BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (10), 2829—2830 (1977)

Graft Polymerization on Pulverized Solid Surface. I. Grafting Polystyrene on a Clay Surface Treated with Silane Coupling Agents

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(Received January 13, 1977)

Synopsis. Styrene was graft-polymerized on kaolin clay treated with silane coupling agents *e.g.* (γ-methacryloyloxypropyl)trimethoxysilane. Although the silane-styrene copolymer was soluble in benzene, the polystyrene-grafted clay swelled in the same medium. A clay-crosslinked, three-dimensional structure is suggested and conditions for gelation are also discussed.

In order to elucidate the interfacial interactions between organic matrices and inorganic fillers in composite materials, studies of the graft polymerization of organic monomers onto inorganic pulverized solid surfaces are of importance.

Many papers appear in the literature dealing with topochemical graft polymerization. But only a single paper has been published on the clay-crosslinked structure of graft polymerization products. Dekking[1] has prepared the adduct of bentonite and 2,2′-azobisisobutyramidine hydrochloride, which initiated the polymerization of vinyl monomers and gave gel-like compositions.

Although silane coupling agents are often used in many composite materials, neither graft polymerization on kaolin clay treated with silane agents nor the characteristic structure of the products has been reported. In the present paper, the crosslinking role of the clay in the polystyrene-silanized clay composition is described.

Experimental

Materials. X-Ray analysis showed that Kaolinite was the principal mineral in the kaolin clay used. (Found: SiO_2, 44.84; Al_2O_3, 39.59; Fe_2O_3, 0.36; TiO_2, 1.12; CaO, 0.14; MgO, 0.06; Na_2O, 0.07; K_2O, 0.20; Ig. loss, 13.99%. Calcd for kaolin; SiO_2, 46.54; Al_2O_3, 39.49; H_2O, 13.96%). The percentage of water adsorbed on the clay under atmospheric conditions was determined to be 0.56% by the Fischer method and, after the desorption treatment procedure described it was found to be 0.02%. The specific surface area was found to be 6.89 m^2/g by the BET method.

(γ-Methacryloyloxypropyl)trimethoxysilane (**1**) was obtained commercially and used without further purification. Benzene was purified in the usual way and styrene was freshly distilled prior to use. Other organic solvents were of reagent grade. The 2,2′-azobisisobutyronitrile (AIBN) used was also of reagent grade.

Procedure. In a 200-ml two-necked round-bottomed flask equipped with a magnetic stirring bar, a condenser and a three way stopcock was placed 2.0 g of clay. The flask was heated to 70 °C under *ca.* 1 mmHg (1 mmHg$\approx$133 Pa) for 1 h, and then allowed to cool down to room temperature at which time nitrogen was introduced into the vessel. After 5.0 ml of benzene and 0.2 ml of **1** were added to the clay, the mixture was stirred at room temperature for 30 min. Moreover, 5.0 ml of styrene and 40 mg of AIBN were added to the mixture, which was heated at 80 °C with stirring in a nitrogen atmosphere for 2 to 4 h. The reaction mixture was poured into hexane and the precipitate was filtered, dried *in vacuo*, and weighed. Non-graft polymer was extracted from the precipitate with benzene for 12 h. Then, in order to determine the graft polystyrene, the residual solid was submitted to pyrolysis gas chromatography whose decomposing temperature was *ca.* 570 °C.

Results and Discussion

As shown by Solomon and Rosser,[2] and Kawasaki *et al.*,[3] kaolin clay can initiate the polymerization of styrene (conv. 93%) by desorption of water from the clay surface, although no graft polymer is observed on the clay surface. The polymerization is inhibited by the addition of either pyridine or **1**. This is probably due to poisoning of the acidic sites on the clay surface.

Table 1. Styrene graft polymerization on clay

Experiment	I[a]	II	III
Clay (g)	2.0	2.0	2.0
Benzene (ml)	5.0	5.0	5.0
1 (ml)	0.2	0.2	0.2
Styrene (ml)	2.0	2.0	2.0
AIBN (mg)	40	41	40
React. temp (°C)	80	80	80
React. time (h)	2	2	4
St. conv. (%)	35	71	79
Free poly-st/free poly-st and graft poly-st wt ratio	0.85	0.94	0.88
Graft efficiency	0.046	0.041	0.084

a) 0.2 ml of pyridine was added.

The data for styrene graft polymerization are given in Table 1. The graft efficiency is indicated by the weight ratio of the graft polystyrene to the polymer-clay composition. These values varied from 0.041 to 0.084. It is noteworthy that the polystyrene-clay products swelled and formed gels in benzene as do vulcanized rubbers. The conditions for gelation were further explored as explained below.

The amount of **1** adsorbed on the clay was determined. Two kinds of procedures were employed for the treatment of **1** on the clay. (A) One procedure was to add **1** in a solution of methanol–water (9: 1) to the air-dried clay. After evaporation, benzene was added to dissolve the non-adsorbed **1**, which was determined by ir spectroscopy (1716 cm^{-1}; ester band of **1**). The amount of **1** adsorbed was calculated from these data. (B) In the other method, the addition of **1** in a benzene solution

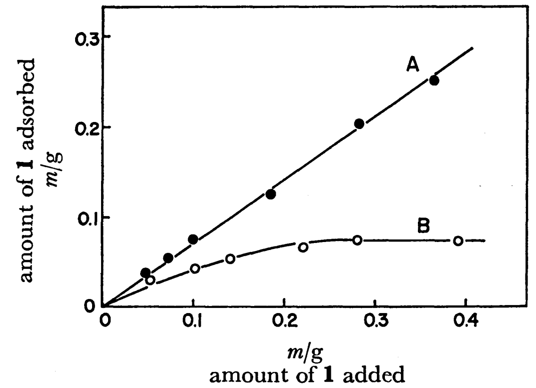

Fig. 1. Amounts of **1** adsorbed on the clay (2.0 g). A) ●: As methanol–water solution (5 ml). B) ○: As benzene solution (5 ml). IR ester band of **1** (1716 cm^{-1}) was used for determination.

was employed. The adsorbed **1** was determined by a similar method. These results are summarized in Fig. 1.

Figure 1 shows that the adsorption of **1** was effective in the presence of enough water to hydrolyze the methoxy moiety of **1** and that the adsorption of **1** increased proportionally to the amount of **1** added in method A. However, in the case of method B, the amount of **1** adsorbed is shown to have a plateau at *ca.* 0.07 g. The specific surface area of the clay is 6.89 m^2/g and the minimum specific surface area of **1** is 314 m^2/g.[4] From these observations, it is considered that **1** forms a multimolecular layer on the clay surface, although it was added as an anhydrous benzene solution.

Subsequently, polymerization was carried out in the presence of the clay which had been treated with various amount of **1** by method A. The results are listed in Table 2. The reproducibility of the graft efficiency and of the amount of *p*-xylene absorbed was rather poor probably due to heterogenity.

As seen in Table 2, when nearly the same amount of **1** was added to the clay, bulk polymerization was found to be preferable to the solution polymerization for the gel compositions. It was also found that gelation of the products brought a considerable increase in the graft efficiency. From the results in Fig. 1, it may be said that the amount of **1** on the clay surface is one of the gelation conditions.

TABLE 2. EFFECTS OF THE AMOUNT OF **1** ON THE GELATION, CROSSLINK DENSITY, AND GRAFT EFFICIENCY OF THE PRODUCTS

1 (ml)	State of products[a]	Absorbed *p*-xylene[b]	Graft efficiency
0.4	g	0.40	0.247
0.3	g	1.17	0.086
0.2	p	1.10	0.041
0.1	n	—	0.002
0.05	n	—	0.002
0.2[c]	g	0.65	0.250
0.1[c]	g	1.03	0.251
0.05[c]	p	2.98	0.236

a) g: gel, p: partially gel, n: non-gel. b) The amount of *p*-xylene absorbed (g-*p*-xylene/g-composition) was determined by glpc.[5] c) Bulk polymerization was carried out in a manner similar to that for solution one, except for benzene.

The crosslink density of the composition was estimated from the amount of the solvent, such as *p*-xylene, absorbed. Table 2 also shows that the density increases for an increase in the amount of **1** added to the clay.[6]

Then, the polystyrene-clay compositions were compared with the styrene-**1** copolymer (**2**) of the same feed composition. The ir spectra of the two polymers were essentially identical in the 3100—1400 cm^{-1} region. However, the decomposition patterns for differential thermal analysis of the two in air are evidently different (250—450 °C). Therefore, a difference in structure of the organic polymer is suggested. Further work on these results is now in progress.

In contrast to the solubility of copolymer **2** in benzene, the polymer-clay composition swelled by the same solvent. These facts are consistent with the clay-bridged, three-dimensional structure illustrated in Fig. 2.

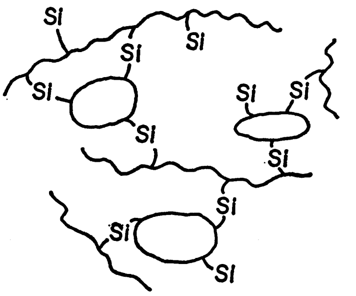

Fig. 2. Model of the polystyrene-clay composition. ⬭: Clay, ∼∼∼: styrene-**1** copolymer.

It was hoped to obtain more information about the crosslinking role of the clay. However, attempts to prepare the polymer-clay gel composition by the reaction of copolymer **2** with the clay were not successful. This appears to be due to the decreased accessibility of the silanols or alkoxysilane groups in the copolymer to the clay surface.

References

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