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Abstract

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INTERACTION OF A POLYESTER AND A POLYAMIDE IN THE MELT

A number of authors have shown that, when two different polyamides ($^{1-3}$) or polyesters (^{4,5}) are fused, interchange reactions lead to the formation of a mixed polymer, the reaction passing through a stage of formation of block copolymers. Korshak, Frunze, and Petrova (^{6}), studying the interaction of hexamethylenediamine and the polyester of sebacic acid with ethylene glycol, established that a polyamido ester is obtained in this process. On the basis of these data, one should expect that, in the interaction of a polyamide and a polyester, as a result of interchain exchange a polyamido ester will be formed. At present there is no information in the literature on this reaction, although the study of such an interaction is of undoubted interest, since it opens up the possibility of obtaining polyamido esters from ready-made polymers. The purpose of the present work was to investigate the exchange interaction of a polyamide and a polyester in the melt, using as an example the reaction of polyethylene sebacinate with polyhexamethylene sebacamide.

Table 1

Change in the properties of the product as a function of the duration of heating of a mixture of polyethylene sebacinate and polyhexamethylene sebacamide at 290°*

No.	Duration of heating, h	Ratio of starting components, mol	Reduced viscosity of the polymer solution in cresol	Melting point**, °C	Amount of extractable substance formed without combustion, %
1	0	1 : 1	0.80	60	45.5
2	1	1 : 1	0.82	195–200	32.2
3	4	1 : 1	0.64	170–175	1.8
4	8	1 : 1	0.50	165–170	3.4
5	12	1 : 1	0.48	165–170	4.5
6	Polyamido ester obtained by aminolysis of polyester	1 : 0.5	0.44	180–185	6.8

* The mixture of polymers was heated in condensation test tubes in a nitrogen atmosphere.
** Determined from thermomechanical curves.

To establish the fundamental possibility of exchange interaction between amide and ester groups, we first investigated, as models, the interaction of acetanilide and benzyl benzoate at various temperatures. It was found that, upon prolonged heating of the starting substances at 290°, benzyl acetate is formed, which is possible only through exchange interaction of the amide and ester groups of the starting substances:

$$C_6H_5NHCOCH_3 + C_6H_5CH_2OCOC_6H_5 \rightarrow C_6H_5NHCOC_6H_5 + C_6H_5CH_2OCOCH_3.$$

At lower temperatures it was not possible to isolate benzyl acetate. Thus, the model experiment shows that exchange between amide and ester groups is possible and proceeds under comparatively severe temperature conditions.

On the basis of these data, we investigated the interaction of polyhexamethylene sebacamide with polyethylene sebacinate in a stream of nitrogen at 290°.

The starting polymers were taken in an equimolecular ratio. The results obtained are summarized in Table 1. From the data in Table 1 it is evident that, upon prolonged heating of the starting homopolymers at 290°, a polymer is formed whose properties are close to those of the polyamidoester obtained by

Fig. 1. Differential curves of turbodimetric titration of samples. 1 —sample No. 1 of Table 1; 2 —sample No. 4 of Table 1

Figure 1: Fig. 1. Differential curves of turbodimetric titration of samples. 1 —sample No. 1 of Table 1; 2 —sample No. 4 of Table 1

Fig. 2. Change in the content of substance extractable with hot benzene in the reaction products as a function of temperature and heating duration: 1 —290°; 2 —280°; 3 —260°

Figure 2: Fig. 2. Change in the content of substance extractable with hot benzene in the reaction products as a function of temperature and heating duration: 1 —290°; 2 —280°; 3 —260°

aminolysis of polyethylene sebacate with hexamethylenediamine (^{6}) (at a molar ratio of polyester to diamine of 1 : 0.5), which undoubtedly indicates the occurrence of exchange interaction between the polyester and polyamide molecules. The presence of exchange interaction is also confirmed by turbodimetric titration data (Fig. 1). Thus, the differential curve of turbodimetric titration for sample No. 1 of Table 1 has two sharply expressed maxima corresponding to the polyamide and polyester portions. The differential curve of turbodimetric titration of the polymer obtained after 8-hour heating of the starting substances has a different form, corresponding, in all probability, to a polyamidoester.

Fig. 1. Differential curves of turbodimetric titration of samples. *1* —sample No. 1 of Table 1; *2* —sample No. 4 of Table 1.

Fig. 2. Change in the content of substance extractable with hot benzene in the reaction products as a function of temperature and heating duration: *1* —290°; *2* —280°; *3* —260°.

Schematically, the process of interaction of the polyester and polyamide in our case may be represented by three principal equations describing an elementary act of exchange:

a) reaction due to interaction of the amide and ester bonds of neighboring chains:

$$\mathrm{H-[-NH(CH_2)_6NHCO(CH_2)_8CO-]_a-[-NH(CH_2)_6NHCO(CH_2)_8CO-]_b-OH+}$$

$$\mathrm{+H-[-O(CH_2)_2OCO(CH_2)_8CO-]_a-[-O(CH_2)_2OCO(CH_2)_8CO-]_b-OCH_3\rightarrow}$$

$$\mathrm{\rightarrow H-[-NH(CH_2)_6NHCO(CH_2)_8CO-]_a-[-O(CH_2)_2OCO(CH_2)_8CO-]_b-OCH_3+}$$

$$+\mathrm{H}-[-\mathrm{O(CH_2)_2OCO(CH_2)_8CO}-]_{\mathrm{a}}-[-\mathrm{NH(CH_2)_6{\cdot}NHCO(CH_2)_8CO}-]_{\mathrm{b}}-\mathrm{OH}\ \text{etc.}$$

b) exchange due to active terminal groups of polymer chains:

$$\mathrm{H}-[-\mathrm{NH(CH_2)_6NHCO(CH_2)_6CO}-]_{\mathrm{n}}-\mathrm{OH}+$$

$$+\mathrm{H}-[-\mathrm{O(CH_2)_2OCO(CH_2)_8CO}-]_{\mathrm{k}}-[-\mathrm{O(CH_2)_2OCO(CH_2)_8CO}-]_{\mathrm{m}}-\mathrm{OCH_3}\rightarrow$$

$$\rightarrow\mathrm{H}-[-\mathrm{NH(CH_2)_6NHCO(CH_2)_8CO}-]_{\mathrm{n}}-[-\mathrm{O(CH_2)_2OCO(CH_2)_8CO}-]_{\mathrm{m}}-\mathrm{OCH_3}+$$

$$+\mathrm{H}-[-\mathrm{O(CH_2)_2OCO(CH_2)_8CO}-]_{\mathrm{k}}-\mathrm{OH}\ \text{etc.;}$$

c) synthetic reactions due to interaction of terminal groups of polymer chains with one another:

$$\mathrm{H}-[-\mathrm{NH(CH_2)_6NHCO(CH_2)_8CO}-]_{\mathrm{n}}-\mathrm{OH}+\mathrm{H}-[-\mathrm{O(CH_2)_2OCO(CH_2)_8CO}]_{\mathrm{m}}-\mathrm{OCH_3}\rightarrow$$

$$\rightarrow\mathrm{H}-[-\mathrm{NH(CH_2)_6NHCO(CH_2)_8CO}-]_{\mathrm{n}}-[-\mathrm{O(CH_2)_2OCO(CH_2)_8CO}-]_{\mathrm{m}}-\mathrm{OCH_3}+\mathrm{H_2O}.$$

Each of the indicated reactions may proceed alongside the others and, ultimately, lead to the formation of a polyamidoester and, consequently, to a change in the basic properties of the original mixture.

The fact that, with increasing duration of heating of the initial polymers, no increase was observed in the reduced viscosity of the solution of the reaction mixture in cresol (see Table 1) undoubtedly indicates that, under the chosen conditions, synthetic processes are not of decisive importance.

As can be seen from the data in Table 1, the flow temperatures of the polymers change with increasing heating time. In the initial period of the reaction, an increase in the flow temperature of the reaction mixture from 60 to 200° is observed. A further increase in the duration of heating leads to a decrease in the flow temperature of the polymer to 165°. This is apparently due to the fact that the block copolymer formed in the first stage of the reaction, as the process proceeds further, is converted into an ordinary blended polymer.

Especially clear evidence for the formation of a polyamido ester in the course of the interaction of the polyamide and the polyester is provided by the data on the change in the solubility of the reaction mixture in hot benzene as a function of the duration of heating (Fig. 2). Of all the components contained in the reaction mixture, only the polyester is completely soluble in hot benzene; the polyamido ester is only slightly soluble in hot benzene, while the polyamide is not soluble at all. Thus, from the decrease in the content of the soluble fraction in the reaction mixture one can judge the rate of formation of the polyamido ester.

Using this method, we decided to determine the lower temperature limit for the occurrence of the exchange interaction between polyethylene sebacate and polyhexamethylene sebacamide (the upper temperature limit is determined by the destruction and crosslinking of the initial homopolymers, which become especially pronounced beginning at 300°).

Table 2

Effect of catalysts on the interaction of polyhexamethylene sebacamide and polyethylene sebacate at 260° and a heating time of 8 hr.*

No.	Catalyst	Reduced viscosity of a 1% solution in cresol	Flow temperature, °C	Amount of polymer fraction soluble in hot benzene, wt. %
1	Without catalyst	0.80	80–85	44.8
2	CH_3–C_6H_4–SO_3H	0.72	80–85	42.8
3	LiOH	1.10	195–200	29.6
4	$NaOH \cdot Al_2O_3$; NH_2	0.54	195–200	33.4
5	naphthalene (structure shown)	0.94	80–85	38.8
6	CH_3COONa	0.80	175–180	31.2
7	$(CH_3COO)_2Cu$	0.56	80–85	38.2
8	$(CH_3COO)_2Zn$	0.82	170–175	17.0
9	$(CH_3COO)_2CC$	1.08	185–190	28.0
10	$(CH_3COO)_2Pb$	0.78	180–185	17.8
11	PbO	0.80	170–175	8.0

* The experiments were carried out in condensation test tubes fitted with a

Figure 3

Figure 3: Figure 3

Figure 4

Figure 4: Figure 4

stirrer, in a nitrogen atmosphere.

It turned out that at 280° the exchange proceeds comparatively slowly, while at 260° it does not occur at all in 8 hr. However, it was found that, in contrast to carrying out the process at 290°, at 280° and, especially, at 260° sufficient homogeneity of the melt is not maintained. To prevent this, all subsequent experiments were carried out with mechanical stirring of the reaction mass, which, as it turned out, somewhat accelerates the exchange process but does not lower the lower temperature limit of its occurrence.

It seemed to us that the lower temperature limit for the exchange interaction under study between the polyamide and the polyester could be lowered through the use of catalysts. For this purpose, the effect of several catalysts, taken in an amount of 1% of the weight of the initial polymer mixture, was investigated. In each case the initial mixture was heated for 8 hr at 260°, i.e., under conditions in which, in the absence of a catalyst, the exchange process does not occur. The data obtained are summarized in Table 2, from which it is evident that the best results (as indicated by the smallest-

a lower content in the polymer of the fraction soluble in hot benzene) are obtained when lead oxide is used as the catalyst.

Investigation of the exchange interaction between the polyester and the polyamide in the presence of various amounts of lead oxide as catalyst (see Fig. 3) showed that the best results are obtained when the catalyst is introduced into the reaction in an amount of 1–2 wt. %. As is evident from

Fig. 3. Change in the content of the substance extracted with hot benzene in the reaction products as a function of the amount of lead oxide

Fig. 4. Change in the content of the substance extracted with hot benzene in the reaction products in the presence of 2% lead oxide at 260° as a function of heating time

Fig. 4, in the presence of 2% lead oxide the exchange interaction between the polyethylene sebacamide practically comes to completion after 6 h. The polyamidoester obtained under these conditions is a horn-like substance of light-yellow color, soluble on heating in a mixture of alcohol and tetrachloroethane, with a flow temperature of about 170°.

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Note: Figure translations are in progress. See original paper for figures.