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Electron-donor-acceptor interactions with cellulosic systems*

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Summary

Using plasticizers with one or two electron donor groups at the alkyl chain end the formation of either ´graft-like´ or ´network-like´ systems with a cellulose acceptor is evidenced. The formation of thermoreversible EDA-complexes is indicated by the modification of the rheological properties of the polymeric systems in the final flow region. There is a great influence of the spacer length between the donor groups of the plasticizer but not of the bulkiness of the endgroups.

Introduction

Cellulose a naturally occuring reproducible polymeric material has gained a wide industrial application. Cellulose and its derivatives are used for paper, fibers, plastics, in food etc. (1,2). Natural cellulose is not directly applicable for thermoplastic processing. Therefore derivatives like esters or ethers are obtained by transformation of the alcoholic groups (3). The disadvantages of these cellulosic materials are both the need of great amounts of plasticizers and their elimination during utilization (4). There are at least two ways to reduce the migration of these additives. On the one hand the use of polymeric plasticizers (4) and on the other hand the improvement of interaction between the cellulose and plasticizer. An useful method is the formation of electron-donor-acceptor complexes (EDA-Complexes) (5).

EDA-complexe formation will seriously influence the rheological behaviour of the polymeric melt (6,7). Additives with one single donor group will result in a ´thermoreversible graft copolymer´, whereas plasticizers with donors groups on both the ends, may conduct to the formation of a ´thermoreversible network´.

The present paper deals with the formation of electron-donor-acceptor complexes between cellulose tripropionate containing about 20 mole% acceptor groups (i.e. an average of one acceptor group for three glycosidic units) and various donor components. Are investigated the influences of EDA-complex formation on the mechanic-dynamic properties of the respective blends and attempted correlations of the rheological properties with the different models of thermoreversible complexation.

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*Dedicated to the 60th birthday of Prof. W. Burchard

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Experimental

1,2-Dibromoethane, 1-Bromo- and 1,6-Dibromohexane, 1-Bromo- and 1,12-Dibromododecane, 1-Bromocyclopentane as well as N-Methyl-N-ethylaniline (Aldrich), N-Methylaniline and 3,5-Dinitrobenzoylchloride (Fluka) were freshly redestilled under nitrogen or recrystallized twice. The cellulose tripropionate (Aldrich) was reprecipitated twice, whereas the ß-Cyclodextrine (Senn Chemicals) was used as recieved.

The acceptor groups containing cellulose was prepared by polymer analogue transformation of the cellulose tripropionate with 3,5-Dinitrobenzoylchloride in dry chloroforme. The product was twice repricipitated from chloroforme into ethanol.

(Mn = 24000, Mw/Mn = 2.6, Mol.weight/acceptor = 1035)

The oligomeric dextrine acceptor (i.e. D-Hepta(glyco-tripropionate) acceptor) was synthesized starting with the ß-Cyclodextrine which was fully esterifyed to ß-Cyclodextrine tripropionate in propionic acid with propione acid chloride. Then the ring was opened (8,9) and the recieved product transformed with 3,5-Dinitrobenzoylchloride to the respective acceptor oligomer. The oligomer was multiple reprecipitated from propanol into petrolether (50-80).

(Mn = 2450, Mol.weight/acceptor = 650)

The alkyl bidonors (1,12-Bis(N-methylaniline)dodecane, 1,6-Bis(N-methylaniline)hexane and 1,2-Bis(N-methylaniline)ethane) were synthesized from the corresponding alkyl dibromides and N-Methylaniline. The recieved producs were at least redestilled under reduced pressure.

The alkyl monodonors (1-(N-methylaniline)dodecane and 1-(N-methylaniline)hexane) were prepared in the same way as the bidonors, starting with the respective alkyl monobromides.

The bipseudodonor (1,6-Dicyclopentylhexane) used as an inert additive of analogous structural dimensions as the hexane bidonor was systhesized from Grignard cyclopentyl magnesiumbromide with 1,6-Dibromohexane. The coupling of the Grignard componente was carried out according to Tamura and Kochi (10).

1-N-Methylaniline-6-cylopentylhexane was synthesized in the same way but using a great exess of the bibromide for the coupling reaction. 1-Bromo-6-cyclopentylhexane was obtained by destillation from the reaction mixture and then transformed with N-Methylaniline to the corresponding monodonor-monopseudodonor.

Both IR, ^{1}H-NMR and elementar analyses of all compounds are in accordance with the expectancies.

The blends of the cellulose acceptor and the oligomer acceptor with the various donor and pseudodonor plastizicers were prepared by freeze drying from dioxane solution. Compositions for all the blends are shown in Table I.

The mechanic-dynamic measurements were carried out on a INSTRON rheometer, Model 3250 using the plate and plate geometry. The plate diameter was of 20 mm and the frequency range was of 50 mHz to 7.5 Hz. The temperature range of the rheological meassurement was of nearly from Tg + 50° to 220°C for the cellulosic material and from 40° to 100°C for the oligomeric material. The isothermes were supperposed to mastercurves according to the usual shift procedure.

Results and Discussion

The mixing of polymer with plasticizer is usually accompanied by a lowering of the Tg of the mixture (4). This behaviour is also confirmed by the data shown in Table I.

Taking into account that EDA-complexation due to CT-interaction will influence the rheological properties of polymeric systems in the final flow region, the retarding influence of the monodonor plasticizers will be effected by the thermoreversible formation of a ´graft-like´ copolymer structure between plasticizer and polymer acceptor backbone, wheras bidonor plasticizers will result in a themoreversible network formation. Both the flow retardation effects of the tangling monodonor ´sidechain´ and of the bidonor thermoreversible network are dependent on the spacer length of the alkyl chain of the respective plasticizer.

In the case of monodonor plasticizer the flow retardation is the higher the longer the alkyl chain. This is confirmed by the mastercurves of the respective loss moduli shown in the upper part of Fig.1. The increase of the loss moduli, i.e. the flow retardation increases with the length of the alkyl group of the interacting monodonor. In the case of the bidonor plasticizer the probability of network formation is also related to the length of the alkyl group between the two donor endgroups.This is shown by the mastercurves of the loss moduli in the lower part of Fig.1. Again the flow hindrance is the higher the longer the alkyl spacer between the two donor endgroups.

There is a surprising similarity between the rheological effects of monodonor and bidonor plasticizers and for discerning between the flow retardation effects of the tangling monodonor sidechains and of the bidonor network in Fig.2 are compared, the respective mastercurves directly. All mastercurves were shiftet along the frequency scale to superpose at the inflection point marking the transition between rubber plateau and glass transition region.

It is evident that the probability of network formation between bidonor plasticizers and the cellulose acceptor increases with the spacer length between the two donor endgroups. For instance the ethanebidonor is too short to act as an effective crosslinker and thus there is no difference between the rheological properties of the respective cellulose acceptor blends with the mono- and bidonor plasticizer. Only starting with the hexane donors the crosslinking effect of the bidonor becomes evident and the flow retardation of the network formation is the higher the longer the spacer between the two donor endgroups.

Comparing the monodonor and the bidonor plasticizer molecules, they differentiate not only by the number of the donor endgroups, but also by the bulkiness of the endgroups. The bidonor is containing two bulky endgroups and the monodonor only one. Thus in a second series of experiences was investigated the influence of the bulkiness of the endgroups of the plasticizer on the rheological properties of the corresponding cellulose blends.

Accordingly were synthesized hexane pseudodonor plasticizer molecules in which one or both donor endgroups were substituted by the inactive cyclopentyle group of nearly identical dimen-

Table I: Composition and glass transition temperature (Tg) of the analysed samples

Pure components	Tg, °C
Cellulose tripropionate acceptor	137.7
D-Hepta(glycotripropionate) acceptor	53.2

Blends of Cellulose tripropionate acceptor

Component	D-A ratio	Weight don.fract.	Tg, °C
Ethane bidonor	1:1	0.091	90.6
Hexane bidonor	1:1	0.110	72.5
Dodecane bidonor	1:1	0.134	88.7
Ethane monodonor	2:1	0.102	104.0
Hexane monodonor 1	2:1	0.137	78.4
Hexane monodonor 2	1:1	0.073	84.7
Dodecane monodonor	2:1	0.186	96.2
Hexane bipseudodonor	---	0.096	109.7
Hexane monodonor-monopseudodonor	1:1	0.114	80.4

Blends of D-Hepta(glycotripropionate) acceptor

Component	D-A ratio	Weight don.fract.	Tg, °C
Hexane bidonor	1:1	0.186	24.3
Dodecane bidonor	1:1	0.226	23.2
Hexane monodonor	1:1	0.128	29.4
Dodecane monodonor	1:1	0.175	28.3

Legends

Figure 1: Comparision of the mastercurves of the loss moduli of the cellulose blends with bidonor- and monodonor plasticizers. The upper part shows the curves of the mono donors the lower of the bidonors.

▲ = Dodecane mono- or bidonor
□ = Hexane mono- or bidonor
△ = Ethane mono- or bidonor
■ = pure Cellulose acceptor

Figure 2: Comparision of the loss moduli of the monodonor- with those of the bidonor plasticizer cellulose blends.

Figure 3: The effect of pseudodonors on the rheological behaviour of cellulose acceptor.

The triangles represent the pure cellulose acceptor (△) or the blend with the bipseudodonor(▲). The squares represent the blends with hexane monodonor (□) or monodonor-monopseudodonor (■). The circles are for the blend with hexane bidonor(●).

Figure 4: Rheological effects in a system with the oligomeric model compound.

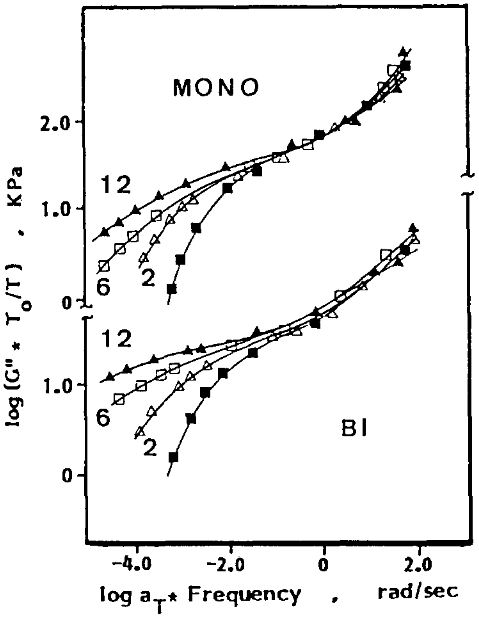

Figure 1

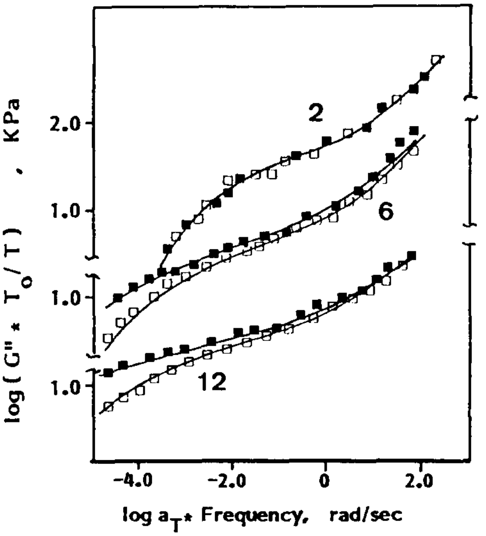

Figure 2

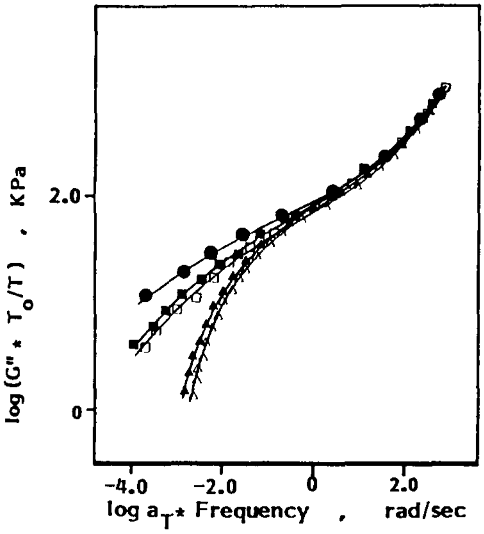

Figure 3

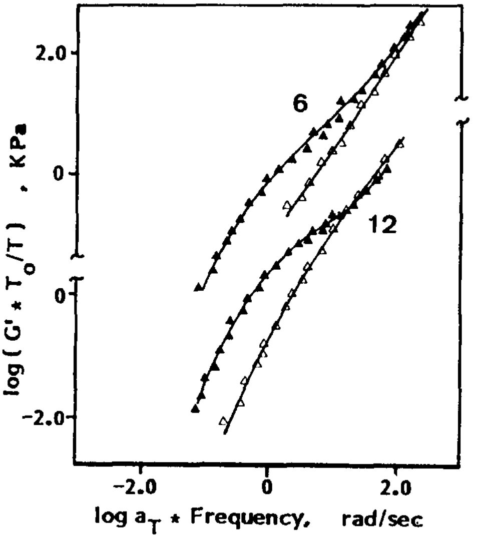

Figure 4

(For clearity, only some representative experimental data-points are shown in the figures.)

sions. The results of the rheological measurements are illustrated in Fig.3. Are compared the respective mastercurves of the loss moduli superposed at the inflection point between rubber plateau and glass transition region. Besides the mastercurves of the pure cellulose acceptor are shown the corresponding curves of the blends with the bipseudodonor, the monodonor and the monodonor-monopseudodonor as well as with the bidonor plasticizer, respectively. It is evident that the prevailing rheological effect is due to the CT-interaction of the EDA-complexes, the retarding action being maximum in the blend with the bidonor plasticizer.

A very last evidence for thermoreversible network formation by EDA-interaction is presented in Fig.4. To reach effectively the flow region, the polymeric cellulose acceptor was substituted in this series of measurements by an oligomeric model compound, obtained starting with the ß-Cyclodextrine, a cyclic saccharide containing seven glycosidic rings.

After ring opening and partially transesterification the corresponding oligomer cellulose acceptor model compound was obtained. In Fig.4 are shown the mastercurves of the storage moduli, superposed at the beginning of the glass transition region. Taking into account that no changes were observed between the mastercurves of the oligomeric cellulose acceptor model and the blends with the monodonor plasticizers, only the mastercurves of the blends with the monodonor plasticizer are compared with those of the respective blends with the bidonor plasticizer. Although low molecular components were blended, the formation of a rubber-like plateau, much more pronounced with the dodecane bidonor, can only be explained by the formation of a thermoreversible network structure.

Acknowledgement

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References

1. J.C. Arthur Jr., ´Encyclopedia of Polymer Science and Engineering´ 2nd. edn. Wiley, New York 1986 Vol.4 p.261.
2. H. de Chardonnet , Fr. Pat. 165349 (1884).
3. Franck A., Biederbick K., ´Kunststoff Kompendium´ 2nd. edn. Vogel, Würzburg 1988 p.234.
4. C.F. Hammer, ´Polymer Blends´ Academic Press, New York 1978 Vol.2 p.219.
5. W. Karcher, G. Haesen, B. Le Goff, K. Figge, Dtsch. Lebensmittel-Rdsch. **80**, 141 (1984).
6. H.A. Schneider, H.J. Cantow, V. Percec, Polym. Bull. **6**, 617 (1982).
7. H.A. Schneider , H.J. Cantow, U. Massen, H. Northfleet-Neto, Polym. Bull. **7**, 263 (1982).
8. B. Pfannemüller, G. Richter, E. Husemann, Carbohyd. Res. **43**, 63 (1976).
9. D. French, J. Amer. Chem. Soc. **71**, 353 (1949).
10. M. Tamura, J. Kochi, Synthesis 303 (1971).

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