

Surface Characterization of a Titanate Coupling Agents Modified Sepiolite

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Synopsis

The surface treatment of a sepiolite with two different titanate coupling agents has been studied. The results obtained from several chemical and physical analytical methods used for the organophylized surface characterization have shown a monolayer reaction has taken place. An attempt to relate the degree of organophylization to the specific surface decrease of filler has been made.

INTRODUCTION

It has previously been proved that sepiolite is a suitable filler for thermoset¹ and thermoplastic² polymers and, in order to improve the mechanical strength and rheological properties of the composites, chemical coupling agents, such as organic titanates³ and other chemical products⁴ have been used with the filler.

Although titanate coupling agents are widely used in the composite field⁵ and their performances from the rheological behavior and mechanical properties⁶⁻¹⁰ points of view have been previously studied, the exact mechanism of bonding is not yet well known.

Earlier studies have shown that when a high proportion of tetra isopropyl titanate is used,¹¹ the titanate hydrolysis and polymerization on the sepiolite surface take place that probably causes a titanium dioxide layer on the mineral surface which does not improve the mechanical properties of the composites.

The influence of temperature, time, and the titanate concentration on the sepiolite organophylization reaction was studied through a statistical procedure.¹² It was shown that the organophylization reaction of silanol groups with titanate coupling agents is strongly dependent on the titanate concentration and hardly influenced by temperature and time.

In this study, we have modified a sepiolite surface through chemical reaction of silanol surface groups with two different titanate coupling agents for the purpose of getting a monolayer organic surface on the mineral filler. In order to compare the results, different chemical and physical methods are used for the characterization of the surface, and attempts are made to relate the specific surface of the filler with the amount of reacted titanate.

EXPERIMENTAL

Materials

Sepiolite, hydrated magnesium silicate, delivered by Tolsa (Spain), was used. The filler was treated with two titanate coupling agents: isopropyl

triisostearoyl titanate (KR-TTS) and isopropyl methacryl diisostearoyl titanate (KR-6) from Kenrich Petrochemicals, Inc.

Organophylization Method

The method of sepiolite organophylization has been described elsewhere.³ The optimum amount of titanate coupling agent required was determined by plotting the decrease in viscosity of a hydrocarbon oil-sepiolite mixture with the increasing concentration of titanate as described by Kenrich Petrochemicals Inc. Briefly, once a ratio is selected of inorganic to organic which gives a measurable Brookfield viscosity, in our case 15 parts of sepiolite by 100 parts of mineral oil, the method consists of filling several jars with the normal oil. In the first jar no titanate is added, and in the others 0.1, 0.5, 1, 2, 4, 5, etc., parts of titanate p.h. filler are added. Into each jar the corresponding sepiolite is let down into the mineral oil (with titanate already blended in) and Brookfield viscosity measures are taken at a constant temperature (in our case 25°C.). Then the viscosity is plotted vs. titanate pph filler.

Moreover, we have also used the stoichimetric amount of sepiolite and titanate, having in mind that we have considered titanates as having only one reactive group, just the isopropyl group.

The surface hydroxyl groups of sepiolite were determined by means of the Armistead-Hockey method,¹³ giving a hydroxyl groups content of 2.624×10^{-4} mol OH/g sepiolite.

The reactions were carried out at room temperature (25°C) for a period of time of 15 min. After filtered, the modified sepiolites were repeatedly extracted with methylen chloryde and dried out at 60°C under vacuum until the solvent was completely eliminated.

Sepiolite Characterization

Untreated sepiolite, as well as the organophylized sepiolites, were characterized by means of different chemical and physical methods. The carbon and hydrogen content was measured in a Perkin-Elmer 240 CHNO. The titanium content was determined by colorimetry, measuring the intensity of the peak at a wave length of 410 nm in a UV spectrophotometer (Perkin-Elmer 554) of a water solution coming from the acid treatment of a sample of sepiolite with fluorhydric and sulphuric conc. acids. Once the pH was adjusted, tyron as an indicator and a few mg of sodium tiosulphite (to eliminate the possible interferences of iron) were added.¹⁴⁻¹⁶

The specific surface was determined by nitrogen adsorption at the temperature of liquid nitrogen (BET) in a Micromeritics Accusorb 2100 D apparatus.

A differential scanning calorimeter (DSC Mettler 2000 system), thermogravimetric analysis, and atomic absorption are other techniques which have been used.

RESULTS AND DISCUSSION

Reaction of Sepiolite with Titanates

In order to arrive at the optimum amount of titanate coupling agent for sepiolite, the Kenrich method of viscosity reduction of a hydrocarbon oil/

sepiolite mixture was employed. The results are graphically represented in Figure 1.

In general, for fine fillers such as silica, carbon black, etc., the manufacturers recommend from 0.5% to 1.5% of titanate. In our case, we have added up to 12–14% of titanate to the dispersion, and two noticeable decreases in viscosity can be observed. We have chosen as an optimum percentage the amount of titanate corresponding to the second fall of viscosity in the curve. Therefore, the optimum amounts of titanate that have been chosen in Figure 1 were 2.75 and 3 pph filler for the KR-6 and KR-TTS, respectively.

On the other hand, keeping in mind the equimolecular reaction between the titanate coupling agents and the sepiolite, the concentrations of titanate that have been used were 19.9 and 25.1 pph filler for the KR-6 and KR-TTS, respectively.

Therefore, and as a function of both criteria, the sepiolite was organophilized using the titanate concentrations that are shown in Table I.

Characterization of Modified Sepiolites

The surface modified sepiolites were characterized by means of the titanium content through colorimetry, and atomic absorption and thermogravimetric analysis, carbon, and hydrogen analysis, differential scanning calorimetry, and specific surface measures.

The amount of organic matter for each different sample was calculated from the thermogravimetric curves (Fig. 2) using the following method: The total weight loss in the range of 50–750°C was decreased in the percentage corresponding to the 50–170°C and the loss percentage corresponding to 170–750°C range of untreated sepiolite is subtracted to the resulting amount. The results obtained for all the samples used in this study are shown in Table II.

As expected, the percentage of weight losses in the 50–170°C range is much higher in the untreated sepiolite.

Actually, in this temperature range, the weight loss of the samples corresponds principally to the absorbed water, and, in the case of the organo-

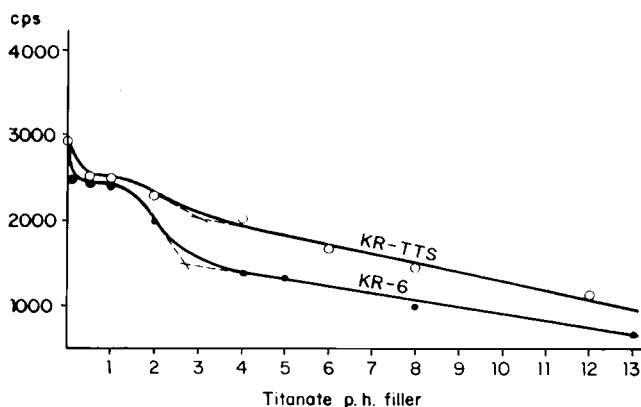


Fig. 1. Effect of titanates on viscosity of the composite.

TABLE I
Amount of Titanate To Be Added for the Organophylization

Sample	Sepiolite	TTS	KR-6
A	100	3	—
B	100	25.1	—
C	100	—	2.75
D	100	—	19.90

phylized materials, the absorption of water is much lower due to their hydrophobic character.

In the 170–750°C temperature range, sepiolite loses the zeolitic and crystallization waters as well as the possible organic matter; therefore, if we subtract this percentage of weight loss from the values corresponding to the different samples at this temperature range, we will get the weight loss due to the organic matter of the samples.

Values of the percentages of organic matter of the samples as well as carbon, hydrogen, and titanate contents are compiled in Table III.

Titanate content has been calculated from thermogravimetric results, having in mind the combustion reaction taking place during the analysis, as well as from UV and atomic absorption measures. The titanate content values compiled in Table III are the average values obtained through the different analytical methods used.

On the other hand, values of the % organic matter/% titanium content and % titanium/% carbon ratios of the samples as well as the specific surface values and number of free hydroxyl groups/nm² of the modified sepiolites are shown in Table IV.

If we compare the % org. mat./% Ti and % Ti/% C ratios of the samples with the corresponding theoretical values of the KR-6 and KR-TTS titanates, it can be concluded that the organophylization has taken place in a monolayer way.

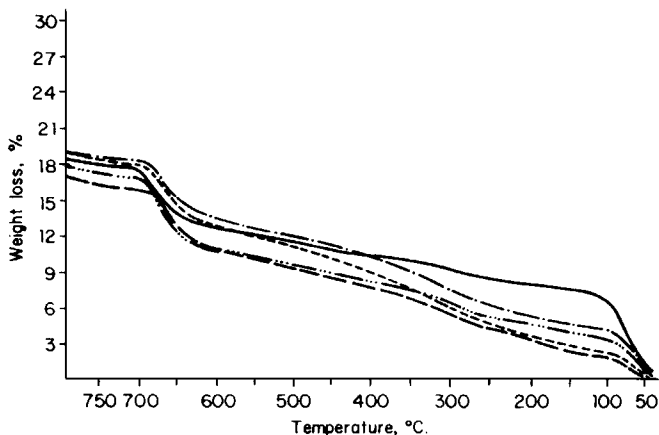


Fig. 2. Thermogravimetric curves of untreated and modified sepiolites: (—) SEP; (— —) A; (— · —) B; (— · · —) C; (· · ·) D.

TABLE II
Weight Loss Percentages at Different Temperature Intervals^a

Temp (°)	Sepiolite	A	B	C	D
50-170	6.42	2.70	3.75	3.99	2.67
170-350	2.34	4.03	4.08	3.33	4.58
350-750	8.11	9.59	9.55	9.85	10.84

^a Heating rate: 10°C/min.

In the case of the sample with the highest concentration of KR-6 titanate coupling agent (sample D), the titanium content seems to be higher than the theoretical value.

The differential scanning calorimetry curves are shown in Figure 3. The differences between the organophylized samples and the untreated sepiolite make the presence of organic matter clear in the first ones. New and more or less wide exothermic peaks appear at 300°C depending on the sample composition. These peaks are due to the organic matter that is present in the organophylized sepiolites, and this is an indication that a chemical reaction between the sepiolite and titanate coupling agents has taken place. This is also made clear if we compare the specific surface values of the samples which are compiled in Table IV.

Organophylation Degree and Specific Surface Interrelations

The change in the interactions between an adsorbate and silica surface with increasing coupling agent coverage have been demonstrated by the variation in the slope of the adsorption isotherms of benzene vapour on Aerosil at various coverages of coupling agent (Trimethyl silyl) groups.¹⁷

The slope of the adsorption isotherms which is an indication of the specific surface value declines as coverage of coupling agent groups increases.

In our case, this effect is very clear and in order to obtain a much better definition of the curves in the titanate pph sepiolite vs. specific surface plots, two more modified sepiolites have been prepared with both titanate coupling agents using 1.5 and 15 parts of KR-TTS and 1.4 and 14 parts of KR-6.

These sepiolites were characterized by means of the same techniques previously described, and the results are shown in Table V.

In Figure 4 we can see the plot of the content of free OH groups/nm² of the samples vs. their specific surfaces. As can be observed, the specific

TABLE III
Chemical Analysis of the Modified Samples in Relation to the Untreated Sepiolite

Sample	% Org. mat.	% C	% H	Mol % Ti × 10 ⁴
A	3.17	1.91	0.52	32
B	3.18	3.46	0.95	40
C	2.71	1.75	0.84	37
D	4.97	3.13	0.91	143

TABLE IV

Sample	% Org. mat./% Ti ^a	% Ti/% C ^b	Spec. surf. BET (m ² /g)	OH/ nm ²
Sepiolite	—	—	205	0.77
A	20.0	0.083	102	0.67
B	16.6	0.055	88	0.65
C	15.4	0.101	115	0.65
D	7.2	0.220	81	0.35

^a Theoretical values: KR-TTS = 18 and KR-6 = 13.9.

^b Theoretical values: KR-TTS = 0.74 and KR-6 = 0.1.

surface tends towards a constant value that in the case of the KR-6-modified sepiolites is about 80 m²/g. The specific surface of the KR-TTS derivatives tends to a similar value, but, in this case, it is more difficult to get a higher degree of modification, probably due to the hindrance effects caused by the bigger molecular size of this titanate.

The same conclusion can be deduced from the plot of titanate content on modified samples (mol) vs. titanate initially added in the organophylization reaction (mol) as can be seen in Figure 5.

Finally, it is very interesting to see how the specific surface of the modified samples changes with the titanate initially added to the sepiolite, as is plotted in Figure 6. From this plot we could assume that the optimal amounts of titanate to be used for the organophylization of the sepiolite are about 3 pph sepiolite. That is to say, the same amount deduced from viscosity measures as can be seen in Figure 1.

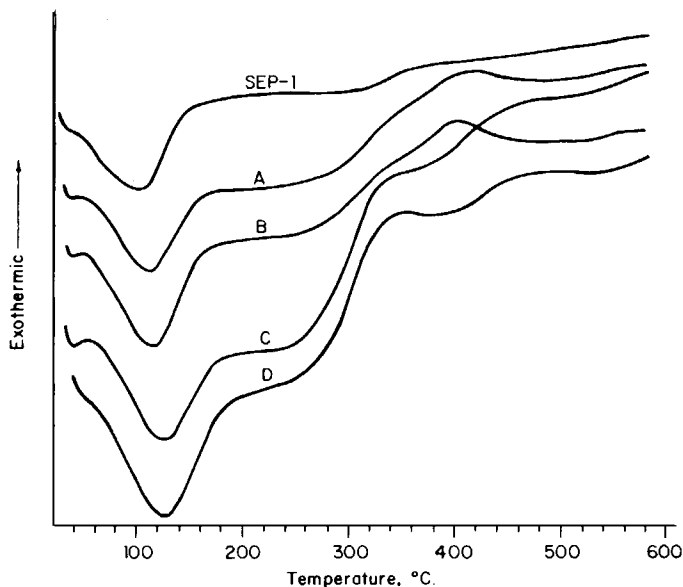


Fig. 3. DSC curves of the sepiolites.

TABLE V

Sample	KR-TTS ^a	KR-6 ^a	% Org. mat.	Mol % Ti × 10 ⁴	Spec. surf. BET (m ² /g)	OH/ nm ²
E	1.5	—	0.33	10	158	0.74
F	15	—	2.01	35	125	0.67
G	—	1.4	0.35	13	172	0.73
H	—	14	2.91	99	115	0.48

^a Parts of titanate p.h. sepiolite.

CONCLUSIONS

From this study it can be concluded that sepiolite organophylization has taken place in a monolayer way and the optimal amount of titanate coupling agent to be used corresponds to the second fall in the viscosity vs. titanate content plots.

On the other hand, the titanate content of the organophylized samples is strongly dependent on the titanate amount initially added to the sepiolite.

Hindrance effects play an important role in the organophylization reaction due to the big molecular size of the titanates, and, as a result, the titanate content of the modified sepiolites tend to a constant value. In a similar way, the specific surface is decreasing until an asymptotic value is reached.

Obviously, these effects may have a great influence on the mechanical and rheological properties of polymer composites based on modified sepiolites. This is the goal of our present studies and will be the subject of future communications.

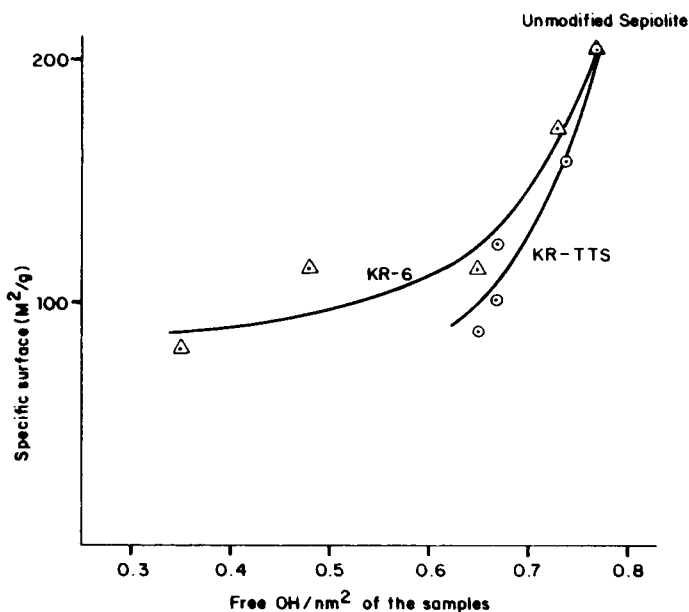


Fig. 4. Specific surface versus degree of modification.

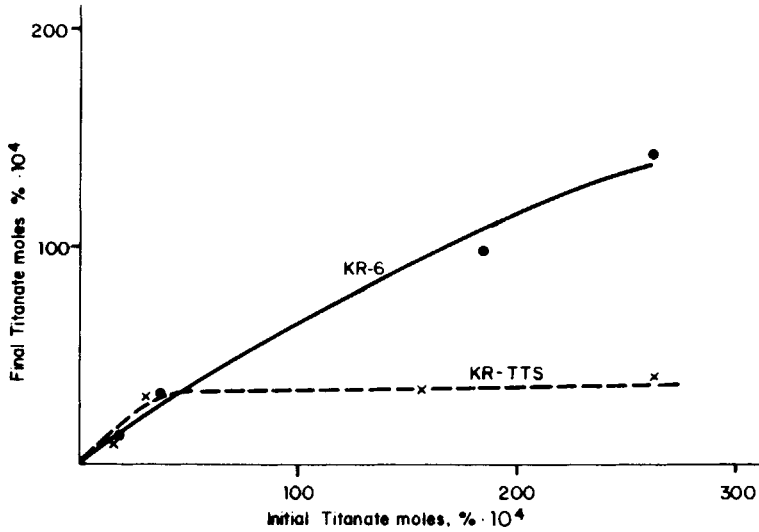


Fig. 5. Degree of modification as a function of initial titanate concentration at 25°C and 15 min. of reaction.

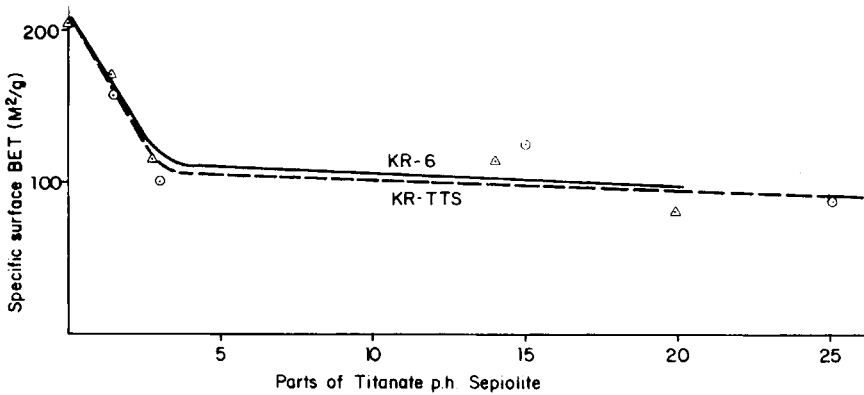


Fig. 6. Specific surface variation of the sepiolites as a function of initial parts of titanate p.h. sepiolite.

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