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Thixotropic compositions: unsaturated polyester resins/modified bentonites

Summary — Nearly 40 quaternary ammonium chlorides were tested as modifiers of a bentonite (smectic clay). The modified bentonite was used as thixotropic agent for a general purpose unsaturated polyester resin. The modification changed the thermal characteristic of bentonites (DSC) and led to increased distance between layers in bentonite grains (X-ray diffraction). The structure of ammonium salt, namely the kind and size of substituents, had a significant effect on thixotropic properties of unsaturated resin compositions. The thixotropic properties were measured by recording viscosity hysteresis by rotary rheometer and evaluating the absolute and standard thixotropic indices. From the point of view of thixotropic properties of unsaturated polyester compositions, the best quaternary ammonium salt modifier had one benzyl and one slightly branched aliphatic hydrocarbon substituent.

Key words: unsaturated polyester resin, bentonite, modification quaternary ammonium salts, rheological properties, thixotropic indexes, viscosity hysteresis.

KOMPOZYCJE TIKSOTROPOWE: NIENASYCONE ŻYWICE POLIESTROWE/MODYFIKOWANE BENTONITY

Streszczenie — Na przykładzie kilkudziesięciu IV-rzędowych soli amoniowych jako modyfikatorów bentonitu oceniono wpływ różnego rodzaju podstawników przy atomie azotu na ich efektywność jako środków tiksotropowych do nienasyconych żywic poliestrowych (tabela 1). Modyfikowane próbki betonitu zastosowano w charakterze środków tiksotropujących konstrukcyjną nienasyconą żywicę poliestrową. Taka organofilizacja spowodowała zmianę termochemicznej charakterystyki bentonitów (badanej metodą DSC, rys. 1) i doprowadziła do zwiększenia odległości pomiędzy warstwami glinki (mierzonej metodą dyfrakcji promieni X, rys. 2). Rodzaj i wymiary podstawników w soli amoniowej w istotny sposób wpływają na obserwowane polepszenie tiksotropowych właściwości uzyskiwanych kompozycji (tabela 2). Właściwości te określano mierząc pętlę histerezy lepkości za pomocą reometru obrotowego oraz wyznaczając bezwzględny i standardowy wskaźnik tiksotropii a także indeks tiksotropii (rys. 3—5). Najkorzystniejszymi modyfikatorami bentonitu okazały się sole amoniowe zawierające podstawnik benzylowy i alkilowy o długim, słabo rozgałęzionym łańcuchu.

Słowa kluczowe: nienasycona żywica poliestrowa, bentonit, czwartorzędowe sole amoniowe, właściwości reologiczne, bezwzględny i standardowy wskaźnik tiksotropii.

The term "thixotropy" describes reduction of liquid viscosity induced by shear forces. The phenomenon was first identified and described by Peterifi, in 1927 [1]. More specifically, one can state that a system is thixotropic when it behaves like a gel at rest and turns into a sol when is subjected to a constant shear stress. The viscosity reduces as the time of shear stress (*e.g.* while mixing of the system) becomes longer. Release of the stress results in return of the system to the initial state: from liquid sol to gel. The viscosity substantially increases again.

Many theoretical papers dealing with thixotropy were published in the last thirty years [2—26]. In 1965 Cheng and Evans [2, 3] presented a phenomenological method of describing of thixotropic liquids. They systematized experimental observations and derived basic flow equations for thixotropic liquids. The ideas of Cheng and Evans were further developed by Kembłowski and Petera [6] who presented a complete phenomenological description of rheology of non-elastic liquid at viscous flow. The liquid was treated as having a rate controlled internal structure characterized by structural parameters (as many as five) responsible for its flowing properties. Their method was suitable for engineering design and calculations, but the structural parameters were not related to any physical properties of liquids. Nevertheless the approach of Kembłowski and Petera is widely applied to describe the properties of many thixotropic liquids [8—17].

Following these ideas we have proposed a new method of characterizing of thixotropic liquids by measuring their "absolute index of thixotropy", I_{at} [18—24].

Details of its definition and physical significance are presented later in this paper.

In this work we concentrated on the effect of chemical structure of a modifier of a thixotropic agent (bentonite) on the properties of unsaturated polyester resin (UP) compositions with this agent.

EXPERIMENTAL

Materials

— Bentonite SN (BSN): a product of ZĘBIEC S.A., (Zębiec n/Starachowice, Poland);

— general purpose unsaturated polyester resin (UP) "Polimal 109" — a product of Organika-Sarzyna Works (Nowa Sarzyna, Poland);

— quaternary ammonium salts (QAS) listed in Table 1 used as modifiers of bentonites.

Table 1. List of quaternary ammonium salts (QAS) of general formula $R_1R_2R_3R_4N^+Cl^-$ used in this work

Number	R_1	R_2	R_3	R_4	Producer
1	CH_3	CH_3	CH_3	CH_3	Fluka
2	C_4H_9	CH_3	CH_3	CH_3	Merck
3	C_8H_{17}	CH_3	CH_3	CH_3	Fluka
4	$C_{12}H_{23}$	CH_3	CH_3	CH_3	Sigma
5	$C_{18}H_{37}$	CH_3	CH_3	CH_3	Merck
6	C_4H_9	CH_3	CH_3	C_4H_9	Lonza
7	C_8H_{17}	CH_3	CH_3	C_8H_{17}	Merck
8	$C_{16}H_{33}$	CH_3	CH_3	$C_{16}H_{33}$	Merck
9	$C_{18}H_{37}$	CH_3	CH_3	$C_{18}H_{37}$	ICSO*
10	C_4H_8OH	CH_3	CH_3	C_4H_8OH	ICSO
11	$C_8H_{16}OH$	CH_3	CH_3	$C_8H_{16}OH$	Merck
12	$C_{18}H_{36}OH$	CH_3	CH_3	$C_{18}H_{36}OH$	Merck
13	CH_2OH	CH_3	CH_2COOH	CH_2OH	ICSO
14	$C_8H_{16}OH$	CH_3	CH_2COOH	$C_8H_{16}OH$	Fluka
15	$C_{18}H_{36}OH$	CH_3	CH_2COOH	$C_{18}H_{36}OH$	Fluka
16	$C_{12}H_{24}OH$	$C_{18}H_{37}$	CH_2COOH	$C_{12}H_{24}OH$	ICSO
17	$C_{16}H_{32}OH$	$C_{18}H_{37}$	CH_2COOH	$C_{16}H_{32}OH$	Lonza
18	$C_{18}H_{36}OH$	$C_{18}H_{37}$	CH_2COOH	$C_{18}H_{36}OH$	ICSO
19	$C_{24}H_{48}OH$	$C_{18}H_{37}$	CH_2COOH	$C_{24}H_{48}OH$	ICSO
20	Ph	CH_3	CH_3	CH_3	ICSO
21	Ph	CH_3	CH_3	C_4H_9	Merck
22	Ph	CH_3	CH_3	$C_{12}H_{25}$	Merck
23	Ph	C_2H_4OH	C_2H_4OH	$C_{10}H_{21}$	Sigma
24	Ph	C_2H_4OH	C_2H_4OH	$C_{12}H_{25}$	Merck
25	Ph	CH_3	CH_3	$C(C_2H_5)_2C_{12}H_{25}$	Sigma
26	$PhCH_2$	CH_3	CH_3	CH_3	Sigma
27	$PhCH_2$	CH_3	CH_3	C_4H_9	Sigma
28	$PhCH_2$	CH_3	CH_3	$C_{12}H_{25}$	Merck
29	$PhCH_2$	CH_3	CH_3	$C_{16}H_{33}$	Merck
30	$PhCH_2$	CH_3	CH_3	$C_{18}H_{37}$	Lonza
31	$PhCH_2$	CH_3	CH_3	C_2H_4OH	Lonza
32	$PhCH_2$	CH_3	CH_3	$C_8H_{16}OH$	Sigma
33	$PhCH_2$	CH_3	CH_3	$C_{12}H_{24}OH$	Sigma
34	$PhCH_2$	C_2H_4OH	C_2H_4OH	C_4H_9	Sigma
35	$PhCH_2$	C_2H_4OH	C_2H_4OH	$C_{10}H_{21}$	ICSO
36	$PhCH_2$	C_2H_4OH	C_2H_4OH	$C_{12}H_{25}$	ICSO
37	$PhCH_2$	CH_3	CH_3	$C(C_2H_5)_2C_6H_{13}$	Lonza
38	$PhCH_2$	CH_3	CH_3	$C(C_2H_5)_2C_{12}H_{25}$	Lonza
39	$PhCH_2$	CH_3	CH_3	$C(C_2H_5)_2C_{16}H_{33}$	Lonza

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Modification of bentonite with QAS

A method of modification of bentonites with QAS developed by us [25, 26] was applied. The modification provided 77.0 to 93.0 % of cation exchange. The modified bentonites were dried at 40—60 °C in a convection and then vacuum oven. The product was grinded to yield a powder of particle size below 0.07 mm.

Modification effectiveness assessment

To assess the effectiveness of modification of bentonites with QAS, the products were tested by scanning differential calorimetry (DSC) and X-ray analysis. DSC measurements were made using "Mettler-Toledo 822e" instrument (Switzerland) in temperature range 20—500 °C in air at heating rate 10 deg/min. Two representative thermograms are presented in Fig. 1 for unmodified bentonite SN (BSN) and for the same modified with benzyltrimethylammonium chloride (QAS No 26 in Table 1) ($BSN_{QAS\,26}$). A well developed exothermic peak appears in the thermogram of $BSN_{QAS\,26}$ which is most probably related to thermooxidative decomposition of QAS built into modified bentonite. Note that in the thermogram of unmodified bentonite there are no thermal effects in the same temperature range. Only an endothermic peak is seen in the range 80—120 °C due to the loss of crystalline water.

A conclusive proof, confirming that bentonite modification indeed took place, provided X-ray diffractograms. They were recorded using Siemens apparatus equipped

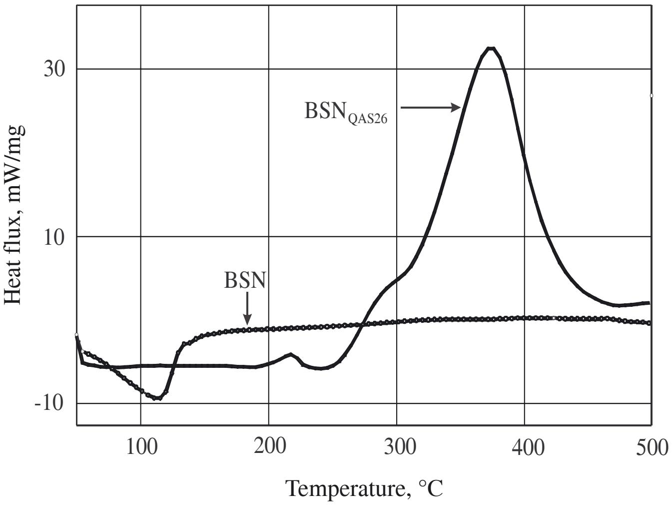

Fig. 1. DSC curves of unmodified bentonite SN (BSN) and the same bentonite modified with QAS No. 26

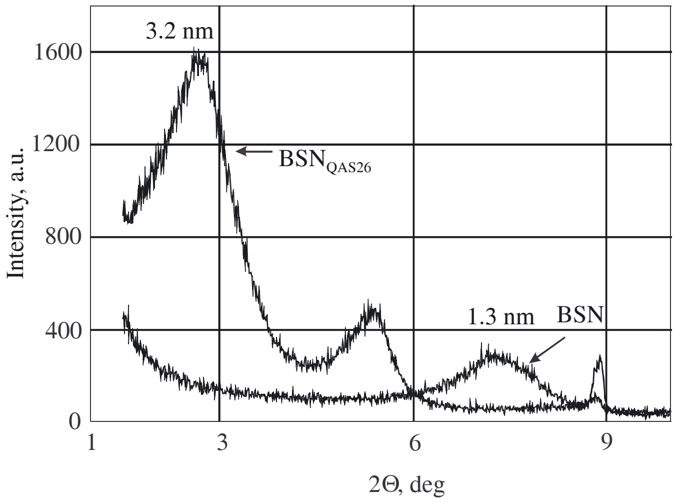

Fig. 2. X-ray diffractograms recorded for unmodified BSN and for BSN$_{QAS26}$, modified with quaternary ammonium salt No 26 (Table 1). The interlamellar distances corresponding to intensity maxima are shown

with 40 kV CuK$_\alpha$ lamp. Two representative diffractograms recorded for bentonites unmodified and modified with QAS No 26, respectively, are presented in Fig. 2. The interlamellar distances that can be calculated from the positions of diffraction peaks are 1.3 and 3.2 nm for unmodified and modified bentonites, respectively. The enlarged distance between the layers in the modified bentonite facilitates penetration of unsaturated polyester resin components between lamellae, good dispersion of bentonite particles in the resins and, eventually, an exfoliation of bentonite particles into individual layers.

Thixotropic properties of compositions

Thixotropic properties were characterized for compositions of unsaturated polyester resin "Polimal® 109" containing 2 wt. % of modified bentonite. This amount of bentonite was found optimal for the compositions [18—26].

Viscosity hysteresis measured by rotary rheometer

The viscosity measurements were made with the use of "Rheotest RV2" (RHEOTEST Messgeräte Medingen GmbH, Germany) and cylinder system S3 at temperature 25 °C, initially for growing and then decreasing rotation rate of the penetration rotor. The shear time at each level of shear rate usually was 60 s. Shear rate at the given level of shear stress changed every 60 s. However, at maximal rate in order to preserve full reversibility of the properties, the shear time did not exceed 3 min in the first series of measurements, and 5 min in the second series. The time of rest between each series of measurements was 30 min, sufficient for the thixotropic structure to be rebuilt. The number of points, *i.e.* different shear rates applied, was 25 in the range from 5.0 to 470 s^{-1}. The same set of cylinders and the same values of shear rates were used for each composition.

The apparent viscosities calculated using the cylinder constants were fitted to the relationship:

$$\eta = \eta_\infty + \eta_1 e^{-\frac{\dot{\gamma}}{\dot{\gamma}_1}} + \eta_2 e^{-\frac{\dot{\gamma}}{\dot{\gamma}_2}} \qquad (1)$$

where: η *and* $\dot{\gamma}$ *— apparent viscosity and shear rate, respectively;* η_∞, η_1, η_2, $\dot{\gamma}_1$, *and* $\dot{\gamma}_2$ *— constants obtained by fitting.*

Empirical equation (1) modified by us provided excellent description of experimental values. The curves were then numerically integrated in the range of applied shear rates. The result obtained for increasing shear rates was subtracted from the value calculated for decreasing shear rates to yield the area of viscosity hysteresis. This surface area can be interpreted as the energy dissipated by the system due to destruction of the liquid structure responsible for thixotropic properties [19, 20, 24].

The absolute thixotropy index

The absolute thixotropy index has been defined as [19, 20]:

$$I_{at} = \frac{\eta_0}{\eta_\infty} \qquad (2)$$

where: η_0 *and* η_∞ *— apparent viscosities of a liquid at rest (zero shear rate) and at infinite shear rate, respectively.*

While the second quantity is available as one of parameters calculated while fitting viscosity measurements [*eq.* (1)], the first one requires careful measurement at as low shear rate as possible. We measured the viscosities "at rest" using a plate-plate oscillation rheometer "Rheo-Stress" (Haake, Germany). The measurements were carried out at 25 °C. The compositions were placed between measuring plates of diameter 20 mm set at the distance of 1.5 ± 0.01 mm. To reach that distance while reducing extra shear, the plates were moved axially to each other at a minimal rate of 0.15 mm/min. The compositions were pre-sheared by rotating of the plates at the rate of 5 s^{-1} and then oscillating at the rate of 0.5 s^{-1}. After 15 min of equilibration, the viscosity was read out. This viscosity was treated as the value at rest (η_0). The whole procedure was controlled by computer.

Since at the rate exceeding 5 s^{-1}, the layer between plates lost their integrity, the values of η_∞ were measured by using cylinder-cylinder setup at "Rheotest RV2". The same cylinders and conditions were used as those described in previous section. Each composition was sheared at given shear rate for 15 min and then the system was switched to next shear rate. Quarter of an hour was sufficient to bring the composition to equilibrium at all shear rates in the range 5.0 to 437.0 s^{-1}. The time of structure restoration between each series of measurements was set to 30 min.

The value of η_0 evaluated in the plate-plate setup was consistent with the viscosity values measured by cylinder-cylinder method and well fitted to the curve calculated with *eq.* (1). The value of η_∞ estimated from this equation was used to calculate the absolute index of thixotropy [*eq.* (2)].

Standard thixotropy index determined using Brookfield viscometer

The standard thixotropy index (Polish Standard PN-73/C-81547) was also measured to compare the results of different methods of thixotropy characterization. A Brookfield viscometer type RVDV II (Brookfield Engineering Labs. Inc. STOUTHTON, USA) was used at 25±1 °C and recommended rotation rates 5 and 50 min^{-1}. Rotor No. 2 was used. Half an hour break was applied between each measurement to rebuilt internal structure of the compositions. The thixotropy index *(IT)* was calculated as:

$$IT = \frac{\eta_5}{\eta_{50}} \qquad (3)$$

where: η_5 *and* η_{50} *are the viscosities obtained at the rotation rate 5 and 50 min*$^{-1}$*, respectively.*

RESULTS AND DISCUSSION

The results of rheological analyses of the compositions of UP containing 2 wt. % of bentonites or modified bentonites are presented in Tables 2—4 and Figs. 3—5. Table 2 collects the data derived from the functions $\eta = f(\dot{\gamma})$ as well as the surface areas of viscosity hysteresis and the energy of breaking bonds forming the structure responsible for thixotropic properties. All these quantities, although differing in values, are consistent, *i.e.* the better thixotropic properties of a composition, the higher the corresponding rheological parameters presented in Table 2.

Table 2. Parameters characterizing the thixotropic properties of UP compositions containing bentonite (BSN) or modified bentonites

Composition*)	Thixotropy index *IT* at 5/50 min^{-1}	Absolute thixotropy index I_{at}	Work of destruction of secondary structure J/m^3	Area of viscosity hysteresis J/m^3	
				t_1**) = 3 min	t_2**) = 5 min
UP+BSN	1.85	3.81	6.8	7.8	12.4
UP+BSN$_{QAS\,1}$	3.28	5.81	24.8	31.6	39.5
UP+BSN$_{QAS\,2}$	3.43	6.12	25.3	37.6	43.0
UP+BSN$_{QAS\,3}$	3.49	6.32	25.6	40.8	46.8
UP+BSN$_{QAS\,4}$	3.62	6.88	26.1	44.0	49.5
UP+BSN$_{QAS\,5}$	3.71	7.14	26.7	46.5	52.3
UP+BSN$_{QAS\,6}$	3.54	6.14	25.5	38.3	44.9
UP+BSN$_{QAS\,7}$	3.58	6.62	25.9	42.3	48.1
UP+BSN$_{QAS\,8}$	3.73	7.18	27.1	47.3	53.2
UP+BSN$_{QAS\,9}$	3.79	7.23	28.6	48.4	55.2
UP+BSN$_{QAS\,10}$	3.56	6.18	25.9	39.1	45.8
UP+BSN$_{QAS\,11}$	3.62	6.78	26.9	43.8	49.8
UP+BSN$_{QAS\,12}$	3.82	7.30	29.4	49.1	56.6
UP+BSN$_{QAS\,13}$	3.57	6.19	26.0	39.0	45.9
UP+BSN$_{QAS\,14}$	3.65	6.83	27.6	44.5	50.8
UP+BSN$_{QAS\,15}$	3.87	7.36	29.9	49.8	57.2
UP+BSN$_{QAS\,16}$	3.93	7.42	31.1	51.2	58.9
UP+BSN$_{QAS\,17}$	3.97	7.49	31.9	52.1	59.5
UP+BSN$_{QAS\,18}$	3.99	7.52	32.1	52.3	59.8
UP+BSN$_{QAS\,19}$	3.95	7.48	31.8	51.9	58.2
UP+BSN$_{QAS\,20}$	4.00	7.94	40.3	84.6	96.8
UP+BSN$_{QAS\,21}$	4.10	7.98	40.9	85.4	98.3
UP+BSN$_{QAS\,22}$	4.32	8.25	44.2	96.3	104.6
UP+BSN$_{QAS\,23}$	4.94	9.32	57.8	106.7	113.9
UP+BSN$_{QAS\,24}$	4.99	9.44	58.9	108.9	117.3
UP+BSN$_{QAS\,25}$	5.08	9.81	61.4	118.3	128.6
UP+BSN$_{QAS\,26}$	4.96	9.42	58.3	108.3	116.8
UP+BSN$_{QAS\,27}$	4.99	9.73	60.0	116.4	125.6
UP+BSN$_{QAS\,28}$	5.20	10.12	63.2	132.6	141.5
UP+BSN$_{QAS\,29}$	5.22	10.24	64.0	131.3	143.2
UP+BSN$_{QAS\,30}$	5.10	9.91	59.9	128.3	132.4
UP+BSN$_{QAS\,31}$	5.09	9.80	61.6	118.2	128.5
UP+BSN$_{QAS\,32}$	5.19	10.10	63.9	133.9	142.9
UP+BSN$_{QAS\,33}$	5.23	10.23	64.2	134.6	145.2
UP+BSN$_{QAS\,34}$	5.26	10.29	64.6	135.1	145.8
UP+BSN$_{QAS\,35}$	5.68	10.84	71.2	138.6	152.3
UP+BSN$_{QAS\,36}$	5.86	11.09	75.9	141.2	155.9
UP+BSN$_{QAS\,37}$	5.89	11.11	76.2	142.3	156.1
UP+BSN$_{QAS\,38}$	6.08	12.88	84.3	148.3	162.6
UP+BSN$_{QAS\,39}$	6.12	13.05	86.2	151.6	164.3

*) Structure of QAS — see Table 1.

**) Shear time at the highest shear rate $\dot{\gamma}_{max}$ = 437 s^{-1}

As can be seen, even the composition containing bentonite modified with the simplest QAS 1 (with all substituents being methyl groups) has better thixotropic quality than that prepared with unmodified bentonite. By extending the length of aliphatic chain R_1 from C_1 through C_4, C_8, C_{12}, to C_{18} (cf. Table 1) one can enhance the thixotropic properties of UP compositions. Among compositions prepared from bentonites modified with all aliphatic QAS, the best properties were observed for compositions containing bentonite SN$_{QAS\,5}$ with R_1 substituent comprising 18 carbon atoms (Fig. 3, curve 1 and Table 2). Further improvement of thixotropic properties of UP compositions was obtained by use of the bentonite

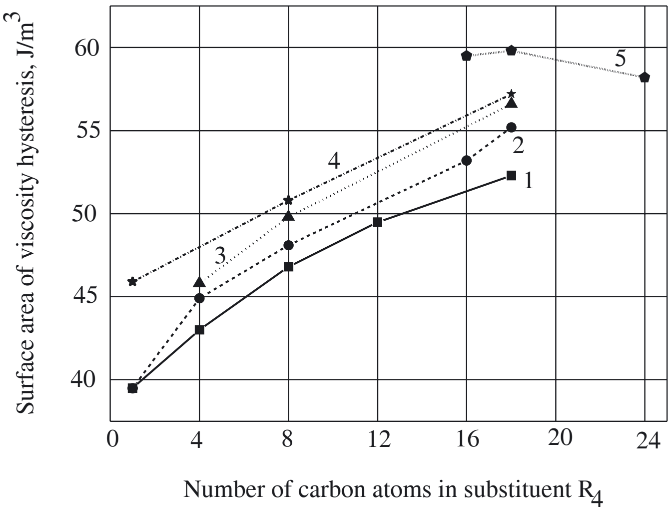

Fig. 3. Thixotropic properties of UP modified with bentonites (expressed as surface area of viscosity hysteresis for t = 5 min, Table 2) vs. number of carbon atoms in aliphatic chains R_4 of QAS. For description of individual curves see the text

modified with QAS having more than one long aliphatic substituent (R_4 with length varying from C_1 to C_{18}), particularly when both R_1 and R_4 were linear C_{18} aliphatic chains (Fig. 3, curve 2 and Table 2). These findings can be interpreted in terms of wider gaps being formed between bentonite lamellae modified with QAS with bigger substituents. The wider gap facilitated penetration of resin into bentonite grains [27, 28]. A replacement of aliphatic substituents R_1 and R_4 in QAS by hydroxyaliphatic ones (Fig. 3, curve 3 and Table 2) and extending of their chains' length from C_4 to C_{18} still further improved the thixotropic properties of compositions. Consequently, the best properties in this group of bentonite modifiers were obtained for compositions containing QAS with R_1 and R_4, both $-C_{18}H_{36}OH$ and R_2 and R_3 both $-CH_3$.

Among the ammonium salts containing carboxylic groups used for bentonites modification QAS similar to those containing hydroxyaliphatic groups, but with R_3 being $-CH_2COOH$ rather than CH_3 provides good thixotropic properties (Fig. 3, curve 4, Table 2). Significant improvement was observed in the case of bentonite modified with QAS in which R_1 and R_4 were both $-C_{16}H_{32}OH$, R_3: $-CH_2COOH$, and R_2: $-C_{18}H_{37}$ (Fig. 3, curve 5, Table 2). It should be noted, however, that extending the length of aliphatic chains from C_{16} to C_{18} an improvement of thixotropic properties was observed, but further increase in the length of aliphatic chain was not advantageous anymore (curve 5).

In the next step, the effect of aromatic substituents on the properties of QAS as modifiers of bentonites for thixotropic UP compositions was studied. Again, the surface area of viscosity hysteresis was a measure of the quality of thixotropic properties. All the results are collected in Table 2, but the effects of QAS structure are illustrated in Fig. 4. The QAS modifiers considered in this group have aromatic substituents as R_1. The remaining substituents R_2 through R_4 are aliphatic. Curve 1 in Fig. 4 is plotted as a reference and refers to all aliphatic substituents in QAS. As it is well seen, curve 1 falls much below the other two curves representing QAS with phenyl (curve 2) or benzyl (curve 3) substituent as R_1. The effect of chain length of the aliphatic substituent R_4 in the range C_1 to C_{12} had a minor effect in the case of phenyl QAS. Benzyl groups present in QAS improved the thixotropic properties of UP compositions most effectively. Increase in the length of R_4 substituent from C_1 to C_{16} markedly improved the thixotropic properties of final UP compositions; further increase in the length was not efficient anymore.

Since UP compositions prepared using bentonites modified with QAS containing benzyl group as substituent R_1 showed the best thixotropic properties, the effect of other substituents (namely aliphatic R_4 substituent) was studied in details.

The relevant results extracted from Table 2 are presented in Fig. 5. Thus, the replacement of purely hydrocarbon substituents (Fig. 5, curve 1) with hydroxyaliphatic ones (Fig. 5, curve 2) clearly improved thixotropic properties of the composition as exemplified by the respective areas of viscosity hysteresis. Again, in both cases, the longer carbon chain of substituent R_4, the better thixotropic properties. Further improvement in thixotropic properties results from the substitution of R_2 and R_3 methyl groups by hydroxyethyl groups ($-C_2H_4OH$) with R_4: $-C_4H_9$ or longer, C_{10} or C_{12} substituents (Fig. 5, curve 3).

Finally, the best modifiers of bentonite SN used in UP thixotropic compositions are QAS with benzyl substituent R_1, two methyl groups as R_2 and R_3 and R_4: $-C(C_2H_5)_2C_6H_{13}$. Still better are the salts with longer chains: $-C(C_2H_5)_2C_{12}H_{25}$ or $-C(C_2H_5)_2C_{16}H_{33}$ (Fig. 5, curve 4). Apparently, these big aliphatic substituents fa-

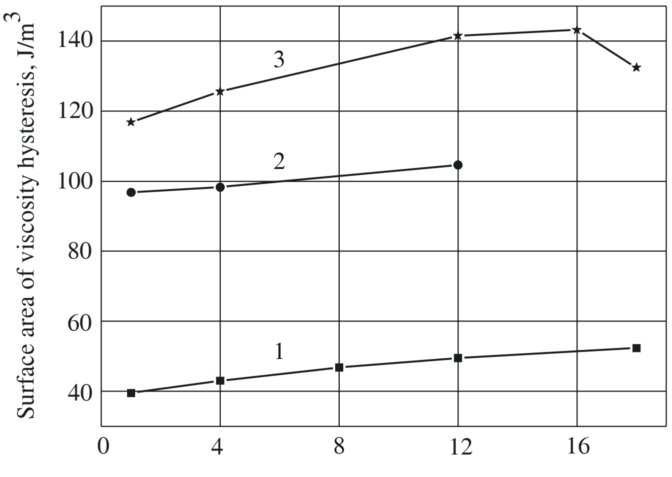

Fig. 4. Thixotropic properties of UP modified with bentonites (expressed as surface area of viscosity hysteresis for t = 5 min, Table 2) vs. number of carbon atoms in aliphatic chains R_4 of QAS. For description of individual curves see the text

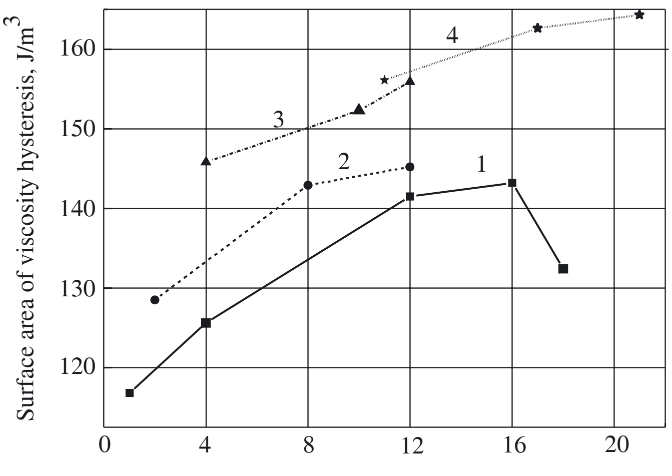

Fig. 5. Thixotropic properties of UP modified with bentonites (expressed as surface area of viscosity hysteresis for t = 5 min, Table 2) vs. number of carbon atoms in aliphatic chains R_4 of QAS. For description of individual curves see the text

cilitate separation of bentonite layers, provide better wetting of grains with UP resin and stabilize the suspension of bentonite in a resin.

The data in Table 2 also suggests that at the time of shear extending at the highest shear rate from 3 to 5 min, one observes only a slight increase in hysteresis surface area (Table 2). The effect is not a big one since the number of temporary links formed between the grains of bentonite is limited. Excessive times of shear at high shear rate or too high shear rate do not improve the thixotropic properties of UP compositions. The reason might be that mechanical destruction of bentonite packets takes place at excessive shear. This mechanical sensitivity of smectic clays is one of the disadvantages of use of bentonites as thixotropic agents.

By taking into account just the values of absolute (I_{at}) and standard thixotropy indices *(IT)* (Table 2), one can conclude that the compositions prepared using bentonites modified with QAS nos. 37 to 39 in Table 1, *i.e.* with those having benzyl substituent and one branched and large hydrocarbon substituent, showed the best thixotropic properties. This conclusion is very much consistent with the results of analysis of viscosity hysteresis surface area, discussed earlier in this paper.

From the absolute thixotropy index measurements one can calculate the energy of secondary bonds destroyed by shear forces [19]. The extrapolated limiting viscosities of the compositions were around 3.0 Pa · s [22]. In the calculations of the work needed to destroy the structure of the so called thixotropic gel, we took the area between the viscosity curve and the line η = 3 Pa · s, assuming that the latter value is the intrinsic viscosity of the liquid not affected by Van der Waals's or other secondary interactions. Among the energies of bonds forming the thixotropic gels listed in Table 2, the highest are those calculated for the compositions prepared using bentonites modified with QAS nos. 37 to 39.

CONCLUSIONS

The chemical structure of substituents in quaternary ammonium salts used for modification of bentonites has a considerable effect on the thixotropic properties of unsaturated polyester resins compositions prepared using these bentonites.

The presence in quaternary ammonium salts of at least one aromatic substituent, preferably benzyl one, and a branched aliphatic substituent with long linear hydrocarbon chain (preferably containing 9 to 19 carbon atoms) gives the modified bentonite clay the best properties, from the point of view of the thixotropic properties of unsaturated polyester resins compositions containing 2 wt. % of the clay.

The compositions of unsaturated polyester resin with 2 wt. % of smectites (bentonites) modified with different quaternary ammonium salts show excellent thixotropic properties and satisfactory fluidity, but also another advantage of almost total lack of sedimentation during storage. As previously reported [25, 26], preaccelerated unsaturated polyester resins' compositions containing bentonites modified with ammonium salts containing benzyl substituents have also an outstanding stability during storage.

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