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Synthesis and Properties of Aliphatic Oligoamides Containing Methionine Fragment

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Abstract—Oligoamides were prepared from dimerized fatty acid, hexamethylenediamine, and an amino acid (methionine). The effect of methionine on the course of polycondensation and properties of the reaction products was examined. New thermoplastic adhesive compounds based on these products were developed.

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Oligoamide products derived from dimerized fatty acid (DFA) and aliphatic diamines are widely used as base components of thermoplastic (hot-melt) adhesives [1–3].

The specific structural features and composition of the DFA used allow preparation of oligoamides exhibiting high adhesion to various materials, high shock resistance, flexibility, and resistance to water and oils [4, 5].

Introduction of various modifying agents (e.g., carbonyl compounds and dicarboxylic acids) into these oligoamides strongly affects the structure and properties of the products and, as a consequence, the characteristics of hot-melt adhesives based on them [6, 7].

Of particular interest in this respect is the modifying effect of methionine (α -amino- γ -methylthiobutyric acid), due to several reasons. First, a fairly bulky substituent, $\text{CH}_3\text{SCH}_2\text{CH}_2$, in the α -position of methionine should affect the physicochemical properties of the products [8–10]. At the same time, methionine plays an important role in biosynthesis processes, and introduction of its fragment into an oligoamide macromolecule may be a route to promising biodegradable materials, which would allow solution of environmental problems associated with the utilization of spent oligo- and polyamides [11, 12].

In this study we prepared a series of oligoamides differing in the content of methionine fragments and examined the specific features of polycondensation and the structure and properties of the products.

EXPERIMENTAL

As starting reagents we used methionine (Met) [GOST (State Standard) 23423–89], DFA of the PRI-POL 1017 brand (the Netherlands, CAS no. 61788–89–4), hexamethylenediamine (HMDA) [TU (Technical Specifications) 6–09–36–73], and wollastonite filler (NordKalk, Finland) FW-70, FW-325, and WIC-10 (mean particle diameter ≤ 90 , ≤ 13 , and ≤ 4.5 μm , respectively).

The procedure for preparing oligo- and polyamides derived from DFA and aliphatic diamines is described in detail in [1, 2] and involves the polycondensation in a nitrogen atmosphere at 160–240°C for 5–6 h without solvents and catalysts.

The synthesis of oligoamides modified with methionine is characterized by certain specific features associated with the fact that at 200–240°C *D*-methionine melts with decomposition; also, the tendency of α -amino acids to cyclize on heating with the formation of 2,5-diketopiperazines [13, 14] should be taken into account.

Therefore, the joint polycondensation of DFA, HMDA, and methionine was performed under milder conditions, which allowed us to minimize the formation of diketopiperazines and avoid thermal decomposition of the amino acid molecules into low-molecular-weight products.

A reactor was charged with the required amounts of DFA and HMDA. The mixture was heated to 80–100°C with stirring until a homogeneous mass was obtained. Then methionine was added, and the mix-

Table 1. Properties of modified oligoamides prepared at different reactant ratios

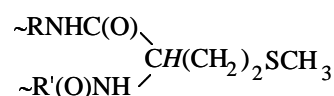
Sample no.	Equivalent ratio of reactants			AmN	AcN	<i>M</i>	<i>T_s</i> , °C
	DFA	HMDA	Met	mg KOH/g oligoamide			
1	0.40	0.50	–	20.5	1.5	5100	85
2	0.40	0.50	0.05	23.5	2.0	4400	80
3	0.40	0.50	0.10	30.3	2.3	3500	75
4	0.40	0.50	0.20	33.8	2.5	3100	68
5	0.40	0.50	0.25	40.8	3.9	2500	62
6	0.40	0.50	0.50	45.4	4.6	2200	56

the adjacent macromolecules and hence in the number of hydrogen bonds between the adjacent oligoamide chains; as a result, the softening point decreases [16].

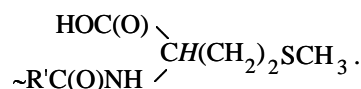
To confirm the incorporation of methionine into the oligomer and determine how methionine is bonded with the oligomer, we examined the chemical structure of polycondensation products formed in the system DFA–HMDA–methionine by IR and NMR spectroscopy. The expected amide structure was confirmed by the characteristic amide vibrations [1]. However, we revealed no specific shift of the absorption bands under the influence of intra- and intermolecular interactions caused by the introduction of the amino acid containing a heteroatomic substituent in the α -position. Furthermore, assignment of S–C bands is complicated by their weak intensity, and identification of this fragment by IR spectroscopy is impossible.

The NMR spectra furnish more information. They convincingly confirm the incorporation of the amino acid into the oligoamide; the methionine fragments were detected in different parts of the oligomer chain:

both in the middle and on the ends. In the ^1H NMR spectrum, along with strong signals belonging to amide groups [1], we additionally detected signals of CH_3S protons at about 2.1 ppm, signals of the methine protons of the fragment



at 4.2 ppm, and signals at 4.6 ppm assignable to the methine protons of the fragment



At the same time, we detected no expected signals of the methine protons of the fragment $\sim\text{RNHC(O)}\cdot\text{CH}(\text{NH}_2)\text{CH}_2\text{CH}_2\text{SCH}_3$ at 3.1 ppm. These signals, however, may be obscured by strong signals of the $-\text{CH}_2\text{C(O)NH}-$ protons.

Examination of the molecular-weight distribution (MWD) of the compounds obtained involved certain problems due to low solubility in THF of higher-molecular-weight samples containing from 0.05 to 0.2 molar equivalent of methionine. It is known that oligo- and polyamides are resistant to the majority of solvents used and dissolve only in substances containing strongly polar groups [17]. Therefore, we determined the molecular-weight parameters only for products containing 0.25 (Table 1, sample no. 5) and 0.50 (sample no. 6) molar equivalent of methionine, which had lower molecular weight (Table 1) and higher solubility in THF. This fact confirms the previous data [17] that the solubility of oligo- and polyamides in common solvents can be increased by performing the synthesis in the presence of components containing a sulfur heteroatom.

The gel chromatograms of the reaction products obtained from DFA, HMDA, and methionine are shown in Fig. 2. It should be noted that calculation of the molecular weights from the polystyrene calibration

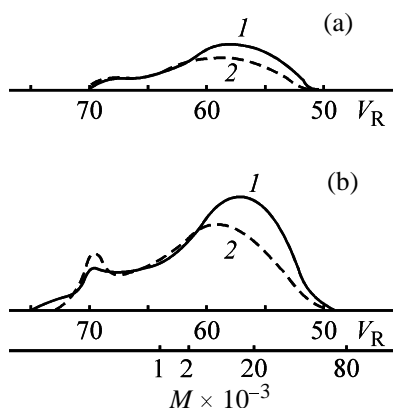


Fig. 2. Gel chromatograms [(a) refractometric and (b) UV detector] of oligoamide samples. DFA : HMDA : Met ratio in the reaction system: (1) 0.40 : 0.50 : 0.25 and (2) 0.40 : 0.50 : 0.50. (V_R) Relative retention volume and (M) molecular weight (polystyrene references).

Table 2. Molecular parameters of sample nos. 5 and 6

Sample no.	Chemical method, M_n	GPC (refractometric detector)		
		\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n
5	2500	2000	7800	3.9
6	2200	1500	5400	3.6

does not give true molecular weights but allows adequate comparison of the MWDs of different samples of similar nature [18].

The chromatographic patterns show that the fractional composition of the samples obtained is nonuniform, with the prevalence of low-molecular-weight and oligomeric fractions; the MWD curves are essentially bimodal. The mean molecular weights M are $600 < M < 40\,000$ for sample no. 5 and $600 < M < 32\,000$ for sample no. 6.

The MWD data for methionine-containing oligoamides are given in Table 2.

A comparative analysis of the molecular weights of methionine-containing oligoamides shows that the number-average molecular weights obtained using various methods are in reasonable agreement. The GPC examination confirms a decrease in M of the oligomer with an increase in the methionine content.

Methionine-modified oligoamides were used for the development of new thermoplastic adhesive formulations. Along with single-component hot-melt adhesives consisting of the base thermoplastic only,

we tested a series of filled adhesives. Here we report the results obtained with wollastonite, one of the most promising fillers. Table 3 shows that introduction of wollastonite considerably expands the working temperature range of adhesive formulations, shortens the curing time, enhances the shear strength of the glue joint, and decreases the cost of the adhesive.

It should be noted that such an effect of wollastonite on the properties of adhesive formulations is determined by a characteristic needle-like shape of its crystals and by the specific chemical composition. Owing to the active surface of the particles, this filler is capable of hydrogen bonding with oligoamide molecules; an important factor is the dispersity of the wollastonite [19, 20]. Our results show that the best physicomachanical and processing characteristics are exhibited by filled hot-melt adhesives containing 20 or 50 wt % wollastonite; the strongest effect is attained with 50 wt % wollastonite WIC-10.

CONCLUSIONS

(1) Addition of methionine to the reaction mixture in the synthesis of oligoamides from dimerized fatty acid and hexamethylenediamine decelerates by a factor of 1.5, on the average, the polycondensation and formation of the final product.

(2) With an increase in the relative amount of methionine, the molecular weight of the product decreases by a factor of 1.2–2.3, and the softening point, by 5–29°C.

Table 3. Composition and properties of hot-melt adhesives based on methionine-modified oligoamide (DFA : HMDA : Met = 0.40 : 0.50 : 0.25)

Component, wt %		T_s	T_{appl}	Curing time, s	Shear strength (Al-Al), MPa
oligoamide	wollastonite	°C			
100	–	62	110–115	4	5.0
	FW-70:				
90	10	66	110–120	3	5.4
80	20	75	120–130	3	6.0
50	50	89	130–140	2	7.3
	FW-325:				
90	10	65	110–120	3	5.3
80	20	74	120–130	3	5.8
50	50	85	130–140	2	6.5
	WIC-10:				
90	10	69	115–120	3	5.6
80	20	78	125–135	3	7.2
50	50	89	140–145	2	8.0

(3) A series of wollastonite-filled thermoplastic adhesive formulations based on methionine-containing oligoamides were developed.

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