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THERMAL PROPERTIES OF COMPLEXES
Metal complexes of saponified products of acrylonitrile terpolymer

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Complexes of saponified polyacrylonitrile with the bivalent metals Ca, Co, Cu, Mg, Ni and Zn, were obtained. Thermal analysis of the complexes was carried out. The highest thermal stability was found for the complexes with Co and Ni.

Keywords: complexes, TA, thermal stability

Introduction

The alkaline hydrolysis of poly(acrylonitrile) has been known for many years to lead to macromolecular compounds consisting of two types of units: acrylic acid and acrylamide. Saponified products of acrylonitrile terpolymer have also been reported [1]. On the other hand, methacrylic acid-methacrylamide copolymers form complexes with metals, and schemes of complexation have been suggested [2].

From a practical point of view, instead of pure polyacrylonitrile it is possible to use wastes from the production of PAN fibres or wastes of PAN fibres from the textile industry as substrates for similar reactions.

The aim of the present study is to examine thermal properties of the complexes with various metals obtained from hydrolysed acrylonitrile terpolymer containing methyl acrylate and itaconic acid.

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Experimental

Materials

The acrylonitrile (AN) terpolymer having the composition AN 92%, methyl acrylate 6% and itaconic acid 2% was supplied by "Anilana" (Poland). Typical hydrolysis was carried out by treating 265 g of terpolymer with 140 g of NaOH and 500 ml of H_2O at 90°C with continuous stirring for 2 h. The product was neutralized with hydrochloric acid to $pH = 7$, precipitated in ethanol and dissolved again in water. The solution for synthesis of the complexes was analysed by conductometric titration. The content of COOH groups was $1.72 \cdot 10^{-3}$mol/g and that of $CONH_2$ groups was $1.10 \cdot 10^{-3}$mol/g. The complex with Cu was obtained as follows: 250 g of the solution of hydrolysed terpolymer was diluted with 2500 ml of H_2O, and 61.7 g of $CuSO_4 \cdot 5H_2O$ dissolved in 500 ml of H_2O was added with stirring. The precipitated complex was filtered off, washed with water and dried at 100°C in vacuo.

Complexes with other metals were prepared in a similar way using for the same amount of the hydrolysed terpolymer: 83.8 g of $MgCl_2 \cdot 5H_2O$, 60.6 g of $CaCl_2 \cdot 2H_2O$, 118.5 g of $ZnSO_4 \cdot 7H_2O$ or 75.0 g of $CoCl_2$. In all cases, the ratio of the number of metal equivalents to the number of moles of COOH groups was slightly higher than one. Additionally, three samples of complexes were prepared with smaller amounts of the metal (copper). The mole ratio Cu^{2+} : COOH was 0.28, 0.14 or 0.07.

Methods

The thermal properties of the complexes were examined with a Hungarian derivatograph under the following conditions: medium air; ceramic crucible; standard substance Al_2O_3; temperature range 25°–800°C; sample size 90 mg; heating rate 7.9 deg·min^{-1}; sensitivity: DTA 1/5, DTG 1/20, TG 100. The thermal stabilities of the complexes were studied both before and after their additional drying at 200°C and 0.06 MPa. The temperature of beginning of mass loss, the temperature of 5% weight loss, t_5, the temperature of 50% weight loss, t_{50}, and the residue after heating to 800°C were determined from the thermal curves.

Results

Results are given in Tables 1 and 2.

TG, DTG and DTA curves for the Zn complex are presented in Fig. 1. Figure 2 shows thermoanalytical curves for the same sample, after additional heating. As can be seen from Fig. 1, mass loss starts at 85 °C. The first period of mass loss is

connected with dehydration. This can be confirmed by a comparison of Fig. 1 with Fig. 2. After additional heating this period disappeared. The following mass

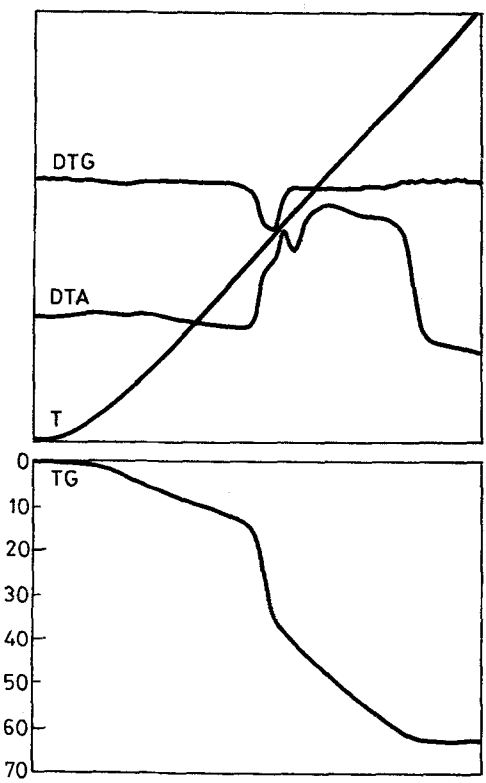

Fig. 1 Thermal curves of complex Zn saponified product of acrylonitrile terpolymer

Table 1 Results of thermal analysis of complexes: metal-saponified products of acrylonitrile terpolymer

Symbol of the sample	Temperature of the outset of the mass loss / °C	Temperature / °C of 5% weight loss t_5	Temperature / °C of 50% weight loss t_{50}	Mass loss at 800 °C/ %
Ca^{++}	85	150	520	74.4
Co^{++}	85	165	435	71.1
Cu^{++}	110	200	440	71.1
Mg^{++}	110	180	450	77.7
Ni^{++}	65	95	390	74.4
Zn^{++}	90	165	520	70.0

loss appears in the temperature range 220°– 440°C and is presumably connected with the formation of anhydride cycles from neighbouring —C(=O)O groups in the complex. The temperature range 440°– 460°C involves a substantial mass loss (about 30%), which is connected with destruction of the macromolecular chain

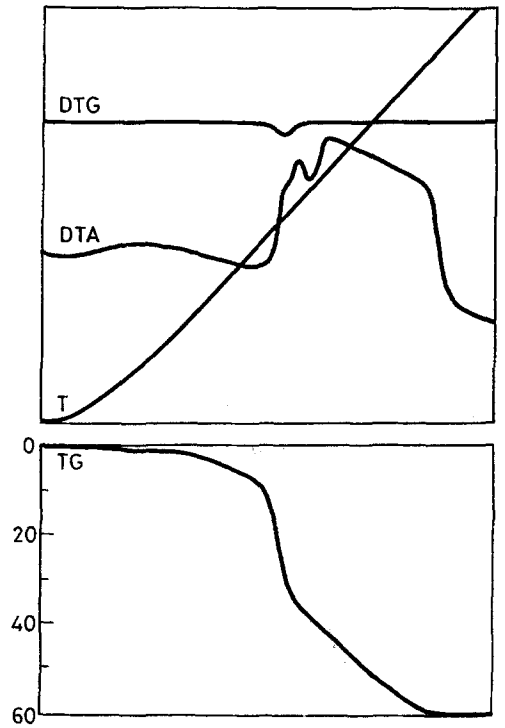

Fig. 2 Thermal curves of complex Zn saponified product of acrylonitrile terpolymer after its additional drying

Table 2 Results of thermal analysis of complexes: metal-saponified products of acrylonitrile terpolymer after their additional drying

Symbol of the sample	Temperature of the outset of the mass loss / °C	Temperature / °C of 5% weight loss t_5	Temperature / °C of 50% weight loss t_{50}	Mass loss at 800 °C/ %
Ca^{++}	220	380	595	71.1
Co^{++}	265	320	440	70.0
Cu^{++}	110	270	460	70.0
Mg^{++}	110	350	455	73.3
Ni^{++}	260	320	585	66.1
Zn^{++}	120	335	530	66.7

and decomposition to yield volatile products. Since the thermal analysis was carried out in an atmosphere of air, in the next period, in the range 460°–650°C, oxidation occurs. This is confirmed by the high exothermic DTA peak in this temperature range. The last part of the curve is the connected with the decomposition of more stable products formed during pyrolysis; in the case of the Ca complex, this is probably $CaCO_3$.

On the thermal analysis of the other complexes (with Co, Ni, Cu, Mg and Zn), the main character of the thermal curves is similar, but the thermal stability is dependent on the metal used for complex preparation. The highest stability is observed for the complexes with Co and Ni (Table 2). The temperature of beginning of mass loss is 260°–265°C, in comparison with 110°–120°C for the Mg and Zn complexes. The following period of decomposition may be catalysed by compounds formed in the course of pyrolysis and is difficult to interpret precisely.

References

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2 S. K. Chatterjee, S. Gupta and K. R. Sethi, Angew. Makromol. Chem., 147 (1987) 133.

Zusammenfassung — Komplexe von verseiftem Polyacrylnitril mit bivalenten Metallen (Ca, Co, Cu, Mg, Ni und Zn) wurden hergestellt und thermisch untersucht. Die höchste thermische Stabilität besitzen die Komplexe mit Co und mit Ni.