Rhone-Poulenc Rhodia AG (Freiburg, Germany). The degree of polymerization was 220 and the degree of substitution 2.5. Lactide and glycolide monomers were supplied by Boehringer Ingelheim (Germany); caprolactone, methoxyethanol, sorbitol, and chitin were supplied by Aldrich (Kehlheim, Ger-

many); glycerol was from Henkel KGaA (Düsseldorf, Germany); corn starch was from Cerestar (Vilvoorde, Belgium); organosolv lignin was supplied by Organocell (Kehlheim, Germany); epoxidized soybean oil, Irganox 1010, and Irganox 168 was supplied by Ciba (Basel, Switzerland); and PEG (600 g/mol) was from Hoechst AG (Frankfurt, Germany). Until otherwise stated, these components were used as received. The catalyst was titanium(IV)butylate supplied by Hüls AG (Marl, Germany).

Batch Mixer

An IKAVIS batch mixer (IKA, Staufen, Germany) was used for investigating variations of polyol and lactone components. The mixer monitors temperature, stirrer revolutions, and torque automatically. The cellulose-2,5-acetate (50 wt %) was mixed with Irganox 1010 (1000 ppm) and Irganox 168 (500 ppm) and heated to 100°C under a 40-mbar vacuum to remove moisture. Under an N_2 atmosphere the temperature was increased to 210°C. Then polyol (25 wt %), lactone (25 wt %), and catalyst (0.5 wt %) were added and kneaded in the N_2 atmosphere. After 30 min a vacuum was applied to remove the remaining volatile monomers or polyol. Then the kneader was cooled to 100°C to recover the product.

Twin Screw Extruder

A CLEXTRAL BC 21 extruder with corotating screws (point 1 in Fig. 2) was used to prepare thermoplastic cellulose-2,5-acetate as depicted in

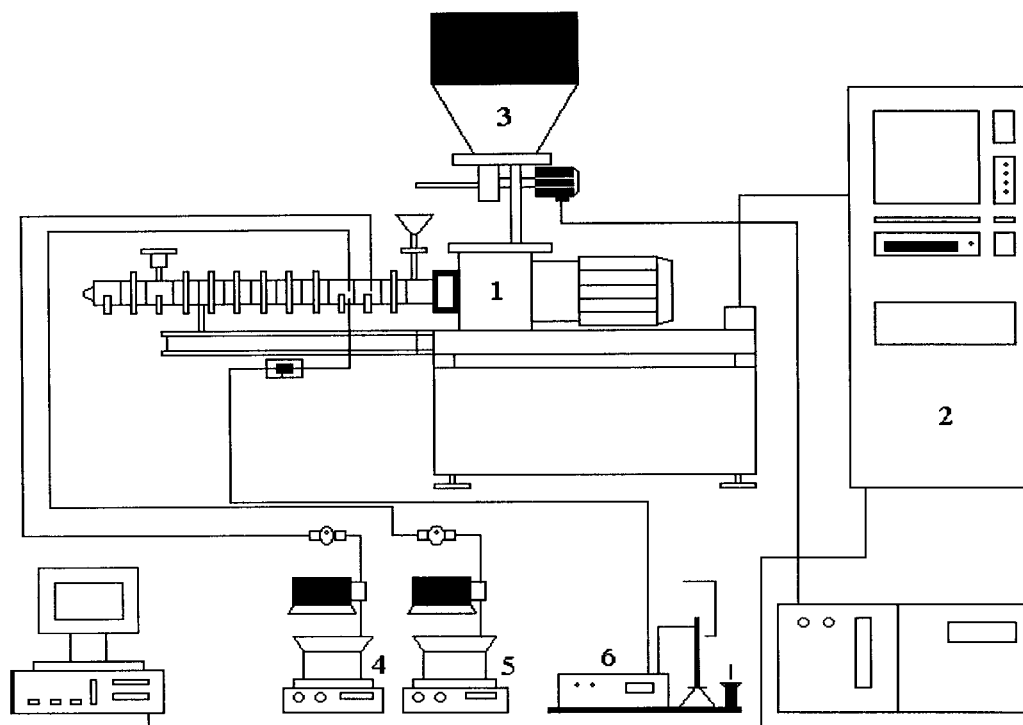


Figure 2 Twin-screw extruder system used to perform *in situ* grafting.

Figure 2. The extruder parameters were set at the control panel (2, Fig. 2) and monitored by a computer. The system was fed by a gravimetric K-Tron KCL24T20 feed system, two Prominent membrane pumps (4 and 5, Fig. 2) and an HPLC pump. The length/diameter (L/D) ratio was 48, $D = 25$ mm. The residence time was approximately 5 min, reaction temperature was 190°C, and screw speed was 250 rpm. To evaluate the resulting data concerning variation of cellulose-2,5-acetate, ϵ -caprolactone, and glycerol, commercially available SAS software (SAS Institute) for the experimental design of experiments was used.

Characterization of Thermal Properties

Thermal properties were recorded by means of a Perkin–Elmer 7 thermal analyzer and a Netzsch STA 409 system. Typically, 10–20 mg samples were used. Differential scanning calorimetry (DSC) gave the glass transition (T_g), three melting points of oligomeric and grafted components (T_1 , T_2 , T_3), and the decomposition temperature (T_z). The resulting phase transitions were determined by means of dynamic mechanical analysis at a heating rate of 5 K/min and frequency of 1 Hz. For evaluation of thermal degradation the weight loss between 170 and 200°C was recorded

by thermogravimetric analysis (TGA) under nitrogen at a heating rate of 10 K/min.

Characterization of Mechanical Properties

According to DIN 53455, samples were cut from compression- and injection-molded material to produce test specimens. Tensile test experiments were carried out with an Instron 4204 Series 9 apparatus, according to DIN 53455, and gave tensile stress at maximum load, elongation at maximum load, and the Young's modulus. Crosshead speed was 10 mm/min.

Characterization of Molecular Mass

Molecular mass was determined by means of size exclusion chromatography. Typically, 10–20 mg of the sample was dissolved in dimethylformamide and fractionated by a microgel C11 column calibrated against polystyrene standards, using refractive index detection. Two fractions, corresponding to grafted cellulose-2,5-acetate and oligomeric fraction parts like grafted polyol, were detected.

Characterization of Residual Cyclic Lactone Content

Typically 200 mg of the powderized material was extracted in tetrahydrofuran for times between 1 and 3 h. The solution contained lactone, alcohol, and low molecular weight components like grafted polyols and oligomers. Their contents were determined by gas chromatography.

Experimental Design

To evaluate the multicomponent system, experimental design was applied. Compositions and extruder parameters were optimized according to Paulus.²⁸ Resulting data were evaluated by the commercial software SAS System for Windows.

RESULTS

Cellulose-2,5-acetate was plasticized by addition of a mono- or polyfunctional alcohol, referred to as polyol, to obtain thermoplastic cellulose-2,5-acetate. Then cyclic lactones such as ϵ -caprolactone, lactide, and glycolide were injected and grafted onto both polyol and polycarbohydrate in the presence of a catalyst, usually titanium(IV)butylate.^{29,30} The corresponding reaction scheme is illustrated in Figure 1 for cellulose-2,5-acetate that was plasticized with glycerol and grafted with ϵ -caprolactone. This reactive processing technology is based upon the well-known catalytic ring-opening polymerization of cyclic lactones that can also form by-products such as cyclic oligomers resulting from a backbiting reaction.³¹ In addition to ϵ -caprolactone, glycolide and lactide were applied as cyclic lactone components. All polylactones are well known as biodegradable plastics.^{32–37} Process conditions, cyclic lactone content, and polyol plasticizer were varied systematically.

Variation of Lactone Component

Simultaneous *in situ* grafting of polyol plasticizer and cellulose-2,5-acetate with ϵ -caprolactone, glycolide, or lactide, respectively, afforded thermoplastic cellulose-2,5-acetate. During the reaction the viscosity increased as a function of the cyclic lactone type, with viscosity increasing in the series ϵ -caprolactone < glycolide < lactide. The maximum viscosity in the kneader was reached 15 min after injection of ϵ -caprolactone and 5 min after injection of lactide. In Table I the composi-

Table I Variation of the Lactone Component

Lactone	Monomer							Oligomer			Tensile Stress (MPa)	Elongation (%)	Young's Modulus (MPa)		
	T_g (°C)	T_1 (°C)	T_2 (°C)	T_3 (°C)	T_z (°C)	Weight Loss ^a (%)	Concentration (%)	M_n (g/mol)	M_w/M_n	Concentration (%)				M_n (g/mol)	M_w/M_n
ϵ -Caprolactone	-53	61	153	200	276	1.6	5.6	137,900	2.3	5	3210	0.62	17.5	64	496
Lactide	-27	62	131	181	252	3.5	2.4	144,300	4.4	6	7510	0.02	14.8	40	434
Glycolide	-46	58	119	210	249	3.7	0.1	57,700	1.2	10	3045	0.06	16.5	81	336

The system was cellulose-2,5-acetate (50 wt %), glycerol (25 wt %), lactone component (25 wt %), Ti(OBut)₄ (0.5 wt %), 210°C, kneader 30 min.
^a 170–200°C; heating rate 5°C/min.

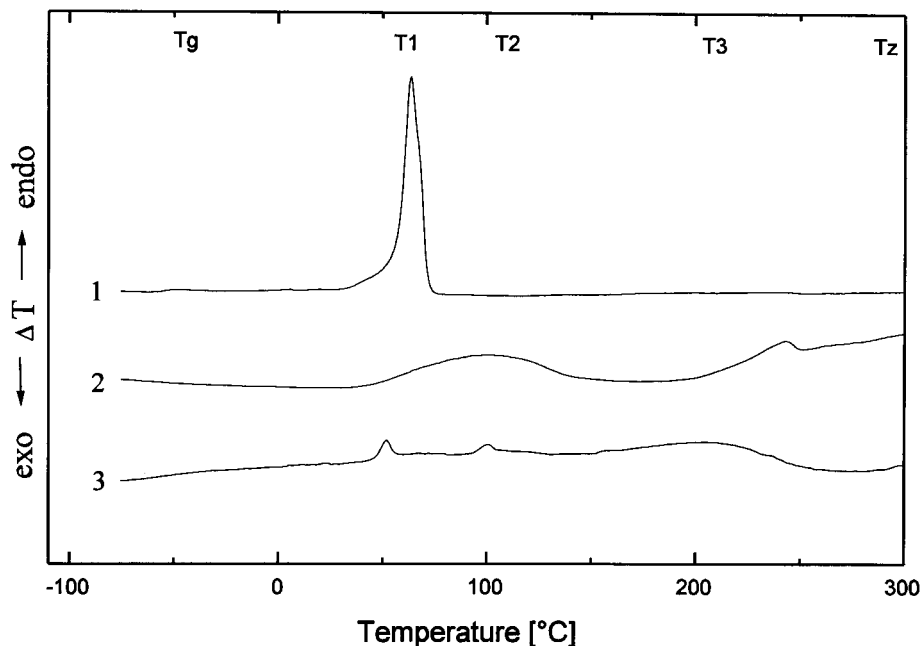


Figure 3 DSC traces of poly(ϵ -caprolactone) (1), cellulose-2,5-acetate (2), and *in situ* grafted cellulose-2,5-acetate (3).

tion, thermal, and mechanical properties of the three different lactone components are summarized. The glass temperature (T_g) of the lactide-based compound is -27°C , whereas those of the other lactones were found to be in the range of -50°C . T_3 corresponds to the melting temperature of cellulose acetate grafted with cyclic lactones and plasticized with *in situ* formed oligocaprolactones. T_1 represents the melting temperatures of oligolactones whereas T_2 is an additional melting temperature, which most likely corresponds to oligomeric cellulose-2,5-acetate grafts. Figure 3 shows DSC traces of poly(ϵ -caprolactone), cellulose-2,5-acetate, and grafted cellulose-2,5-acetate.

Softening temperature ($T_2 = 153^\circ\text{C}$) decreased from ϵ -caprolactone to lactide ($T_2 = 119^\circ\text{C}$). The lactide containing sample gave the lowest melting temperature ($T_3 = 181^\circ\text{C}$) with respect to $T_3 = 200^\circ\text{C}$ for ϵ -caprolactone grafted cellulose-2,5-acetate. All decomposition temperatures were well above those melting temperatures, thus affording good processability. The residual monomer content was decreased as expected for cyclic lactone reactivity: 5.6 wt % of ϵ -caprolactone and 0.1 wt % of glycolide; oligomer content, determined by extraction, increased from 5 to 10 wt %. Highest grafting yield or lowest residual monomer and oligomer content, respectively, were found for lactide grafting. Molecular mass of the

lactide oligomer (7510 g/mol) was much higher than the 3210 and 3045 g/mol for ϵ -caprolactone and glycolide, respectively. Molecular mass of grafted cellulose-2,5-acetate was found to be 144,300 g/mol for lactide and only 57,700 g/mol for glycolide. Likewise the mechanical data showed lower tensile stress (14.8 vs. 17.5 MPa) and elongation (40 vs. 64%) when comparing lactide- with ϵ -caprolactone-based compounds. This was in accord with observations of low oligomer content detected in the case of the lactide-based compound.

Variation of Hydroxyfunctional Plasticizer

Methoxyethanol, diethylene glycol, glycerol, and sorbitol were used as mono-, di-, tri-, and poly-functional plasticizers. When added to cellulose-2,5-acetate together with cyclic lactone, all of them gave thermoplastic cellulose-2,5-acetate. With increasing functionality, viscosity build-up was smaller. Methoxyethanol and diethylene glycol were stripped in a vacuum, thus accounting for the 4–5 wt % lower alcohol content. Sorbitol-containing samples gave much better color. Thermal properties, listed in Table II, showed an increase of thermal transition temperature (T_1 , T_2 , T_3) as well as decomposition temperatures (T_z) with increasing numbers of hydroxy groups. The diethylene glycol containing sample exhibited a

Table II Variation of Hydroxyfunctional Plasticizer

Hydroxyfunctional Plasticizer	T_g (°C)	T_1 (°C)	T_2 (°C)	T_3 (°C)	T_z (°C)	Weight Loss ^a (%)	Monomer			Oligomer			Tensile Stress (MPa)	Elongation (%)	Young's Modulus (MPa)
							Concentration (%)	M_n (g/mol)	M_w/M_n	Concentration (%)	M_n (g/mol)	M_w/M_n			
Methoxyethanol	-45	57	92	180	258	1.4	0.5	113,500	6.0	5	7480	0.1	12.9	8	583
Diethylene glycol	-44	63	110	222	293	2.3	3.0	93,900	5.0	(26.4)	—	—	11.5	27	458
Glycerol	-53	61	153	200	276	1.6	5.6	137,900	2.3	5	3210	0.6	17.5	64	496
Sorbitol	-30	71	127	211	290	2.0	0	117,900	2.6	6	8590	0.03	29.3	5	1408
Sorbitol/glycerol ^b	-61	57	102	183	269	2.7	0.3	106,700	2.9	5	5980	0.1	34.0	14	932

The system was cellulose-2,5-acetate (50 wt %), hydroxyfunctional plasticizer (25 wt %), ϵ -caprolactone (25 wt %), Γ (OBut)₄, (0.5 wt %), 210°C, kneader 30 min.

^a 170–200°C, heating rate 5°C/min.

^b 12.5/12.5 wt %.

higher melting point (T_3) and higher content of oligomers. A mixture of glycerol and sorbitol resulted in markedly lower thermal transition temperatures. When vaporization was taken into account, during degassing the residual monomer content decreased with increasing functionality while there was no change in the oligomer content. The elongation at maximum load increased in the series methoxyethanol (8%) and glycerol (64%), but was much lower for sorbitol (5%). Tensile stress and Young's modulus increased with increasing functionality of the polyol from 13/583 MPa for methoxyethanol to 29/1408 MPa for sorbitol, respectively. The mixture of sorbitol and glycerol gave considerably higher tensile stress of 34 MPa. The molecular masses of the oligomeric fractions was 7480 g/mol for methoxyethanol and 8590 g/mol for sorbitol.

Scale-Up and Variation of Contents of Cellulose-2,5-acetate

The compound cellulose-2,5-acetate, plasticized with glycerol and *in situ* grafted with ϵ -caprolactone, was scaled up in a twin-screw extruder with corotating intermeshing screws. The extruder system is displayed in Figure 2. The resulting grafted materials exhibited much smaller weight loss in TGA than conventional compounds with low molecular weight plasticizer. Figure 4 shows TGA traces of pure cellulose-2,5-acetate, ϵ -caprolactone grafted cellulose-2,5-acetate containing 24 wt % glycerol-/ ϵ -caprolactone-based (1 : 1) plasticizer, and cellulose-2,5-acetate containing 26 wt % diethylphthalate as a conventional low molecular mass plasticizer. While pure cellulose-2,5-acetate decomposed at temperatures above 275°C, the diethylphthalate-based compound exhibited three stages of weight loss. The first two stages from 140 and 280°C resulted from plasticizer devolatilization and the last one from 325°C resulted from the decomposition of the cellulose-2,5-acetate. In contrast, thermal decomposition of the compound containing grafted plasticizer was similar to pure cellulose-2,5-acetate with weight losses shifted approximately 25°C to lower temperatures. The grafted plasticizer was not volatile and decomposed well above 240°C.

Figure 5 shows Young's modulus and elongation as a function of the screw speed. With screw speed increasing from 100 to 500 rpm, Young's modulus dropped by 15% from 650 to 550 MPa, elongation nearly tripled from 35 to 110%, and color deteriorated. In Figure 6 the amount of

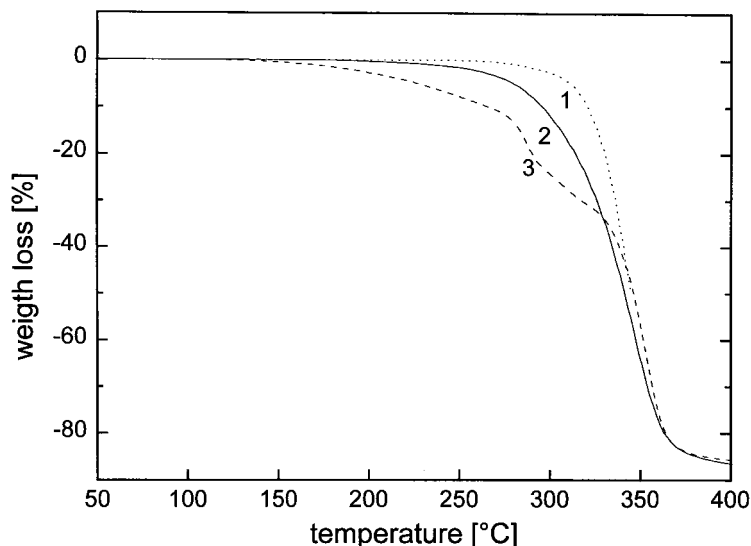


Figure 4 Thermogravimetric analysis of cellulose-2,5-acetate (1), ϵ -caprolactone grafted cellulose-2,5-acetate containing 24 wt % glycerol/ ϵ -caprolactone) (2) (1 : 1), and cellulose-2,5-acetate containing 26 wt % diethylphthalate (3).

oligomeric plasticizer increased slowly with higher screw speeds and the residual monomers dropped sharply from 9 to 2 wt %. This clearly indicates that much better grafting can be obtained with higher screw speeds.

Experimental design was applied to evaluate the multicomponent system. To minimize the number of experiments, several parameters were changed simultaneously. In Figure 7 the tensile

stress is plotted against the cellulose-2,5-acetate content. The vertical lines are not error bars but show the area for a certain cellulose-2,5-acetate concentration in which the tensile stress was varied by simultaneously changing other parameters like the ratio of glycerol to ϵ -caprolactone or specific extruder parameters. With increasing cellulose-2,5-acetate content the tensile stress increased.

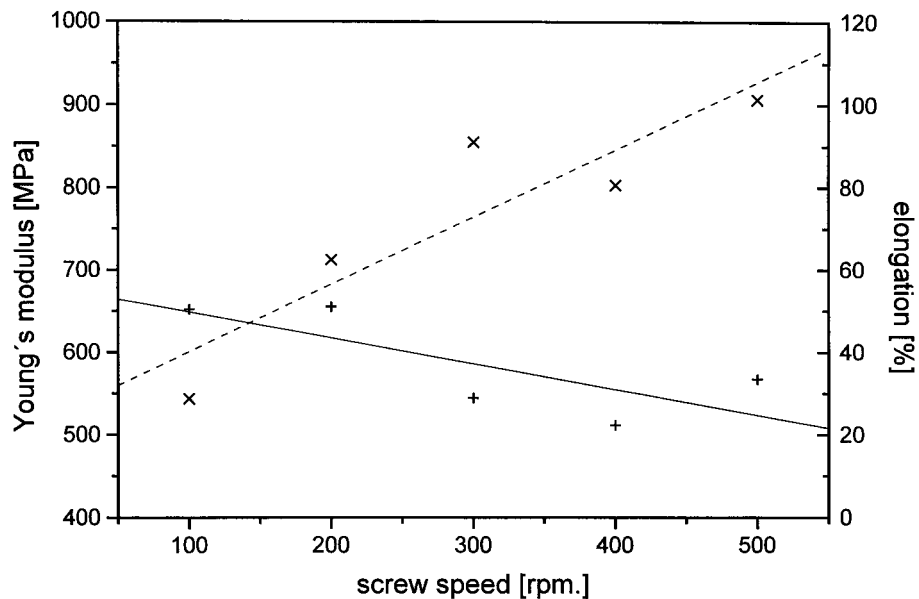


Figure 5 Influence of screw speed (rpm) on Young's modulus (+) and elongation at maximum load (\times).

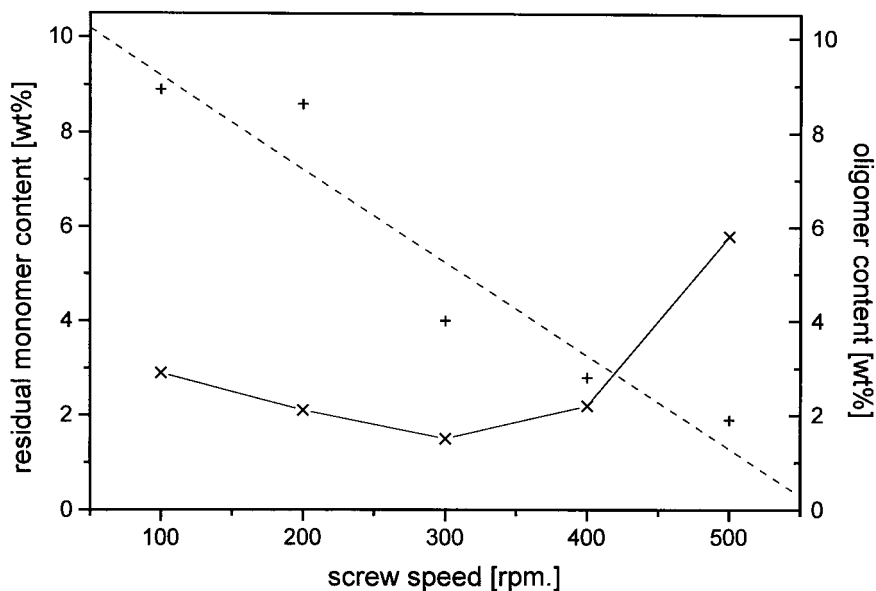


Figure 6 Influence of screw speed on monomer (+) and oligomer (x) content.

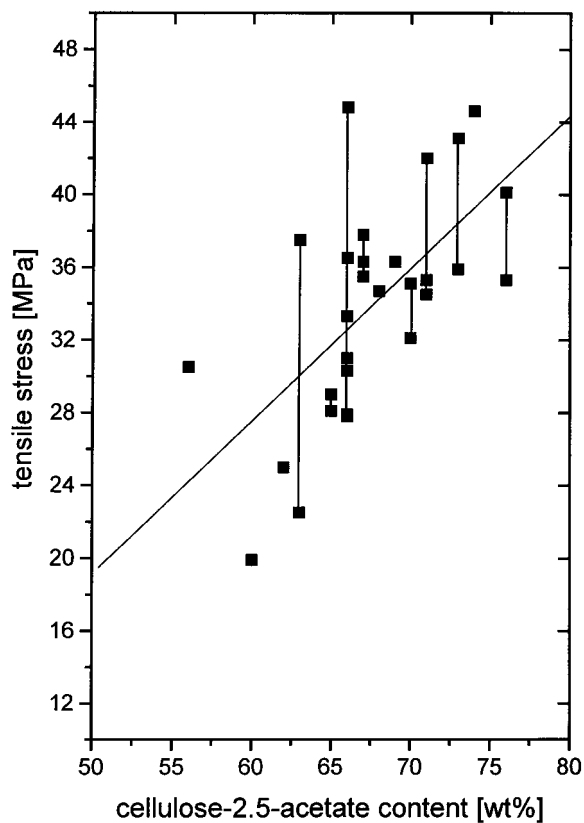


Figure 7 Tensile stress at maximum load as a function of cellulose-2,5-acetate content.

Over 200 experiments were evaluated with the commercially available SAS system for experimental design. A nonlinear model was used to

produce the plots displayed in Figures 8 and 9. For the plots the following parameters were kept constant until otherwise stated: throughput at 1.5 kg/h, screw speed 200 rpm, 190°C barrel temperature, catalyst content 1 wt % titanium(IV)butylate, ϵ -caprolactone content of 20 wt %, and 14 wt % glycerol/sorbitol (50/50 wt %). In Figure 8 the elongation is plotted against barrel temperature and screw speed. To achieve grafting a certain minimum energy is needed, which is either supplied by heating or by shearing. Maximum elongation was reached at approximately 185°C. A further increase of temperature led to lower elongations and finally to thermal decomposition. A rise of screw speed resulted in higher elongation, and the elongation maximum was shifted to lower barrel temperatures. The tensile stress in Figure 9 was highest when no plasticizer was present, which was not practically feasible because the resulting compound was not thermoplastic. With increasing amounts of either ϵ -caprolactone or glycerol plasticizer, the tensile stress decayed. The decline was more pronounced for ϵ -caprolactone than for glycerol. This indicates that *in situ* ϵ -caprolactone grafting is very important for plastification.

Compounding

Mixture modifiers were added to the cellulose-2,5-acetate/ ϵ -caprolactone. Lignin, starch, cel-

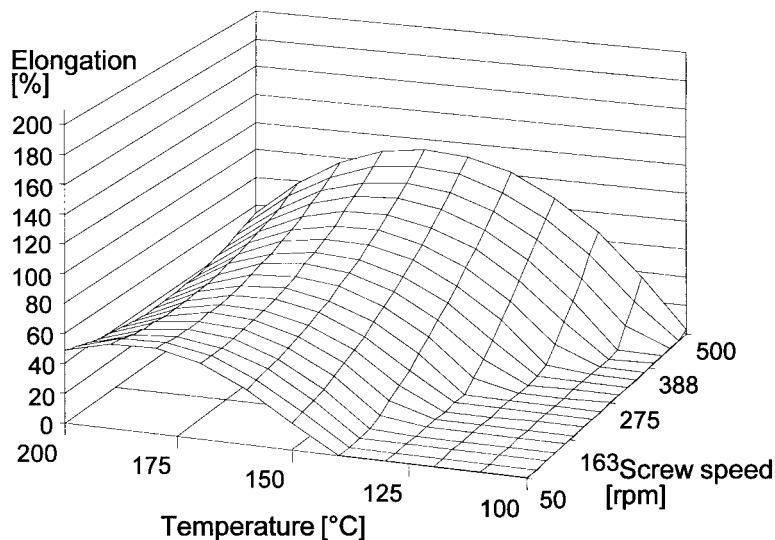


Figure 8 Elongation at maximum load as a function of temperature and screw speed.

lulose, and chitin were added as hydroxyfunctional reactive fillers, which were incorporated in the matrix as a separate phase, as visualized by means of scanning electron microscopy (SEM). ESO, PEG, and polyethylene glycol mono-methylether (PEGME) gave homogeneous materials, where PEG and PEGME represent polyol plasticizers. In addition to the constant feed ratio of cellulose-2,5-acetate (1 kg/h) and ϵ -caprolactone (0.5 kg/h), 5, 9, and 13 wt % of PEG and PEGME modifiers were fed. Temperature in the reaction zone was kept constant at 190°C and the screw speed was 250

rpm. Table III summarizes the properties of the resulting materials. For comparison, the non-modified compound is also listed. The modifier added in all cases caused a rise of the thermal transitions compared with those of the reference sample. When modifier content was increased, T_1 and T_3 decreased while weight loss, oligomer, and residual monomer content increased. Interestingly, T_2 increased from 91°C for the reference sample to 164°C for the chitin-containing sample, and the melting point T_3 increased from 124 to 210°C when 5 wt % chitin was added and decreased to 167°C when the

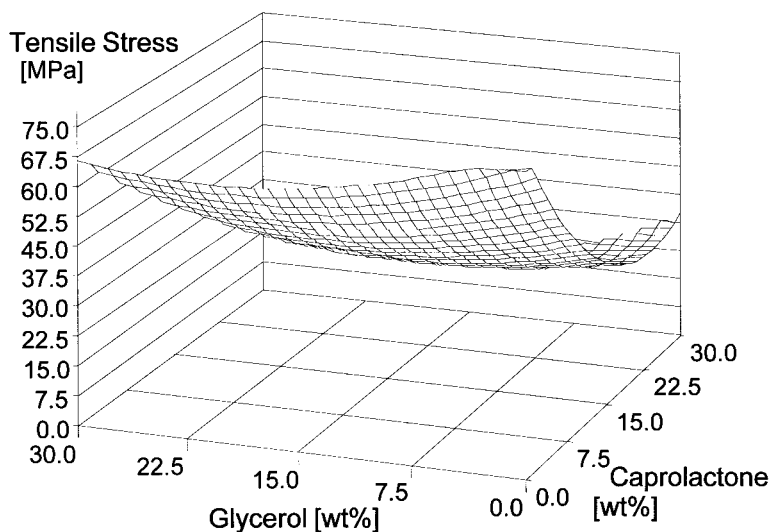


Figure 9 Tensile stress at maximum load as a function of glycerol and ϵ -caprolactone content.

Table III Cellulose-2,5-acetate Compounding

Modifiers (wt %)	T_1 (°C)	T_2 (°C)	T_3 (°C)	T_z (°C)	Weight		[Monomer] (%)	M_n (g/mol)	M_w/M_n	[Oligomer] (%)	M_n (g/mol)	M_w/M_n	Tensile Strength (MPa)	Elongation (%)	Young's Modulus (MPa)
					Loss (%) ^a										
—	65	91	124	243	0	0.2	91000	1.6	1.8	8700	1.1	27.3	44.6	401.7	
Lignin ^b															
5	66	—	165	261	0.2	0.3	142500	1.5	2.7	7040	1.2	16.8	3.9	457.0	
9	85	119	243	291	0.5	1.2	147200	1.6	2.0	6620	1.3	34.3	9.4	550.0	
13	—	111	203	291	0.5	0.7	141400	1.5	3.7	6090	1.3	46.2	11.2	626.6	
Starch															
5	—	1187	219	>250	0	2.5	148100	1.8	2.4	7660	1.1	40.3	11.8	605.8	
9	62	126	225	>250	0.2	0.5	219000	1.4	2.3	7920	1.1	35.6	17.8	570.6	
13	—	119	191	265	0.2	0.3	147300	1.7	3.6	9060	1.1	33.2	8.4	595.0	
Cellulose															
5	66	—	244	292	0	0.4	123400	1.5	2.1	8510	1.1	25.4	36.7	403.2	
9	—	120	229	266	0.3	0.5	146800	1.7	2.5	7690	1.1	41.8	10.0	624.4	
13	70	111	173	259	0.5	2.7	142400	1.8	3.7	7890	1.1	45.9	9.1	718.8	
Chitin															
5	73	164	210	234	0.1	0.8	147000	1.6	1.7	6390	1.2	33.5	11.7	522.5	
9	65	126	202	244	0.4	0.8	141700	1.8	1.2	6390	1.1	40.6	7.7	685.1	
13	—	114	167	265	0.4	1.8	—	—	2.6	—	—	37.5	6.6	693.6	
PEG ^c															
5	103	157	253	272	0.1	0.8	131900	1.6	4.3	7280	1.2	36.7	53.2	585.2	
9	115	157	268	287	0.3	3.9	138200	1.5	2.6	8470	1.2	29.5	85.4	284.3	
13	62	157	260	263	0.2	0.5	147600	1.5	3.7	10000	1.1	23.2	83.7	287.2	
PEGME ^d															
5	118	157	245	280	0	0.4	123400	1.4	4.9	—	—	26.5	35.5	306.1	
9	63	175	245	290	0	0.4	122400	1.6	4.2	10300	1.1	20.5	43.5	266.7	
13	101	175	224	277	0.4	nu.	123900	1.5	2.5	8260	1.1	25.4	79.6	322.7	
ESO ^e															
11	67	163	214	285	0.1	0.3	142700	1.6	1.9	8060	1.1	28.2	64.5	442.8	

The system was cellulose-2,5-acetate (63/60/57 wt %), ϵ -caprolactone (31/30/29 wt %), Ti(OBut)₄ (0.5 wt %), 190°C, extruder, 250 rpm.

^a 170–200°C, heating rate 5°C/min.

^b Organosolv lignin.

^c Polyethylene glycol.

^d Polyethylene glycol monomethyl ether.

^e Epoxidized soybean oil.

chitin content was further increased to 13 wt %. The oligomer content was highest for PEG- and PEGME-containing compounds because PEG and PEGME are oligomers themselves. For starch, chitin, and PEG tensile stress and Young's modulus increased and elongation decreased. In the case of lignin and cellulose, tensile stress increased with the modifier content. The incorporation of starch and cellulose gave more brittle materials whereas PEG and PEGME appeared to be efficient plasticizers, producing softer materials. Lignin was best suited as a filler because all mechanical properties improved with higher lignin content; for example, the tensile stress increased from 17 to 46 MPa, the elongation from 4 to 11%, and the Young's modulus from 457 to 627 MPa when lignin contents were increased from 5 to 13 wt %. In all cases the molecular mass of the grafted material increased compared to the reference sample, while molecular mass of the oligomeric fraction was always much lower than that of the nonmodified reference sample.

DISCUSSION

It was demonstrated that cyclic lactones such as ϵ -caprolactone, glycolide, and lactide were successfully grafted simultaneously onto the rigid polysaccharide backbone and hydroxyfunctional plasticizers. This simultaneous *in situ* grafting was carried out in the melt without solvent addition. Low molecular weight hydroxyfunctional plasticizers were *in situ* converted into nonmigrating higher molecular weight oligoester plasticizers. Moreover, the simultaneous grafting of cellulose-2,5-acetate and hydroxyfunctional plasticizer substantially improved compatibility between these two components. In addition compatibility between oligolactone-modified cellulose-2,5-acetate and fillers such as lignin, starch, cellulose, and chitin were markedly improved when fillers were added during this reactive extrusion process. As a result of the excellent compatibility of poly(ϵ -caprolactone) with numerous polymers, it was possible to prepare a wide range of polymer blends. In addition to ϵ -caprolactone, lactide (3,6-dimethyl-1,4-dioxan-2,5-dione) or glycolide (1,4-dioxan-2,5-dione) could be used as cyclic lactones. Grafting reactivity, as expressed by time required for maximum viscosity build-up, reflected the reactivity of the cyclic lactones with lactide > glycolide > ϵ -caprolactone. However, higher reactiv-

ity appeared to favor homopolymerization of the cyclic lactone with respect to grafting. Hydroxyfunctional plasticizers such as methoxyethanol, diethylene glycol, glycerol, sorbitol, and especially glycerol/sorbitol blends were used successfully. With increasing hydroxyfunctionality the viscosity build-up of the resulting compound was much smaller because molecular masses of oligolactones, formed *in situ*, were much smaller. SEM studies revealed that the lighter color of sorbitol-containing compounds is associated with formation of pores in the range of 1–10 μm average diameter. These pores may have resulted from phase separation due to crystallization of sorbitol and sorbitol-based oligocaprolactones. With increased grafting efficiency and increased chain length of the grafts, mechanical and thermal properties reflected those of polycaprolactones. At higher ϵ -caprolactone content the resulting compounds were flexible and had lower melting temperatures. It was possible to control polymer properties over a very wide range as a function of process conditions, for example, temperature and screw speed. Also ESO, PEG, and PEGME can be used as plasticizers. Starch, chitin, cellulose, and lignin are fillers that upon *in situ* grafting with oligolactones are quite compatible with the grafted cellulose-2,5-acetate compounds. Attractive properties such as higher stiffness, strength, and elongation were obtained when organosoluble lignin and cellulose were added during cyclic lactone grafting. In conclusion, novel families of thermoplastic cellulose-2,5-acetate compounds were obtained when cyclic lactones were grafted *in situ* onto cellulose-2,5-acetate, hydroxyfunctional plasticizer, and hydroxyfunctional fillers. This technology is not restricted to cellulose-2,5-acetate but can be applied to a broad range of carbohydrates to produce thermoplastic biodegradable polysaccharides.

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