Chemosetting Resins Containing Fillers. I. Unsaturated Polyester Resin Compositions Containing Modified Smectites

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ABSTRACT: Smectic clays with quaternary ammonium salts (QAS) were subjected to hydrophobization, whereupon we applied the products in attempts to modify various polymers. The clays were of natural origin and contained a large proportion of montmorillonite and an original method of modification was applied. A significant improvement of the stability of unsaturated polyester (UP) resins, modified with clays modified with QAS, was observed with essentially no change in the reactivity of resins. The compositions of polyester resins containing 2 wt % of modified smectites had excellent thixotropy. The presence of modified bentonites in a cured commercial UP resin (2–4 wt %) improved its tensile strength (by 21–62%), Brinell hardness (23–70%), and unnotched impact strength (23–100%), depending on the type of bentonite used. The compositions of UP resins with modified clays had certain properties typical for nanocomposites: improved stiffness, strength, transparency, and fine-lamellar morphology of the fracture as found by electron scanning microscopy. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 793–801, 2005

Key words: unsaturated polyester; organoclay; gelation; shelf-life time; resins

INTRODUCTION

As reported in a number of recent publications,[1–12] both natural and synthetic minerals, having a layer structure, can be used as specific fillers for polymeric materials. Natural smectic clays are minerals containing mostly layered material with aluminosilicate components that are capable of exchanging cations. The most common are bentonites with montmorillonite as their main component, usually accompanied by kaolinite and illite and, in small quantities, also the products of crystallization of silicate gels.[13]

The properties of montmorillonite minerals can be modified by making them lyophilic (organophilic) through covering the surface of grains with organic compounds or ions containing organic substituents. One of the methods of modification is linking organic compounds to clay through metal cations. The method is used in the case of nonswelling minerals. Another method consists of creating intracrystalline complexes in which organic components fill the spaces between packets of smectic clays (interlamellar complexes).[14]

Particular attention was devoted to complexes of illitic minerals with amines.[15–18] Aliphatic short-chain primary, secondary, or tertiary amines, when converted into cationic form, as well as quaternary ammonium salts, readily enter the interlayer sections in clays by cation exchange. The cations play a role of "pilasters " pushing away and determining the minimal distance between layers.

The free interlayer space can be filled with water, glycerin, or other liquids. Barrer and Macleod[19] increased the interlayer distance in a montmorillonite by replacing natural cations with $[N(CH_3)_4]^+$ or $[N(C_2H_5)_4]^+$. Then, the clay selectively adsorbed large organic molecules such as paraffinic or aromatic hydrocarbons.

The smectic clays modified with *N*-alkylammonium ions easily swell in organic solvents and they are applicable in many fields of modern technology. The methods of their preparation are protected by numerous patents.[20–25]

In short, it is possible to treat smectic clays in a special way that aims at improving certain properties such as compatibility with organic resins, stability of their suspension in organic liquids, thixotropy, and thickening effect of liquids in which they are dispersed.

In recent years an increasing number of reports have been published on the application of smectic clays as nanofillers for organic polymers.[26–30] These

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TABLE I
Chemical Composition of Quaternary Ammonium Salts (QAS) of General Formula $R^1R_2R_3R_4N^+X^-$ [a]

Symbol of QAS	R_1	R_2	R_3	R_4	X
A1	$PhCH_2$	CH_3	CH_3	C_nH_{2n+1} $n = 10$, 2% $n = 12$, 57% $n = 14$, 23% $n = 16$, 11% $n = 18$, 7%	Cl^-
A2	$C_{10}H_{21}$ ($C_{10} > 95\%$)	CH_3	CH_3	$C_{10}H_{21}$ ($C_{10} > 95\%$)	Cl^-
A3	$PhCH_2$	CH_3	CH_3	C_nH_{2n+1} $n = 12$, 70% $n = 14$, 26% $n = 16$, 4%	Cl^-
A4	C_8H_{17} ($C_8 > 95\%$)	CH_3	CH_3	C_8H_{17} ($C_8 > 95\%$)	Cl^-

[a] All salts are the products of Lonza Group AG, Visp, Switzerland.

nanocomposites appear in the literature under various names. In general, one can distinguish two limiting types of nanocomposite structures depending on the type of polymer and that of nanofiller[30–37]:

1. *Intercalated* structures in which a polymer is placed between parallel layers of otherwise unaffected mineral.
2. *Delaminated* or *exfoliated* structures in which mineral particles are disintegrated and individual aluminosilicate layers are randomly distributed in polymer matrix.

Although unsaturated polyester (UP) resins are widely used, very few articles have been published on nanocomposites based on this group of chemosetting materials. Kornmann et al.[38] published a report in which they described silylation as a method of modifying montmorillonites. The resulting composites had improved mechanical properties. They also modified natural clays with quaternary ammonium chloride containing two 2-hydroxyethyl substituents.[39] The authors studied morphology, thermal stability, and both mechanical and barrier properties of the composites obtained using various amounts of the modified clay. Suh et al.[40] indicated some disadvantageous features that may accompany modification of UP with organophilic monomorillonites. Styrene penetrates the spaces between clay layers with greater facility than it penetrates polyester chains and this may lead to an unintended reduction of crosslink density of the final material. To avoid this they proposed to mix the polyester first with modified clay and then to introduce styrene at about 60°C soon before curing the mixture.

Good results were also obtained when modified clays were used as fillers of epoxy resins, including the inflammable variants of these resins and other types of chemosetting resins.[41,42]

Existing reports on the application of modified smectic clays as nanofillers concentrate on the methods of their use and on the properties of cured composites. Less is known about the properties of the nanocomposites before they are cured, that is, about their stability during storage, reactivity in the curing process itself, and rheological properties. Some of these aspects have already been described in our earlier reports.[1,2,46–48] Herein we also report on new results with respect to the presetting state of nanocomposites based on UP and modified smectic clays. In particular we deal not only with the shelf life of the compositions UP-modified clays but also with improvements in mechanical properties of the UP-based composites. Several commercial bentonite clays were used in the study.

EXPERIMENTAL

Materials

Quaternary ammonium salts (QAS) and commercial bentonites used in the work are listed in Tables I and II, respectively.

The reference polyester resin was preaccelerated (i.e., containing polymerization accelerator) Polimal® 109–32RpyK resin, a product of Organika-Sarzyna Chemical Plants (Nowa Sarzyna, Poland). The polymerization initiator was Luperox K-1, a commercial product also supplied by Organika-Sarzyna.

Modification of bentonites with QAS

An original method of modification of smectic clays, previously developed in our laboratory,[1,2] was used. The process of modification of clays provided 77.0 to 93.0% of cation exchange. It should be pointed out that for all bentonites studied (Table II) no problems re-

TABLE II
Characteristics of Bentonites Used in the Studies

Parameter	Type of bentonite					
	SN	"Special extra" based on Ukrainian bentonite	"Special extra"	"Special"	"Wyoming"	Ukrainian bentonite
Code	BSN	BSEUZU	BSEUZ	BS	BW	BU
Montmorillonite content, wt %	75	75	80	70	90	70
Carbonates, wt %	5	5	5	5	na	na
Water, wt %	9	9	12	12	15	14
Swelling factor, cm^3/2g	8	22	18	17	na	na
Total ion-exchange capacity (Z)[a], mmol/g	26.1	25.9	25.4	27.1	26.0	23.2
Producer/supplier	Zębiec Co., Poland				Cetco Ltd., Poland	

[a] Determined using a procedure recommended by a Polish Standard.[50]

lated to rinsing and filtering the products were encountered, which is important from a practical perspective because these minerals are known to form thixotropic suspensions in water that are difficult to process.

All modified clays were dried at 40–60°C in a vacuum oven, after which they were ground to grain diameters < 0.07 mm.

To gain information on the extent of clay modification, thermochemical [differential scanning calorimetry (DSC) and thermogravimetry (TG)] and X-ray analyses were made. DSC studies were made by using a STAR 822e DSC analyzer (Mettler-Toledo International, Zurich, Switzerland), over a temperature interval of 50 to 500°C at a heating rate of 10°C/min. TG studies were made by using Paulik–Paulik EMG system type 2895 analyzer (MOM, Budapest, Hungary), over a temperature interval of 20 to 1000°C at a heating rate of 10°C/min.

Two representative examples of the results are presented in Figure 1, where DSC thermograms are compared for unmodified bentonite (Wyoming) and the same product after modification with QAS of symbol A1 (Table I). For the latter sample one can observe a clear exothermic peak at 250–450°C, most probably related to the thermooxidative degradation of the QAS. The only endothermic signal in DSC of unmodified bentonite is that attributed to removal of adsorbed and/or crystalline water at 80–120°C.

The amount of QAS modifying individual clay samples was assessed by TG (Fig. 2). In the temperature range 100–700°C the differences between mass losses, read out from thermogravimetric profiles recorded for modified and unmodified samples, was used to calculate this amount. The amount of water present in the unmodified bentonites was estimated from the heat of evaporation measured by DSC. The humidity peak for modified samples was comparatively very small and

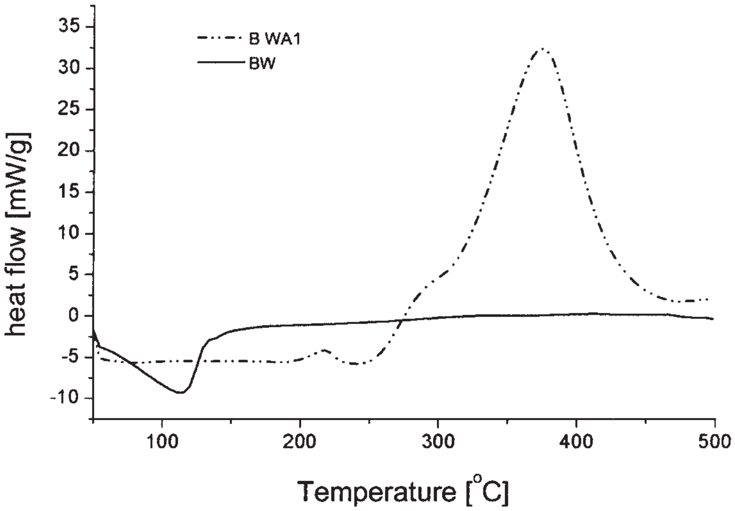

Figure 1 DSC thermograms for unmodified bentonite "Wyoming" (BW) and for the same bentonite modified with quaternary ammonium salt A1 (BWA1).

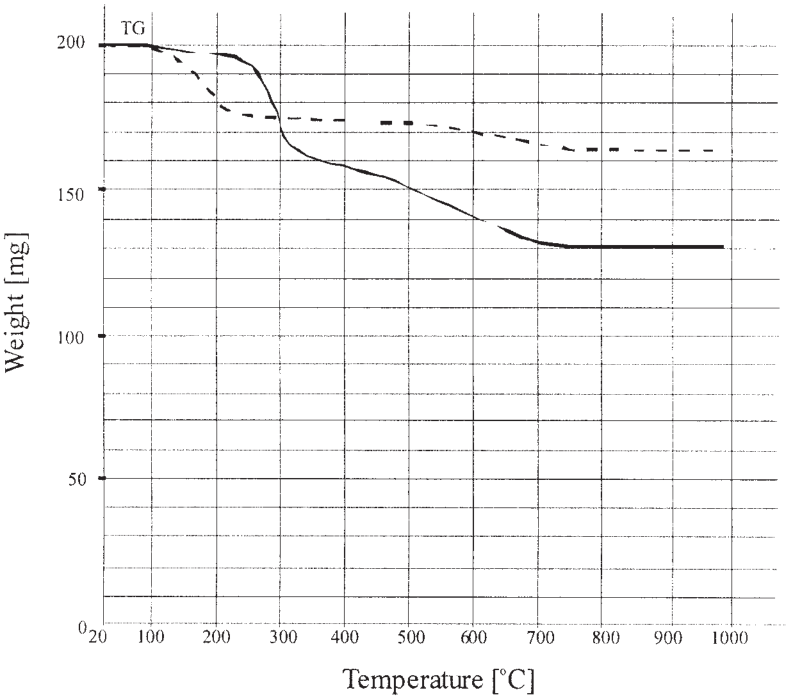

Figure 2 TG curves for unmodified bentonite "Wyoming " (dashed line) and for the same bentonite modified with QAS A1 formula (solid line).

thus neglected. The estimated amounts of QAS incorporated into bentonites ranged between 15 and 20.5 wt % and are shown in Table III for individual clay samples and ammonium salts.

The final evidence of QAS penetrating the interlamellar positions in the clays was provided by X-ray studies. In the unmodified Wyoming bentonite the interlamellar distances are about 1.1 nm, whereas after modification with QAS A1, the distances are about 1.9 nm (measured on a Siemens X-ray diffractometer; X-Ray source: Cu–K_α radiation at 40 kV) (cf. Fig. 3).

Processing of the modified smectites with standard commercial UP resin

The modified bentonites were processes into UP resins in two stages. First a concentrate was prepared containing 10 wt % of bentonite in UP (Polimal® 109–32RpyK) resin. The component was homogenized with a laboratory homogenizer equipped with a grinding set, at a grinding rate of 750 rpm. The compositions were then kept at 4°C until used. The concentrate was then diluted with more resin to prepare test samples of the composites.

TABLE III
Content of QAS in the Modified Bentonites

Bentonite[a]	Content of QAS in bentonites (%)			
	Type of QAS[b]			
	A1	A2	A3	A4
BSN	19.0	18.5	19.0	18.5
BS	20.0	19.0	20.5	19.5
BSEUZ	18.0	17.5	18.0	17.5
BSEUZU	18.0	17.5	18.5	17.5
BU	16.0	15.0	16.0	15.5
BW	18.0	17.5	18.0	17.5

[a] Bentonite symbols are listed in Table II.
[b] Symbols of QAS are listed in Table I.

Stability and reactivity of compositions

The so-called shelf life of UP–clay compositions was determined by measuring the time before the composition (kept at 50 or 70°C) spontaneously gelled.[49] Because the compositions in question were very stable we used the higher temperature (70°C) among those recommended by the standard procedure.[49]

The reactivity of compositions was measured according to another standard procedure[50] by recording the temperature versus time for the reacting sample after a predetermined amount of initiator was added.

Test samples

The compositions contained 2 or 4 wt % of modified smectites and were prepared by mixing and thorough homogenization of UP resin with the concentrate and 1–2 wt % of Luperox K-1 initiator. The compositions were placed in silicon rubber molds and cured at 20 ± 1°C for 2 h and postcured at 80°C for another 2 h. Clear transparent samples were obtained after the curing.

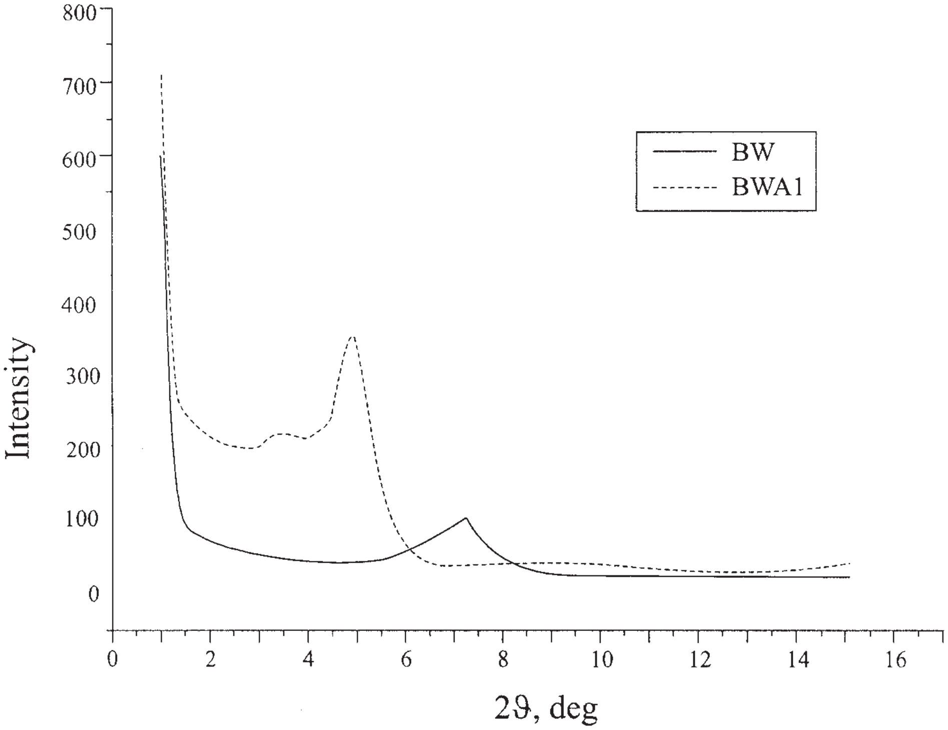

Figure 3 X-ray diffraction curves recorded for "Wyoming " bentonite unmodified and modified with quaternary ammonium salt A1.

The samples (oar or beam shape) were used to determine the basic mechanical properties of the composites. The basic measurements, tensile strength, Brinnel hardness, and unnotched Charpy impact strength, were made according to the respective standard procedures.[51–55]

The morphology of brittle fracture was observed in an electron scanning microscope (Novoscan 30, Zeiss, Oberkochen, Germany) after breaking the sample frozen in dry ice. Fractured surfaces were sputtered with gold.

RESULTS AND DISCUSSION

Stability and reactivity

The results of stability and reactivity measurements (at 70°C) are detailed in Tables IV and V, respectively. The addition of QAS in the amount of about 0.8 wt % introduced with modified bentonite slightly reduces the reactivity of UP, but significantly improves its stability. As already shown,[46–48] the stabilizing effect of the QAS depends on the type of salt and, to a lesser extent, the type of bentonite. The most effective in stabilizing the UP are salts A1 and A3, each having a benzyl substituent and a long aliphatic chain. The stability of UP-containing bentonites, modified with these QAS, increases the stability time by the factor of 16. At the same time the gelation time, a measure of the reactivity of a resin, increases by not more than 25%. The proposed mechanism of QAS effect on the shelf-life stability of UP was previously described[46] and is summarized here in Figure 4.

Mechanical properties

As follows from the results presented in Table VI, the tensile strength of the cured composites, both contain-

TABLE IV
Stability Time (Measured at 70°C) of the Compositions Containing Unsaturated Polyester Resin Polimal 109-32RPyK (UP) and 2 wt % of Unmodified and Modified Bentonite

	Type of QAS used for modification of bentonite[b]				
	Unmodified	A1	A2	A3	A4
Type of bentonite[a]	Stability time,[c] (h)				
BW	9	158	73	135	65
BU	8	149	70	128	60
BSN	9.5	163	75	140	66
BSEUZ	8	148	69	129	59
BS	9	159	73	131	65
BSEUZU	8.5	152	71	129	61
Unfilled UP	12	208	106	198	98

[a] Bentonite symbols are listed in Table II.
[b] Symbols of QAS are listed in Table I.
[c] The stability time was determined according to a Polish Standard.[51]

TABLE V
Gelation Time at 25°C of Unstaturated Polyester Resin Polimal 109-32RPyK (UP) Containing 2 wt % of Bentonite

	Type of QAS used for modification of bentonite[b]				
	Unmodified	A1	A2	A3	A4
Type of bentonite[a]	Gelation time,[c] (s)				
BW	204.6	251.3	340.2	264.2	356.8
BU	205.2	256.6	342.6	266.6	360.2
BSN	201.2	250.3	341.8	261.8	353.4
BSEUZ	203.3	252.0	343.4	262.0	354.6
BS	202.6	250.4	340.0	260.4	350.1
BSEUZU	204.0	252.7	341.6	262.9	356.2
Unfilled UP	133.3	151.6	180.4	160.2	189.3

[a] Bentonite symbols are listed in Table II.
[b] Symbols of QAS are listed in Table I.
[c] The gelation time was determined according to a Polish Standard[52] with 1 wt % of Luperox K-1 as initiator.

ing 2 and 4 wt % of unmodified bentonite, remained unchanged compared with the plain cured polyester resin. The elongation at break improved slightly (by 8 to 9.5%) over that of unfilled resin. The composites containing bentonites modified with QAS A1 through A4 were characterized by tensile strength improved by 16 to 40% and, at the same time, the elongation at break also increased by 16 to 34%. A significant improvement of the mechanical strength provided the higher amount of filler (4%). Then, the tensile strength was higher by 21 to 62% and elongation at break by 42 to 58% compared with those of unfilled resin. The best mechanical properties were observed in compositions containing bentonite "Special " modified with QAS A1 and A3 (cf. Table VI).

Impact strength

The results of impact strength measurements, made using a Charpy tester for unnotched samples, are

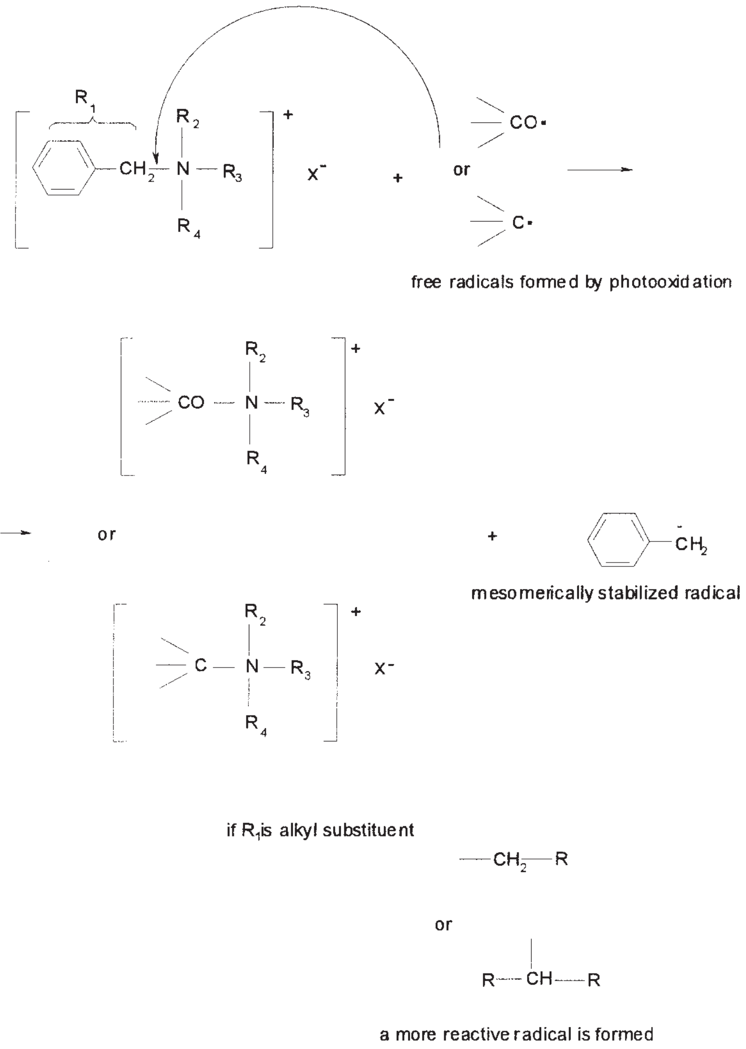

Figure 4 Proposed mechanism of quaternary ammonium salts on the shelf stability of unsaturated polyester resins.

TABLE VI
Mechanical Properties of Cured Unsaturated Polyester–Bentonite Composites with Bentonites Modified with Different Quatermary Ammonium Salts (QAS)[a]

Type of bentonite[b]	Property[c]	Types of QAS used for bentonite modification[d]									
		Unmodified		A1		A2		A3		A4	
		2%	4%	2%	4%	2%	4%	2%	4%	2%	4%
BSN	σ_r, MPa	20.5	21.0	24.8	30.1	24.0	27.4	25.0	30.3	24.6	28.0
	ε_r, %	4.1	4.2	4.6	5.4	4.5	5.4	4.7	5.1	4.6	5.2
BS	σ_r, MPa	20.8	21.3	27.2	31.1	25.5	30.3	27.9	32.3	26.0	30.7
	ε_r, %	4.2	4.4	5.0	6.2	4.7	6.1	5.1	6.0	4.7	6.2
BSEUZ	σ_r, MPa	20.0	20.3	25.1	30.7	23.2	26.5	25.3	30.4	23.4	25.1
	ε_r, %	4.1	4.2	4.8	5.5	4.5	4.9	4.9	5.6	4.5	4.6
BSEUZU	σ_r, MPa	20.6	20.9	25.0	30.4	23.5	25.4	25.7	30.1	24.0	26.1
	ε^r, %	4.1	4.2	4.4	5.4	4.4	4.9	4.6	5.3	4.4	4.9
BU	σ_r, MPa	20.0	20.2	23.6	27.4	23.0	24.1	24.0	27.1	23.7	26.3
	ε_r, %	4.0	4.1	4.4	4.9	4.4	4.8	4.5	4.8	4.5	5.0
BW	σ_r, MPa	20.1	20.5	24.9	30.1	24.0	29.5	25.0	26.4	24.4	27.1
	ε_r, %	4.1	4.2	4.6	5.4	4.5	5.1	4.7	5.0	4.5	5.0

[a] Samples prepared from plain unsaturated polyester resin have tensile strength 19.9 MPa and elongation at break 3.8%

[b] Bentonite symbols are listed in Table II.

[c] σ_r, ultimate tensile strength; ε_r, elongation at break.

[d] Symbols of QAS are listed in Table I.

listed in Table VII. For compositions containing 2 and 4% of unmodified bentonites, the increase of impact strength was 7–14 and 23–28%, respectively, compared to those of unfilled UP resin. A significant increase of the impact strength was observed for composites containing 2 and 4% of modified bentonites. The impact strength of compositions containing 4% of bentonite "Special " modified with QAS A3 was twice that of the plain UP resin.

Brinnel hardness

Addition of unmodified bentonite to UP, in the amount up to 4 wt %, only slightly improved (by 6–8%) the Brinnel hardness. Again, the use of bentonites modified with QAS substantially improved this important property (cf. Table VIII). The increase depends on the type of both bentonite and modifier. The increase reached 24–38 and 30–70% for the composites containing 2 and 4 wt % of modified bentonite, respectively. The best results were obtained for the composition containing bentonite "Special," modified with QAS A3.

To summarize the results on mechanical properties one can state that these depend on the ion-exchange capacity of bentonites and the type of QAS used for modification. The relationship between the ion-exchange capacity of smectic clays and the mechanical properties of composites derived from them seems particularly striking. The same applies to the rheological properties of the compositions before the cure. The latter will be described in greater detail in a forthcoming report.

TABLE VII
Charpy Impact Strength of Composites Based on Unsaturated Polyester Resin Containing Bentonite Modified with QAS[a]

Type of bentonite[b]	Charpy impact strength (kJ/m^2)									
	Type of QAS used for modification of bentonite[c]									
	Unmodified		A1		A2		A3		A4	
	2%	4%	2%	4%	2%	4%	2%	4%	2%	4%
BSN	1.5	1.8	1.9	2.3	1.8	2.3	2.0	2.4	1.9	2.2
BS	1.6	1.8	2.0	2.4	2.0	2.2	2.4	2.8	2.1	2.2
BSEUZ	1.6	1.8	2.0	2.5	1.8	2.3	2.2	2.7	1.9	2.3
BSEUZU	1.5	1.7	1.9	2.3	1.9	2.2	1.9	2.4	1.9	2.3
BU	1.5	1.7	1.9	2.2	1.8	2.1	1.9	2.2	1.8	2.1
BW	1.6	1.8	2.0	2.4	1.9	2.3	2.1	2.5	2.0	2.3

[a] Samples prepared from plain unsaturated polyester resin have impact strength of 1.4 kJ/m^2.

[b] Bentonite symbols are listed in Table II.

[c] Symbols of QAS are listed in Table I.

TABLE VIII
Brinell hardness of composites based on unsaturated polyester resin containing bentonites modified with QAS[a]

Type of bentonite[b]	Brinell hardness (MPa)									
	Type of QAS used for modification of bentonite[c]									
	Unmodified		A1		A2		A3		A4	
	2%	4%	2%	4%	2%	4%	2%	4%	2%	4%
BSN	40.1	41.8	48.2	55.8	45.7	49.4	48.2	53.2	48.0	52.4
BS	40.4	42.9	51.3	61.6	49.2	55.0	50.0	66.6	49.0	54.4
BSEUZ	40.3	42.6	49.9	56.6	45.1	48.8	49.5	53.6	48.9	50.4
BSEUZU	39.9	41.4	48.4	54.8	48.2	53.2	48.9	54.4	47.7	50.4
BU	39.2	40.8	47.7	51.3	45.5	49.4	47.3	50.0	47.7	51.0
BW	40.0	41.6	48.6	55.6	48.3	53.9	48.4	53.0	47.7	51.0

[a] Samples prepared from plain unsaturated polyester resin have Brinnel hardness of 38.3 MPa.
[b] Bentonite symbols are listed in Table II.
[c] Symbols of QAS are listed in Table I.

Clearly, the amount of modifier incorporated into the clay (Table III) improves compatibility of the aluminosilicate with UP resin. With respect to the chemical structure of QAS modifiers, apparently the presence of benzyl and large aliphatic substituents results in a widening of the distance between the layers of smectites, thus facilitating penetration of the polyester chains.

When the amount of clays is at 4 wt % of the composites, the mechanical properties of the cured composites show a greater degree of improvement than when the amount of clays is at 2%, which seems optimal with respect to the rheological behavior of the compositions.

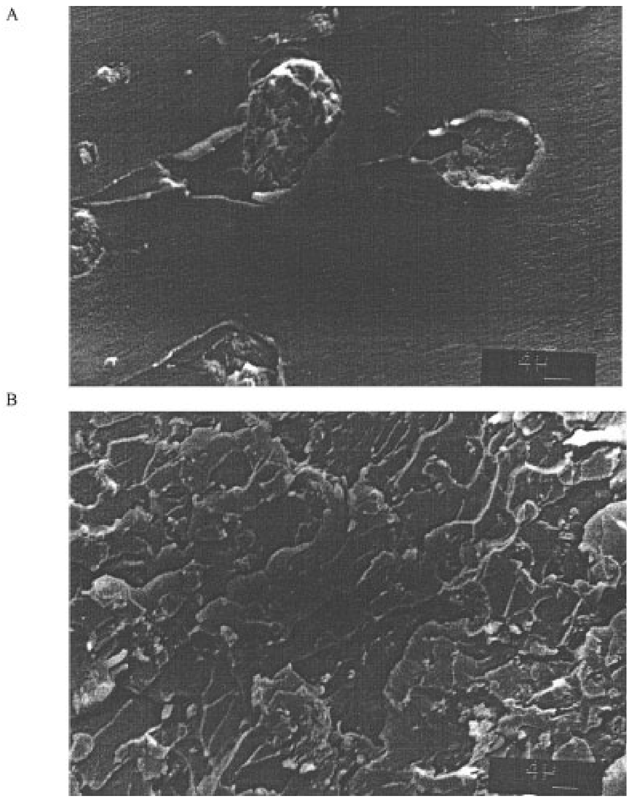

Figure 5 Morphology of UP filled with unmodified (A) and UP filled with QAS A1 modified (B) bentonite "Special."

Morphology of composites

Scanning electron micrographs of brittle fractures of cured composites revealed significant differences in the morphology of those containing unmodified and modified bentonites (Fig. 5). In the fracture of the composite prepared from unmodified clays one can clearly see the filler particles (size 2–10 μm) unevenly distributed in the UP matrix. The same bentonite modified with QAS has a much different morphology. Shattered pieces of plates are seen in the fracture and it is difficult to distinguish the aluminosilicate material from the polyester matrix, which once again confirms the substantially improved compatibility of the composite components when bentonite has been modified.

CONCLUSIONS

All bentonites used in this work contained large proportions of montmorillonite (as claimed by the supplier) and a considerable ion-exchange capacity.

The presence of a quaternary ammonium salt, introduced directly into UP or the modified bentonites, significantly improved the stability of preaccelerated resins, barely affecting the reactivity of resins. The stabilizing effect is related to the chemical structure of QAS. The presence of benzyl and large aliphatic substituents is advantageous in the structure of QAS.

By using bentonites modified with QAS as fillers of UP resins, an obvious improvement of the mechanical properties of cured composites can be obtained, including tensile strength, elongation at break, impact strength, and Brinnel hardness.

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