

Dedicated to Prof. Antonius Kettrup on the occasion of his 60th birthday

INVESTIGATION OF THE PLASTICIZING EFFECT OF DICARBOXYLIC ACID DIESTERS ON STARCH ACETATE

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Abstract

A study was made of the applicability of dicarboxylic acid diesters for the plasticization of starch acetate. The ratio of the carboxyl and methylene groups was found to be the most important criterion for the use of this group of substances. This ratio should have values between 0.45 and 0.66. From the available dicarboxylic acid diesters, the diethyl esters and dibutyl esters were investigated.

Keywords: dicarboxylic acid, DSC, glass transition temperature, mechanical parameters, plasticizer

Introduction

In the search for biodegradable or compostable materials, starch as a readily available, renewable raw material is achieving increasing importance in the field of thermoplastic materials. Materials based on or combined with starch already exist. Some examples are:

- starch-filled conventional plastics
- foamed or pressed starch materials
- thermoplastic starch compounds and blends

There are significant limits to the applicability of all these materials, governed by the hydrophilic properties of the starch. To achieve a considerable decrease of these hydrophilic properties, the starch used at BSL Olefinverbund GmbH was acetylated. The demand for compostability did not lead to a triacetate, but to the synthesis of a starch acetate with a degree of substitution (DS) between 2.0 and 2.4. Acetylation results in a white, amorphous powder with a glass transition temperature of about 165°C. The glass transition temperature is slightly correlated with the DS.

The degradation of starch acetate starts at about 220°C and so the plasticizing is very important for good thermoplastic processing, as it is well known for PVC

and cellulose acetate. Of the well-known plasticizers for commercial plastics, the dicarboxylic acid esters are very interesting because of their environmental digestibility. A first idea about the plasticizer digestibility of starch acetate may be obtained from analogous considerations of cellulose acetate [1]. So it can be assumed that starch acetate is not digestible if the carbon chains contain more than one or two carbon atoms in both the acid and the alcoholic part of the ester.

The aim of our investigations was to establish the optimum carbon chain length of the acid and the alcoholic components of the dicarboxylic esters. To describe the effects plasticization, measurements of the glass transition temperature were carried out and compared with the results of mechanical testing.

The glass transition temperature is a well-defined and easily measurable property, which can reflect the influence of plasticization. The admixture of low molecular mass substances to plastics decreases the glass transition temperature. In the region up to 40% of the plasticizer in a polymer, the decrease in the glass transition temperature is directly proportional to the amount of the plasticizer [2].

The effectiveness of the plasticizer results from its constitution and its interaction forces. To decrease the glass transition temperature, it is required to increase the versatility of the chain segments. To obtain such an effect, the plasticizer has to be digestible with the polymer matrix. A good solubility results from strong intermolecular interactions between the plasticizer molecules with the polymer matrix. However, solvation increases the stiffness of the chain. This means that a plasticizer should be a poor solvent but not a non-solvent.

On the other hand, the stiffness is higher, the bigger the plasticizer molecules are. *The molecules of the plasticizer should be small for good softening to be attained.* However, small molecules have a high vapour pressure and therefore a high volatility, which is not desirable for the processing.

Another important point is that the interaction between the molecules of the plasticizer should be slight. Slight interactions lead to a low viscosity.

All these considerations show that there is a discrepancy between the demand for a high softening effect and a poor solubility, small molecules, low viscosity and technical usefulness. This means that a real technical plasticizer represents a compromise between desired and tolerable properties.

Substances

The plasticizer used for our investigations was selected on the following criteria:

- short chain length for the acid and the alcoholic components
- high boiling point
- commercial availability

Pretests were performed with the BRABENDER Plastograph. The selected substances are shown in Table 1. These dicarboxylic acid diesters are charac-

Table 1 Substances used as plasticizer

Dicarboxylic acid diethyl ester	Dicarboxylic acid dibutyl ester
adipic acid diethyl ester $C_2H_5OOC(CH_2)_4COOC_2H_5$ (AADE)	adipic acid dibutyl ester $C_4H_9OOC(CH_2)_4COOC_4H_9$ (AADB)
heptanedicarboxylic acid diethyl ester $C_2H_5OOC(CH_2)_7COOC_2H_5$ (HADE)	ethanedicarboxylic acid dibutyl ester $C_4H_9OOC(CH_2)_2COOC_4H_9$ (EADB)
sebacic acid diethyl ester $C_2H_5OOC(CH_2)_8COOC_2H_5$ (SADE)	propanedicarboxylic acid dibutyl ester $C_4H_9OOC(CH_2)_3COOC_4H_9$ (PADB)

terized by a ratio of the molecular weight of the carboxyl to the CH_2 groups of 0.45 to 0.66. Substances with shorter chains were not used because of the too low boiling point, and substances with longer chains could not be processed at temperatures below 200°C.

Sample preparation

The starch acetate (DS=2.3) was processed with the plasticizer into a dry blend using a fast lab mixer from THYSSEN-HENSCHERL, and then granulated in a lab twin-screw extruder from COLLIN. The content of the plasticizer in the starch acetate varied from 0 to 30%. For determination of the glass transition temperature, the above mentioned granules were used. The mechanical testing was carried out with an ISO-stick (80×10×4 mm), made from the granules by injection molding.

Experimental

The glass transition temperature was determined with a DSC-2C from Perkin-Elmer under the following conditions:

Mass:	about 8 mg
Crucible:	aluminium
Temperature range:	-40 – (+200)°C
Heating rate:	10 K min ⁻¹
Cooling rate:	40 K min ⁻¹
Purge gas:	20 ml argon min ⁻¹
Cooling agent:	CO ₂ /ethanol

Two heating runs were carried out for each sample, but only the second one was used to determine the glass transition temperature. Within the mechanical

testing, the following parameters were determined: impact bending strength, flexural strength, flexural modulus, tensile strength, tear resistance, ball indentation hardness, temperature of deformation under flexural load (HDTA) and melt flow index (MFI).

Results and discussion

The dependence of the glass transition temperature on the content of the plasticizer in the starch acetate is shown in Table 2. For comparison, Table 2 includes the values for the plasticizer polyethylene glycol with a molecular weight of 400 g mol^{-1} , which displayed the best processing parameters.

Table 2 Dependence of the glass transition temperature on the content of plasticizer

Softener	Glass transition temperatures at the given percentages of plasticizer/ $^{\circ}\text{C}$				
	0%	91%	16.7%	23.1%	28.6%
AADE	165.9	134.0	108.7	97.8	96.0
HAE	165.9	126.8	103.2	87.4	73.0
SADE	165.9	123.4	105.1	101.6	101.1
AADB	165.9	119.4	110.4	106.3	107.0
EADB	165.9	127.4	109.0	99.6	98.5
PADB	165.9	129.9	104.3	90.2	86.4
PEG 400	165.9	114.9	87.4	66.3	50.6

The determined glass transition temperatures show that most of the investigated plasticizers possess only partial digestibility with starch acetate. In most cases the increase of the plasticizer content above 20% does not lead to a proportional decrease in the glass transition temperature. The dicarboxylic acid diethyl and dibutyl esters can be used for technical applications only in the concentration range up to 20%. Figures 1a and 1b show the dependence of the glass transition temperature on the number of CH_2 groups in the dicarboxylic acid for each concentration of dicarboxylic acid diethyl ester (a) and dicarboxylic acid dibutyl ester (b). For the dicarboxylic acid diethyl esters, it is seen that 5 or 6 CH_2 groups in the dicarboxylic acid can lead to a significant decrease of the glass transition temperature, and thereby to an improvement of the plasticizing effect for starch acetate. In the case of dicarboxylic acid dibutyl esters it is seen that a number of CH_2 groups in the acid higher than 2 does not result in an improvement of the softening effect for the starch acetate. This partial digestibility leads to the conclusion that samples with a plasticizer content higher than 16.7% are not suitable for mechanical testing. The described ISO-sticks were made only from granules containing 16.7% of the plasticizer.

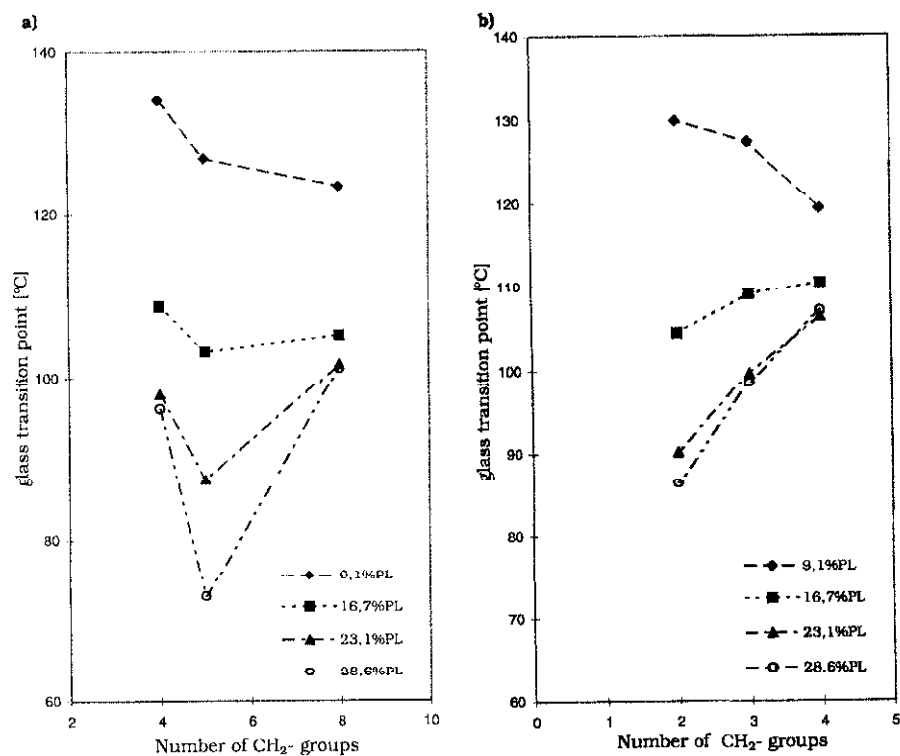


Fig. 1 Dependence of glass transition temperature of starch acetate on the number of methylene groups in the dicarboxylic acid; a) in the dicarboxylic acid diethyl ester, b) in the dicarboxylic acid dibutyl ester

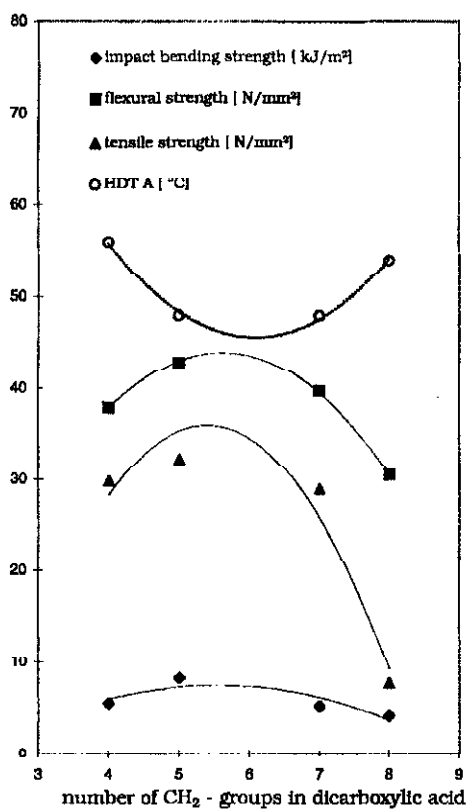
The processing of the granules by injection molding yielded clear and transparent testing sticks. This is in good accordance with the results of the glass transition measurements. The determined values of the mechanical parameters are shown in Table 3.

The values for the impact bending strength, the flexural modulus and the ball indentation hardness vary only slightly. In contrast, the flexural strength and the tensile strength display significant differences (Fig. 2). The first three selected parameters for the dicarboxylic acid diethyl esters in Fig. 2 show a maximum at 5 to 6 CH₂ groups in the dicarboxylic acid, while the HDTA shows a minimum. The maximum in the strength, in accordance with the minimum in the glass transition temperature at the given concentration, means that the investigated plasticizers exert nearly the same effect as that in cellulose acetate.

The partially polar side-chain of the acetylated starch undergoes specific intermolecular interactions. As the digestibility occurs in only a small range of the ratio of the carboxyl and CH₂ groups, only a comparison between the diesters of adipic acid made sense. A longer chain length caused the decrease of the flexural

Table 3 Mechanical parameters

Parameter	Plasticizers						
	AADE	HADE	SADE	AADB	EADB	PADB	PEG 400
Impact bending/ kJ m^{-2}	5.5	5.2	4.2	6.9	5.4	5.4	4.1
Flexural strength/ N mm^{-2}	37.9	39.7	30.5	21.7	42.3	43.0	48.8
Flexural modulus/ N mm^{-2}	1640	1560	1540	1680	1560	1520	1581
Tensile strength/ N mm^{-2}	29.8	28.9	7.7	8.1	21.6	20.4	22.5
Tear resistance/ N mm^{-2}	16.5	16.1	–	–	–	–	8.3
Ball indentation hardness/ N mm^{-2}	57	68	60	72	64	65	70
HDTA/ $^{\circ}\text{C}$	56	48	54	56	51	51	45
MFI/ g 10 min^{-1}	2.8	–	4.7	0.7	2.4	2.4	4.5

**Fig. 2** Dependence of some properties of Seonacell A on the chain length of the dicarboxylic acid

strength and the impact bending strength, as expected. In parallel with these effects, we registered a fast decrease of digestibility.

Figure 1b demonstrates that the possible chain length of the acid group for the dibutyl esters is shorter than for the diethyl esters. While the digestibility of the plasticizer passes through a maximum at 5 to 6 CH_2 groups, a good digestibility is observed only at 4 CH_2 groups and only for a concentration of 15% plasticizer in the case of dibutyl esters. Nevertheless, the effective part of the plasticizer of the dibutyl esters made a higher impact on the glass transition temperature and the tested mechanical parameters than in the case of the diethyl esters.

The dependence of the strength of the material on the content of AADB (Fig. 3) confirmed the good plasticizing effect of AADB up to 16%. The significant decrease in the flexural and tensile strength as for the tear resistance reveal that free drops of plasticizer were present, which disturb the structure of the material.

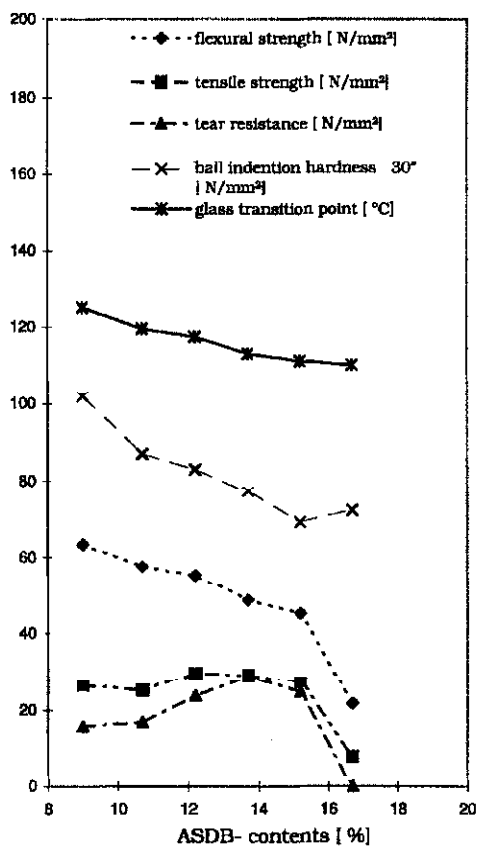


Fig. 3 Dependence of some properties of starch acetate on the ASDB content

Conclusions

Dicarboxylic acid diesters were studied to assess their ability to plasticize starch acetate. The ratio of the carboxyl and methylene groups was found to be the most important criterion for the use of this group of substances. This ratio should have values between 0.45 and 0.66.

From the available dicarboxylic acid diesters, the diethyl esters and dibutyl esters were investigated. For the ethyl esters, the tested properties showed optima at 5 to 6 CH₂ groups for the acid group of the dicarboxylic acid ester. For the butyl esters, the properties improved with increasing chain length in the acid group, but simultaneously the digestibility of the esters decreased.

Accordingly, the use of pimelic and sebacic acid diethyl ester seems to be of great promise. The ready availability of adipic acid seems to afford a good compromise.

References

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