

Polymerization and Characterization of Acrylonitrile with γ -Methacryloxypropyltrimethoxy-Silane Grafted Bentonite Clay

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ABSTRACT: Novel natural clay–polymer hybrid materials are prepared from natural bentonite that was modified with silane-coupling agent, γ -methacryloxypropyltrimethoxysilane (A-174), and acrylonitrile. By changing the molar ratio of acrylonitrile in the initial monomer feed, several clay–hybrid materials were prepared. The structure and thermal stability of hybrid materials were investigated by various methods. The A-174-modified bentonite was dispersed in a solution of acrylonitrile in toluene. In this system, radical polymerization in the presence of AIBN was carried out. Product formed at the particle surface was either physically bound by entanglement or chemically bound by covalent bonding to the silane. In this way, core–shell morphology was obtained with an inorganic core and a polymer shell. The results showed that bonding at the surface of bentonite took place by hydrolytic cleavage of methoxy groups of A-174 with hydroxy groups of bentonite. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 164–171, 2002; DOI 10.1002/app.10289

Key words: hybrid materials; clay; bentonite; polyacrylonitrile

INTRODUCTION

The ability of layered silicates to undergo intercalation by a wide variety of monomers or polymers was extensively employed to obtain composite materials that are important in industry.^{1–10} Recently, the development of a new class of composite materials with characteristic features has gained interest, owing to the new techniques available for carrying out structural and property characterization. The improved mechanical, ther-

mal, optical, and other properties hold promise for novel technological applications.^{11–15} These materials can exhibit unusual and astonishing properties compared with the natural materials with unique structures.^{16–18} The interaction of layered silicates with polymers leads to two classes of hybrid materials. In the first class, denoted as intercalated hybrids, one or more polymer chains are inserted between host layers. In the second, silicate layers are exfoliated and dispersed in polymer matrix.^{19–25}

The controlled modification and patterning of clay will continue to be the basis of the advancement of chemical technologies in the future. Such engineered clay minerals are crucial elements for the development of clay polymer hybrid materials.

In the context of potential uses of clays, it was demonstrated that variation of polymer can affect

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the properties and end-use of the resulting hybrid materials. Furthermore, it is known that the nature of the clay also plays a significant role in controlling the properties of the product. One approach to varying the nature of the matrix is to use bentonite because of their high-cation exchange capacities, surfaces areas, surface reactivities, and adsorptive properties.²⁶

Synthesis of clay minerals in the presence of organic, organometallic, and polymeric intercalant were studied.^{26–40}

This work concerns the preparation of novel composite materials from pillared clays, which were functionalized by treatment with surface-coupling agent, γ -methacryloxypropyltrimethoxysilane, with an aim to obtain clay-hybrid materials with polymerizable end groups. The grafting of γ -methacryloxypropyltriethoxysilane on bentonite was optimized under various conditions. Several parameters, such as solvents, pH, and γ -methacryloxypropyltrimethoxysilane concentration, were studied to determine grafting efficiency of A-174 on bentonite.

Our efforts were focused on the preparation of poly(γ -methacryloxypropyltrimethoxysilane-co-acrylonitrile)-bentonite sol-gel materials and structural elucidation by means of X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and differential thermal analysis (DTA).

In this article, we examined the preparation and physicochemical properties of bentonite hybrid materials obtained from bentonite grafted with the appropriate silane coupling agent and acrylonitrile. In addition, the change in structure was revealed and the effect of polyacrylonitrile content in hybrid materials are investigated.

EXPERIMENTAL

Chemical Analysis and Characterization

Preparation of Methanesulfonic Acid-Treated Bentonite (BP-1)

Natural bentonite clay from the Reşadiye region of Tokat, Turkey was used in this work (325-mesh sieve). The clay was obtained by the methods of dispersion and sedimentation and various chemical treatments were applied to natural clay. The clay (20 g) was treated with 100 mL 10% methanesulfonic acid ($\text{CH}_3\text{SO}_3\text{H}$; $d = 1.48 \text{ g mL}^{-1}$, Sigma) solution for 4 h at 353 K with slow agitation. It was further treated with 10% $\text{CH}_3\text{SO}_3\text{H}$ and 0.5 mol dm^{-3} potassium permanganate solu-

tion for 5 h at 353 K. Finally, it was washed with water until neutral pH was obtained. The material was dried in an oven at 353 K for 24 h. Composition and specific surface area of the treated clay was found as SiO_2 , 88%; Al_2O_3 , 5.2%; Fe_2O_3 , 2.7%; CaO , 0.26%; MgO , 0.17%; Na_2O , 0.1%; K_2O , 0.48%; MnO_2 , 0.08%. CEC was 76.4 mequiv/100 g. S_{BET} was $112.3 \text{ m}^2 \text{ g}^{-1}$. Composition and surface area of the natural bentonite was determined as SiO_2 , 63.2%; Al_2O_3 , 18.2%; Fe_2O_3 , 11.7%; CaO , 0.56%; MgO , 0.55%; Na_2O , 0.17%; K_2O , 4.8%.

Grafting of A-174 onto the BP-1 Particles

Grafting was carried out under nitrogen atmosphere by using Et_3N as the catalyst with different amounts of A-174, toluene, and BP-1 (sieved between 70 and 200 mesh). After dispersing BP-1 (1 g) in 50 mL toluene, 2–10 mL A-174 and 0.15 mL Et_3N were added to the solution. The resulting solutions were refluxed for 4–18 h. The modified particles were then poured off and extracted with dichloromethane in a Soxhlet apparatus for 12 h. Finally, the particles were dried under vacuum at 120°C for 24 h. The grafting efficiency of A-174 was determined as a function of A-174 concentration.

Preparation of TAG-64 to TAG-67 Hybrid Materials

Grafting of A-174 on BP-1 was achieved by dispersing the A-174 modified BP-1/A-174 particles (1 g) in 50 mL toluene. Then, an appropriate amount of acrylonitrile was added to the mixture under nitrogen atmosphere. The sample was heated to 50°C , and a radical initiator, AIBN (in 10 mL toluene), was added to the mixture. Finally, the mixture was heated to 85°C for 18 h and the extent of reaction was monitored by FTIR. The crude product was poured off and extracted with dichloromethane in a Soxhlet apparatus to remove unreacted monomers. Obtained hybrid materials were dried at 120°C under vacuum. The chemical composition of the hybrid materials are given in Table I.

Characterization

X-ray powder diffraction patterns of the products were recorded on a Rigaku RAD-B diffractometer by using monochromatic $\text{Cu-K}\alpha$ radiation. DTA result was determined by a Shimadzu System 50 thermal analyzer. The SEM images of the prod-

Table I Chemical Compositions of Bentonite/A-174/AN Sol Gel Materials

Sample Code	AN in the Materials (wt %)	SiO ₂ ^a (Calc wt %)	SiO ₂ ^b (Obs wt %)
BP1-A174	—	27.2	29
PAN	100	—	—
TAG-67	10	62.3	64
TAG-66	25	24.5	27
TAG-65	50	86.1	84
TAG-64	75	81.7	83

^a The SiO₂ contents of A-174 unit in bentonite calculated from compositions.

^b Determined by TGA at 700°C.

ucts were recorded on a JEOL scanning electron microscope. FTIR absorption spectra were obtained with a ATI Unicam Mattson 1000 system.

RESULTS AND DISCUSSION

To obtain the optimum conditions for attachment of A-174 to activated bentonite clay particles, several parameters, such as solvents and A-174 concentration, were changed. The amount of required silane was calculated according to:

$$g(\text{silane}) = \frac{[g(\text{clay}) \times \text{surface area of clay}]}{(\text{spec. wetting area of the silane})}$$

$$g(\text{A-174}) = \frac{[10 \text{ g} \times 112.3 \text{ m}^2 \text{ g}^{-1}]/314 \text{ m}^2 \text{ g}^{-1}}{=} = 3.576 \text{ g}$$

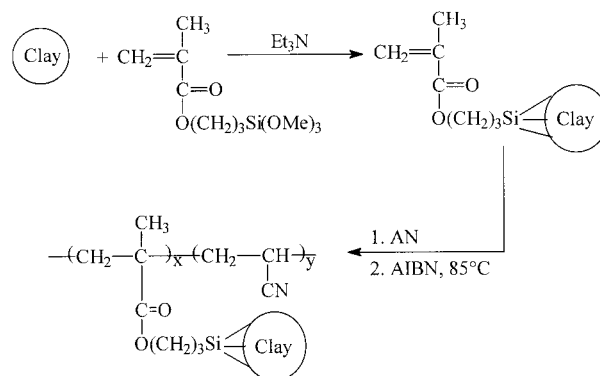
Theoretically, 3.57 g A-174 was required for 10 g bentonite to obtain optimum grafting efficiency. Furthermore, the grafting efficiency was calculated from the thermogravimetric analysis. For A-174-modified BP-1, the weight loss was < 1% between 50 and 250°C. This was very similar behaviour, as observed for the pure BP-1. However, the total weight loss was 24.45% between 250–700°C. This was considered to be due to grafting of A-174 on BP-1. By subtracting these two values (3.56 and 24.45%), we obtained 20.89% weight loss caused exclusively by grafted A-174. The grafting efficiency of A-174 on BP-1 was 20.89%.

All the evidence obtained from FTIR, DTA, and XRD analysis supported the successful grafting of A-174 onto the surface of BP-1 clay. According to the results, it was found that the amount of A-174 for optimal grafting was very close to the amount calculated by the formula. The grafting efficiency

of A-174 on BP-1 was studied as a function of reaction time (from 4 to 18 h). In this time range, the reaction time had nearly no influence on the grafting efficiency of A-174. The results indicated that grafting reaction on BP-1 was completed within 6 h.

As an extension of this work, acrylonitrile was chosen as a monomer for the polymerization at the surface of the A-174-grafted BP-1 clay. To confirm the function of A-174 on the polymerization process of acrylonitrile, a comparative study of the polymerization of acrylonitrile with pure BP-1 was also performed. After polymerization reaction, the A-174-modified BP-1 solution became very viscous, but the pure BP-1 solution kept its original viscosity. This showed that acrylonitrile could be successfully copolymerized via the reaction of the functional end group of A-174 with acrylonitrile. The changes in FTIR, DTA, SEM, and XRD analysis were confirmed in the structure.

According to the procedure established in this work, the results showed that acrylonitrile was



TAG-63 to TAG-67

Scheme 1 Synthetic outline.

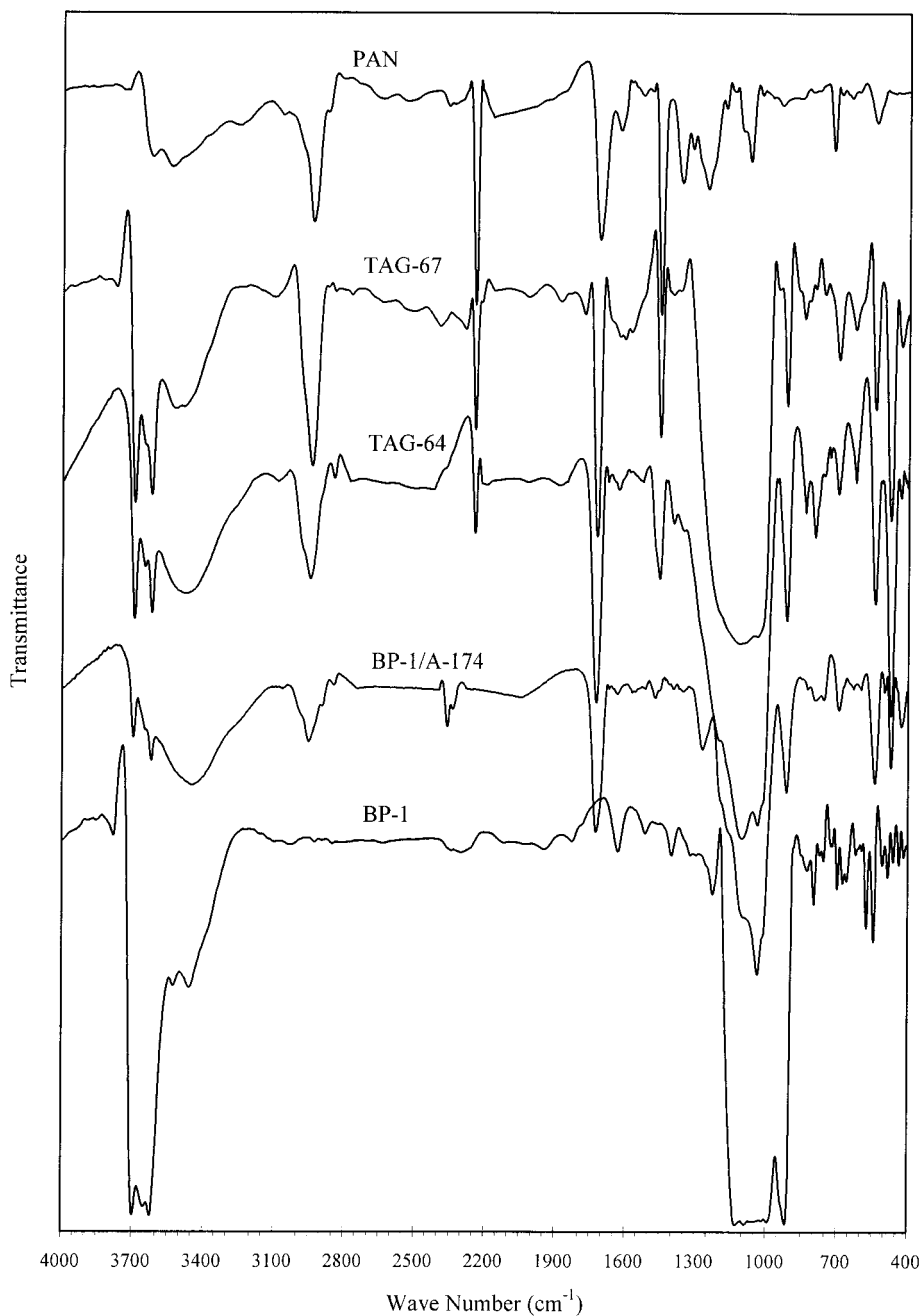


Figure 1 FTIR results of the clay-hybrid materials.

bonded to the acrylate end group of γ -methacryloxypropyltrimethoxysilane via the polymerization process shown in Scheme 1.

FTIR Characterization

Infrared absorption curves for a variety of hybrid materials, BP-1 and polyacrylonitrile, are given in Figure 1. For BP-1, the layer silicate structural

OH groups show absorption bands at 3600–3700 cm^{-1} , whereas the adsorbed water appears at 3400 and 1640 cm^{-1} . A strong absorption band between 3600 and 3700 cm^{-1} , which was not lost on heating to 200°C, is correlated with structural OH groups. The band at 3677 cm^{-1} is attributed to the basal plane OH groups. Typical characteristics of the absorption band for polyacrylonitrile (PAN) at 2250 cm^{-1} corresponding to $\text{C}\equiv\text{N}$ as

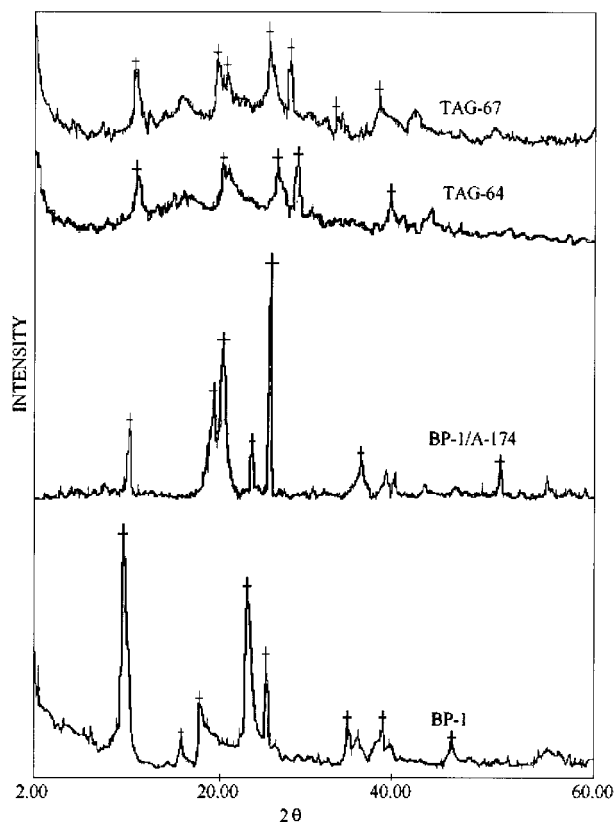


Figure 2 XRD diffraction patterns of bentonite and the materials prepared.

well as absorption band 1620 cm^{-1} corresponding to $\text{C}=\text{N}$ was clearly visible. In addition, PAN shows strong absorption peaks at 2590 cm^{-1} ($\text{C}-\text{H}$ stretching), 1460 cm^{-1} ($\text{C}-\text{H}$ bending), $1360\text{--}1390\text{ cm}^{-1}$, and 1260 cm^{-1} . In the case of hybrid materials, TAG-64 and TAG-67, the OH bands at $3600\text{--}3700\text{ cm}^{-1}$ diminished, whereas peak at 1090 cm^{-1} increased in intensity. This absorption occurs mainly because of $\text{Si}-\text{O}$ stretching. The peak at 2250 cm^{-1} was attributed to CN groups.

XRD Characterization

Diffraction patterns corresponding to pure BP-1, BP-1/A-174, PAN, and hybrid materials prepared with different ratios of the acrylonitrile in copolymers were given in Figure 2. The pure BP-1 has triclinic unit cell and the following cell parameters: $a = 5.155\text{ \AA}$, $b = 8.959\text{ \AA}$, $c = 7.407\text{ \AA}$, $\alpha = 91.68^\circ$, $\beta = 104.87^\circ$, $\gamma = 89.94^\circ$. Observed data of the BP-1 and calculated peak position by using cell parameters and related indices were shown in

Table II. XRD provides a look into the extent of clay crystallization and in some cases a clue as to the organic incorporation by the (001) basal spacing. Figure 2 includes BP-1 for the comparison purposes with BP-1/A-174.

The XRD pattern of bentonite is clearly affected by the incorporation of A-174, as evidenced by the change in 001 reflection. The 001 spacing proves that A-174 partially enters into the interlayer of the BP-1. It is clearly evident that 001 reflection of the BP-1/A-174 is broad compared to the pure BP-1, but the intensity is not changed. This means that A-174 is partially entered into the interlayer of the BP-1; however, covalent bonding is not formed with the interface atoms. On the contrary, as shown in the (002) peak, covalent bonding is formed because the (002) peak was diminished in the BP1-A174 sample. Actually, the structure of the bentonite was not changed because the original peak positions of the samples BP1-A174 and bentonite are the same. When the covalent bonding is formed by the interaction between bentonite and A-174, some structural distortions occur at the plane atoms in the bentonite. As a result of these distortions, the (002) peak in the BP1-A174 is diminished.

Sample PAN, as shown in Figure 2, is a largely amorphous material. It has three main reflections marked (a), (b), and (c). These plane reflections may have occurred when the orientation between the atoms or atomic groups is strong as the polar nature of the amorphous material PAN. It is shown that plane peaks of the PAN strongly interacted with BP1-A174 and covalent and hydrogen bonding between $-\text{CN}$ groups of PAN and surface hydroxyls of bentonite might take place. It is evident that for the samples TAG-67 to TAG-64 (c), the peak disappeared, which indicates that PAN is linked via covalent bonding to BP1-A174. This linking does not take place with

Table II Diffraction Data for the Bentonite Sample and Related Indices^a

2θ	d (\AA)	hkl
12.00	12.98	001
19.75	4.51	013
24.64	4.47	002
26.44	4.30	012
34.84	4.27	131

^a X-ray powder diffraction patterns of the products were recorded using monochromatic $\text{Cu}-\text{K}\alpha$ radiation.

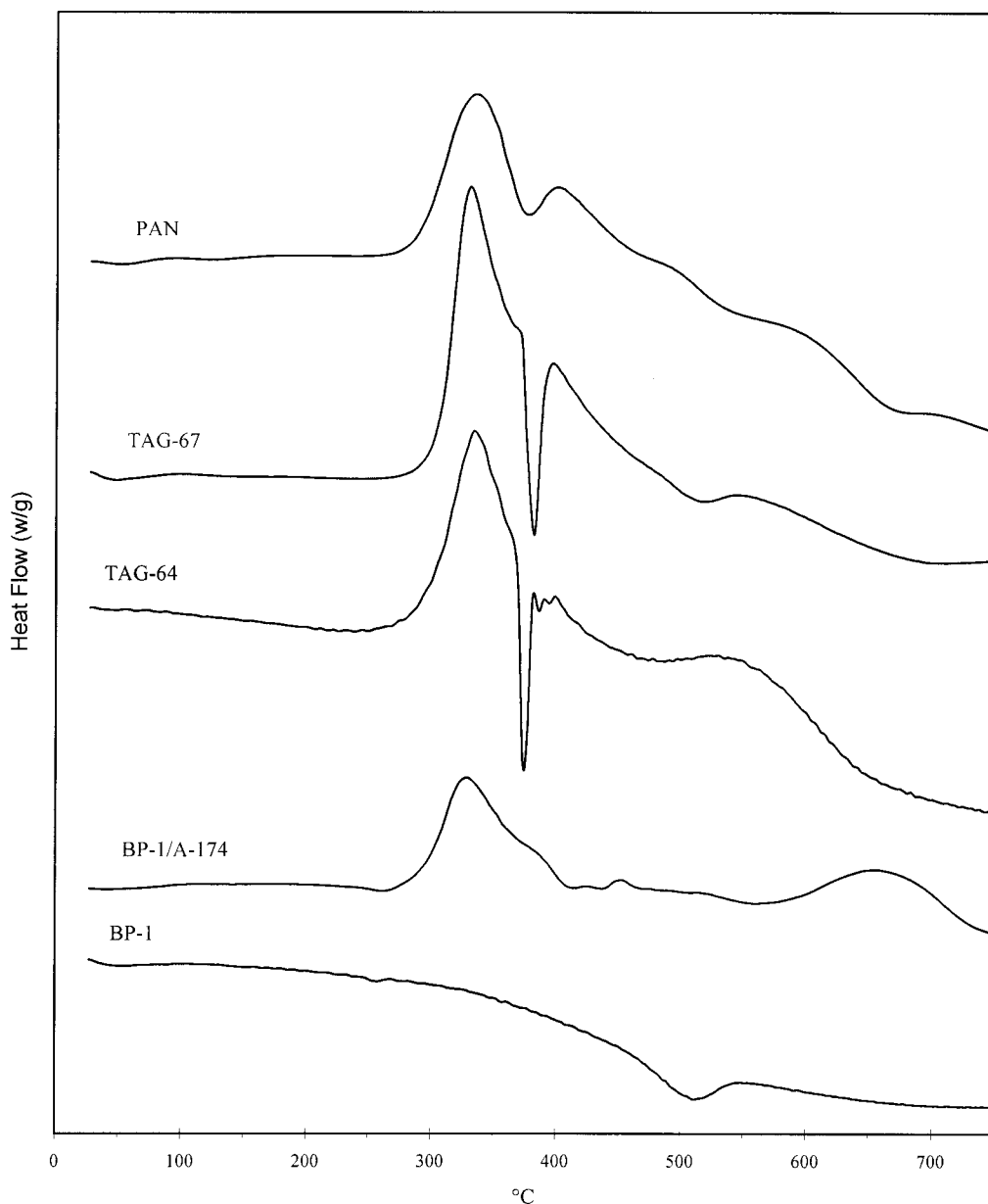


Figure 3 DTA results of the bentonite and bentonite-hybrid materials.

(a) peak-forming atoms, which are present in all samples. In all cases, XRD patterns of the samples showed that characteristic bentonite peaks are present except the peak (a), which is attributed to the nonbonding plane symmetry. In addition, there exists the possibility of an intercalated PAN-clay composite in the interlayer gallery of the bentonite. This was confirmed with the interlayer spacing that increased because of insertion of the PAN polymer. The results were in accord with the results given by Choi et al.⁴¹

DTA

Figure 3 shows the DTA diagrams of BP-1, PAN, TAG-64, and TAG-67. BP-1 shows characteristic thermal behavior at 596.3°C, which corresponds to a loss of interlattice hydroxyl groups. For PAN, organic groups leave the structure at 330.16°C and the structure starts to melt at 348°C. The exothermic peak at 330.16°C and the endothermic peak at 384.84°C indicate that polymer degradation starts at 330.16°C. Figure 3(b) shows that, in the case of hybrid materials, decomposi-

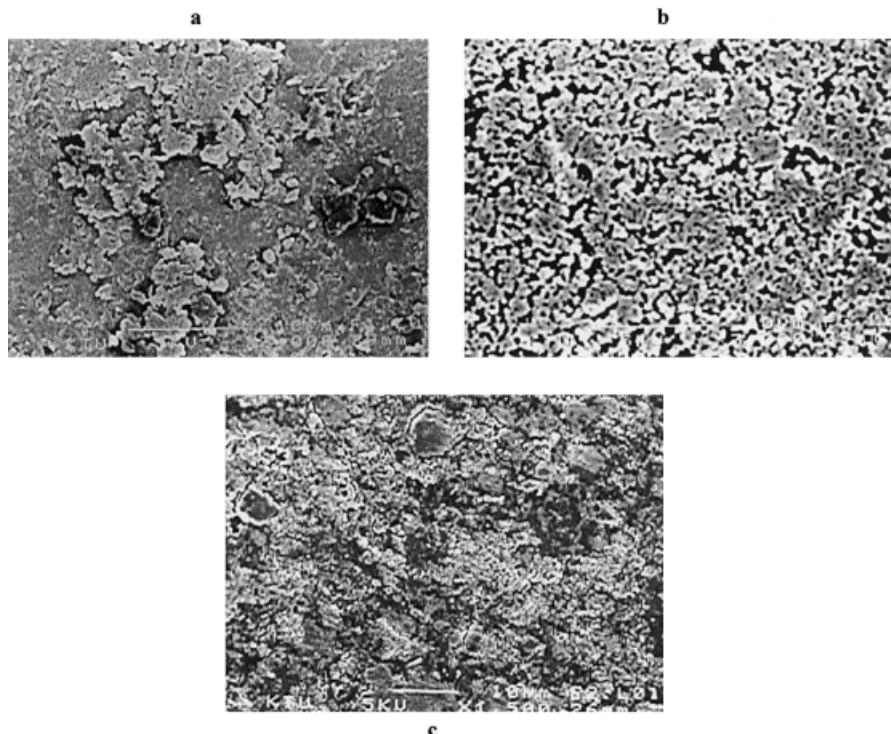


Figure 4 SEM images of (a) BP-1, (b) PAN, and (c) TAG-64.

tion of the polymer shifts to 480°C, meaning that the thermal stability of polyacrylonitrile is elevated at about 100°C.

SEM

Figure 4(a–c) shows SEM photographs of the surface cross section of the BP-1, PAN, and hybrid material TAG-64. SEM photographs have shown the effect of polyacrylonitrile composition on the morphology of clay. In the case of TAG-64, the SEM image shows no microscopic voids. This indicates that the polymeric components do not agglomerate and retain their integrity.

CONCLUSION

The present study of the reaction of bentonite with A-174 and acrylonitrile has revealed surprisingly novel composite materials. Present evidence in combination with our previous results indicates that covalent bond formation has taken place mostly at the surface of the bentonite clay. By interaction of the organofunctional group of the silane with the functional group of bentonite and polymer, bonds were formed which connect

the inorganic substrate via the silane, acting as a bridge, with the polymer, and the thermal stability of the polyacrylonitrile was elevated.

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