Polymer Encapsulation of Colloidal Asbestos Fibrils

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Synopsis

The free-radical polymerization of several monomers in an aqueous suspension containing chemically opened chrysotile asbestos fibrils was investigated with the intention of promoting complete encapsulation of the individual colloidal fibrils. The degree of polymer deposition on the colloidal substrate is dependent upon several factors including monomer and polymer solubility, initiator type, ionic comonomers, and degree of interfacial wetting. Successful encapsulation was achieved by the addition of novel unsaturated polyelectrolytes which served a dual role as dispersing agent and comonomer. Such methods are useful for the preparation of reinforced composites with controlled interfacial properties. In one example, it is shown that asbestos fibrils surrounded by a rubbery layer can impart greater toughness to a reinforced composite, compared to a composite in which the rubbery phase is dispersed at random or isolated from the interface. The technique can be extended to other types of fillers. The various methods of chemically "opening" asbestos are summarized.

INTRODUCTION

There are numerous references in the literature describing methods of encapsulating inorganic or organic particles.[1-6] However, when such methods were applied to the encapsulation of submicroscopic asbestos fibrils in aqueous suspension, visual inspection with the electron microscope revealed that fiber coverage was either incomplete or nonexistent. The extreme subdivision of the asbestos fibrils having average diameters of only 500 Å meant that, to be successful, polymer encapsulation must proceed by the formation of a uniform coating built up polymer molecule by polymer molecule rather than by massive coprecipitation. Therefore, the objective of this study was aimed at discovering methods for uniformly coating inorganic fillers (such as asbestos fibrils) with a hydrophobic polymer and preferably in aqueous suspension. Such coated fillers were required for preparing reinforced plastic composites and for investigating the role of the interface in composite materials, particularly the influence of an interfacial layer on toughness and impact strength.

Some of the most successful encapsulation methods have been achieved through growth of a polymer film from the vapor phase on a substrate dispersed in organic media by employing Ziegler-Natta catalysts.[3,7] The uniformity and thickness of the film can be accurately controlled. Initia-

tion by γ-ray irradiation[8] or free-radical catalysts[4-6] has been also reported. Aqueous encapsulation is usually preferred because the solvent need not be recovered and because it provides an inexpensive system which is easily handled by suspension or emulsion polymerization equipment. However, in most previous investigations, particles of macroscopic dimensions were reported to be encapsulated, and in such cases the polymeric coatings were thick and easier to deposit uniformly without special precautions. Use of redox[4,5] and thermally decomposing initiators[6,9] in aqueous media has been suggested for the polymerization-encapsulation using vinyl monomers. Creation of active sites on the substrate by an ion exchange reaction between the substrate and one component of the redox system is the accepted polymerization mechanism in the first case; in the second case, encapsulation results from the tendency of the unstable monomer–polymer particle to agglomerate on the surface of the dispersed filler until complete coverage is obtained even though the polymer does not preferentially wet the filler surface.

The use of a colloidal substrate results in the reduction of the surface area per particle. Because of the difficulties arising from the reduced area per particle associated mainly with the droplet size and creation of active sites, several other variables were examined in the present work. Aqueous monomer solubility, polymer glass transition temperature (T_g), and ionic interactions between oppositely charged polymer chains were found to be of importance. Modification of the hydrophilic characteristics of the substrate surface by using polyelectrolytes as asbestos-dispersing agents and initiator solubility are also variables examined in the present work.

Chrysotile asbestos fibrils of colloidal dimensions have largely been overlooked until recently[10,11] as potential reinforcing agents for plastics and foams. There are several reported methods for chemically "opening" asbestos to its ultimate fibrils. Previously used dispersing agents are detergents or wetting agents,[12] inorganic salts,[13,14] acids,[15] and polar organic compounds.[11,16] These are summarized in Table I along with the

TABLE I
Chrysotile Asbestos Fibrillating Agents

Dispersing agents	Reference
Soaps, detergents, wetting agents (Aerosol OT, sodium oleate, long-chain cationic reagents, etc.)	12, 18
Inorganic salts (aluminum chloride, ferric chloride, barium chloride, sodium aluminate and acetic acid, etc.)	13, 14
Monocarboxylic acids (lactic acid, acetic acid, etc.)	15
Fatty amines (tallow-1,3-propylene diamine)	17
Polar organic compounds (glycerol, diethanolamine, dimethyl sulfoxide, etc.)	11, 16
Anionic polyelectrolytes [poly(acrylic acid), poly(methacrylic acid), poly(styrene-co-acrylic acid), etc.]	this work

Fig. 1. Electron micrograph of chrysotile asbestos (Plastibest No. 20) dispersed with sodium polyacrylate. 10,450×.

preferred method used in this investigation. It was found that anionic polyelectrolytes (i.e., poly(acrylic acid) and copolymers thereof) are particularly effective fibrillating agents (Fig. 1), yielding dispersions of excellent stability. Such polyelectrolytes could be neutralized with a variety of inorganic bases (NaOH, KOH, NH₃) or an organic base such as triethylamine, diethanolamine, or piperidine. Dimethylaminoethyl methacrylate (DMAEMA) can also be employed to neutralize the polyacid, thereby converting the polymeric dispersing agent into a polyfunctional comonomer.

The flexural properties of thermoplastics reinforced with randomly oriented chrysotile fibrils have been already investigated.[10] In the present work, a comparison is made between properties of composites containing encapsulated asbestos and others prepared by latex compounding techniques. The effect of an elastomeric layer at the fiber–matrix interface on the toughness of these composites was also examined by introducing a poly(ethyl acrylate) layer on the asbestos surface.

EXPERIMENTAL

Preparation of Asbestos Dispersions

Chrysotile asbestos (Plastibest 20, Canadian Johns-Manville Co. Ltd.) was the type used in all the described experiments. The colloidal dispersions were prepared by adding the desired quantities of water, dispersing agent, and asbestos to a high-speed blendor (Osterizer) and subjecting the mixture to vigorous agitation for several minutes.

Chemical opening was carried out by the method of Barbaras[13] or by the use of water-soluble salts of poly(acrylic acid) or copolymers contain-

TABLE II
Polyelectrolyte Dispersing Agents

Polyelectrolyte	Source	Composition
Poly(acrylic acid)	Rohm and Haas (Acrysol A-1 to A-3)	100% PAA
Poly(methacrylic acid)	synthesized[19]	100% PMAA
Poly(styrene-co-acrylic acid)	synthesized[a]	0.82 to 0.63 equiv/100 g[b]
Poly(MMA-co-acrylic acid)	synthesized[a]	0.76 to 0.54 equiv/100 g[b]
Poly(styrene-co-maleic anhydride)	Sinclair SMA 1420	acid number 300

[a] Prepared in heptane at 60°C with AIBN as initiator. The polymer was recovered by filtration.
[b] Determined by titration with alcoholic KOH in pyridine.[20]

ing a polymerizable acid as a major component. Inorganic bases or monomeric amines (DMAEMA) were used to neutralize the carboxylic polyelectrolytes. The polymers used in this investigation are listed in Table II. The amount of polyacid varied from 0.15 to 2.0 g per gram of asbestos. A 1% asbestos dispersion was used in all experiments.

Polymerization-Encapsulation

The colloidal asbestos suspensions were mixed with a weighed quantity of a freshly distilled monomer and polymerized for 12–48 hr at 60°C, using either azobisisobutyronitrile (AIBN) or benzoyl peroxide as oil-soluble initiator or potassium persulfate as a water-soluble initiator. The polymerizations were conducted in pop bottles which were flushed with nitrogen and placed in a bottle polymerization unit at constant temperature. The polymerized mixture was filtered, washed with water, and dried in an air oven at 60°C. Samples of the suspended matter were diluted 50-fold

TABLE III
Polymerization Systems Yielding
Complete Encapsulation of Asbestos Fibrils

Components	Group A	Group B	Group C	Group D
H_2O, g	100	100	100	100
Asbestos, g	1	1	1	1
PAA, g	0.15–0.5	0.15–0.5	—	0.15–0.21
DMAEMA, g	0.32–1.02	0.32–1.02	—	0.32–0.46
Basic aluminum[1] formate, cc (0.1M solution)	—	—	1	—
Styrene, g	0.96–2.91	—	1.1–1.75	0.96–1.38
MMA, g	—	0.96–2.91	—	—
EA, g	—	—	0.4–0.9	0.28–0.84
AIBN, % (based on monomer concn.)	0.5	0.5	0.5	0.5

and placed on a 200-mesh copper grid supporting a film of carbon. Examination of the dried suspension was carried out with a Philips EM 300 electron microscope.

Typical formulations which gave complete encapsulation are shown in Table III. In Table III, groups A and B refer to two-component compositions, whereas groups C and D refer to three-component compositions. In group C, after the ethyl acrylate polymerization and the determination of its conversion, a calculated amount of styrene was added. The inverse procedure was followed in group D where ethyl acrylate was added after the polymerization-encapsulation with styrene.

DISCUSSION

For charged surfaces, stabilization of dispersions with polyelectrolytes is due to both the strong adsorption of the long-chain ions at the oppositely charged surface and the projection of unadsorbed charged segments into the aqueous phase.[12,21] Since the outer layer of chrysotile is essentially magnesium hydroxide, a similar mechanism is applicable explaining the absorption of the polyacrylate chains which results in a negative charge of the overall structure.

Although the classical "electrostatic stabilization" explains adequately the stability of these dispersions, a steric mechanism should also be considered.[22] The flexible polymer chains sterically prevent the particles from approaching close enough, thereby functioning as a mechanical as well as an electrostatic barrier to prevent coalescence or flocculation.

Homopolymerization

The presence of the poly(acrylic acid) salts adsorbed on the surface of the asbestos fibrils did not promote sufficient wetting by the monomer–polymer mixtures and consequent growth of a uniform polymer layer on the surface. In the case of homopolymerization, polymer deposition of water-soluble monomers (MMA, AN) was not affected by the type or nature of the polyelectrolyte dispersing agent. These ionomers function more or less as conventional emulsifiers controlling the size and number of the formed polymer particles and contributing to the stability of the resulting dispersion. In the case of oil-soluble monomers, the presence of such agents favors emulsion or suspension polymerization depending upon the emulsifier efficiency and the choice of initiator, as shown in Table IV.

The effect of the type of initiator and the emulsifier efficiency on the polymerization of an oil-soluble monomer (styrene) is shown in Figures 2, 3, and 4. The number of the formed particles depends upon the type of initiator (Figs. 2 and 3). Sodium polyacrylate functions in the case of $K_2S_2O_8$ as a conventional emulsifier in emulsion polymerization (although inefficient), or as suspending agent (AIBN as initiator). On the other hand, a copolymer of styrene–acrylic acid behaves as a true emulsifier; this is confirmed by the number and size (average diameter 1500 Å) of

TABLE IV
Summary of Polymerization Behavior of Different Monomers in the Presence of Colloidal Asbestos

Monomer	Initiator	Dispersing agent	Type of polymerization	Coating of fibrils
St[a]	$K_2S_2O_8$	PAA or PMAA	emulsion-inefficient emulsifier	partial
MMA[b]	$K_2S_2O_8$	PAA or PMAA	aqueous precipitation	incomplete
MMA[c]	$K_2S_2O_8$	PAA or PMAA	aqueous precipitation and emulsion-inefficient emulsifier	incomplete
St[a]	AIBN	PAA or PMAA	suspension	no coating
MMA[b]	AIBN	PAA or PMAA	aqueous precipitation	incomplete
MMA[c]	AIBN	PAA or PMAA	aqueous precipitation and suspension	incomplete
St[a]	AIBN	Basic aluminum formate	suspension	no coating
MMA[c]	AIBN	Basic aluminum formate	aqueous precipitation and suspension	incomplete
St[a]	AIBN	Poly(St-co-AA)	emulsion-efficient emulsifier	no coating
MMA[c]	AIBN	Poly(MMA-co-AA)	emulsion-efficient emulsifier	no coating
AN[b]	$K_2S_2O_8$ or AIBN	PAA or PMAA	aqueous precipitation-inefficient stabilizer	incomplete
EA[c]	$K_2S_2O_8$ or AIBN	PAA or PMAA or basic aluminum formate	aqueous precipitation-inefficient stabilizer	massive encapsulation
St[a]/ DMAEMA(3/1)	$K_2S_2O_8$	PAA or PMAA	aqueous precipitation-formation of non-stabilized at high concentration polyelectrolyte complex.	incomplete
MMA[b,c]/ DMAEMA(3/1)	$K_2S_2O_3$	PAA or PMAA		fairly uniform coating
St[a]/ DMAEMA(3/1)	AIBN	PAA or PMAA		complete encapsulation
MMA[b,c]/ DMAEMA(3/1)	AIBN	PAA or PMAA		complete encapsulation

[a] Monomer concentration greatly exceeding its solubility limit.
[b] Monomer concentration within its solubility limit.
[c] Monomer concentration slightly exceeding its solubility limit.

polymer particles (Fig. 4) which generally in emulsion polymerization is related to the amount and efficiency of the surface-active agent.

Although it is generally accepted[23] that the site of polymerization is the interior of the micelles, attempts have been made to explain the mechanism of particle formation at emulsifier concentrations below the C.M.C.[24-26] Roe[26] has shown that the presence and concentration of
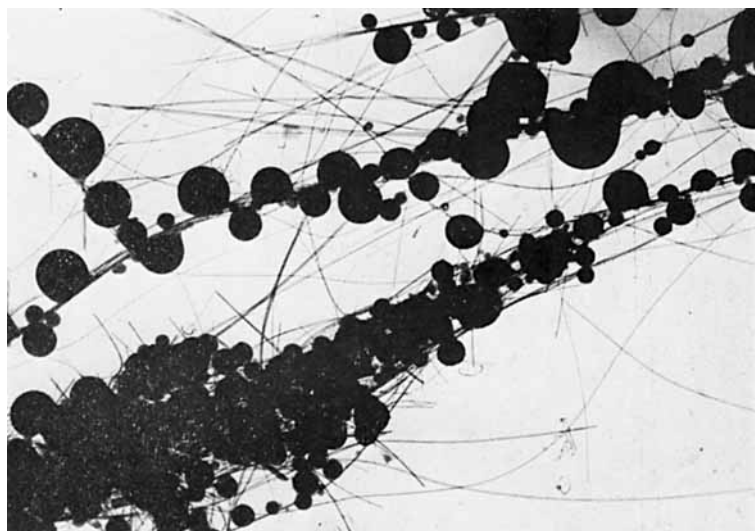

Fig. 2. Polystyrene particles formed in the presence of asbestos dispersed with sodium polyacrylate ($K_2S_2O_8$ as initiator). 3,230×
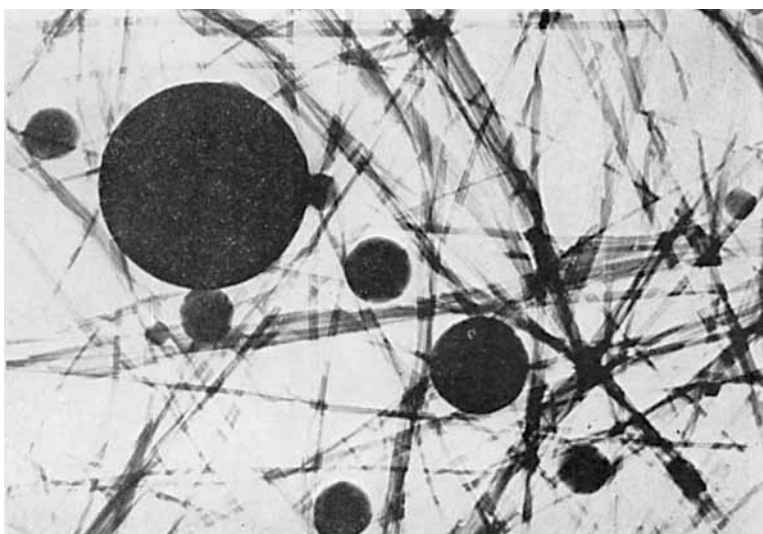

Fig. 3. Polystyrene particles formed in the presence of asbestos dispersed with sodium polymethacrylate (AIBN as initiator). 10,450×.

micelles are of trivial importance in emulsion polymerization; particles are generated from the interaction of a free radical and a monomer molecule dissolved in the aqueous phase. The inherent properties of the emulsifier control the size and stability of the growing latex particles.

Considering the absence of micelles (St–PAA–$K_2S_2O_8$ system), the experimental results can be interpreted according to Roe's theory. Initiation takes place in the aqueous phase where initiator radicals attack disssolved
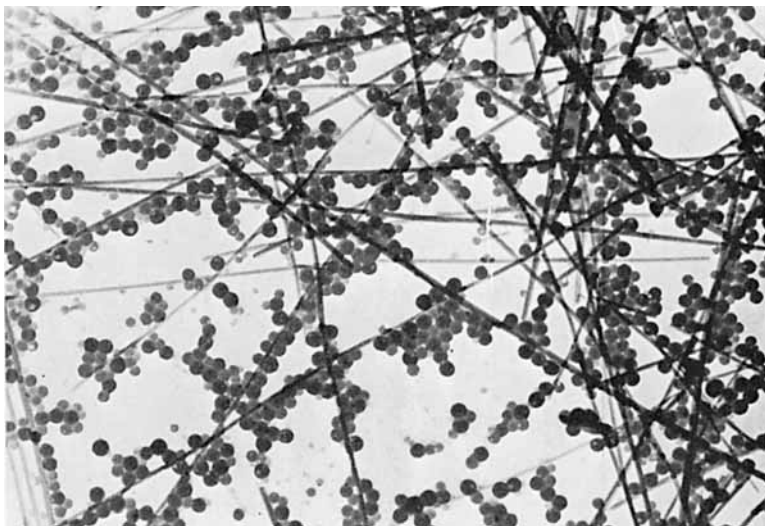

Fig. 4. Effect of poly(St-co-AA) as asbestos dispersing agent on the size and distribution of polystyrene particles (AIBN as initiator). 10,450×.

Fig. 5. Poly(methyl methacrylate) particles formed in the presence of asbestos dispersed with sodium polyacrylate ($K_2S_2O_8$ as initiator). 16,500×.

monomer to form growing radical oligomers.   The growing oligomers may either deposit immediately on the asbestos surface and then continue to grow or may grow until they become larger particles, whereupon they may become unstable and deposit on the fibril surfaces.   Because of the weak stabilizing efficiency of the PAA, coalescence of the polymer particles with each other and on the asbestos surface probably occurs.
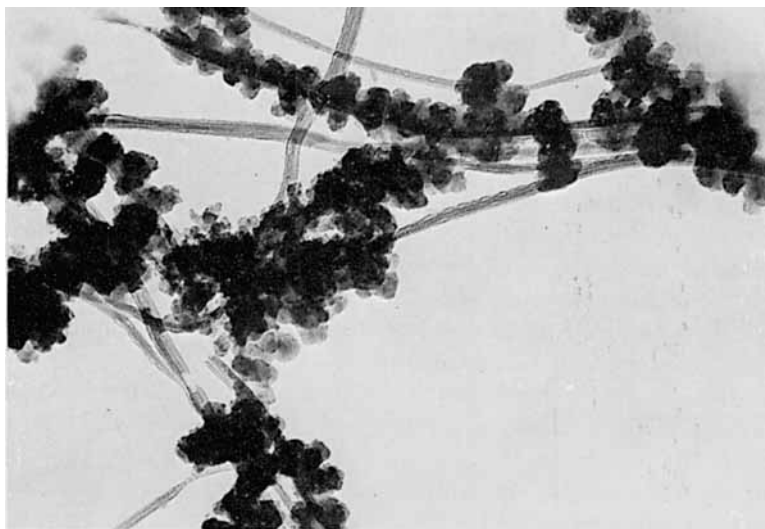

Fig. 6. Polyacrylonitrile particles formed in the presence of asbestos dispersed with sodium polyacrylate (AIBN as initiator).   28,000×.
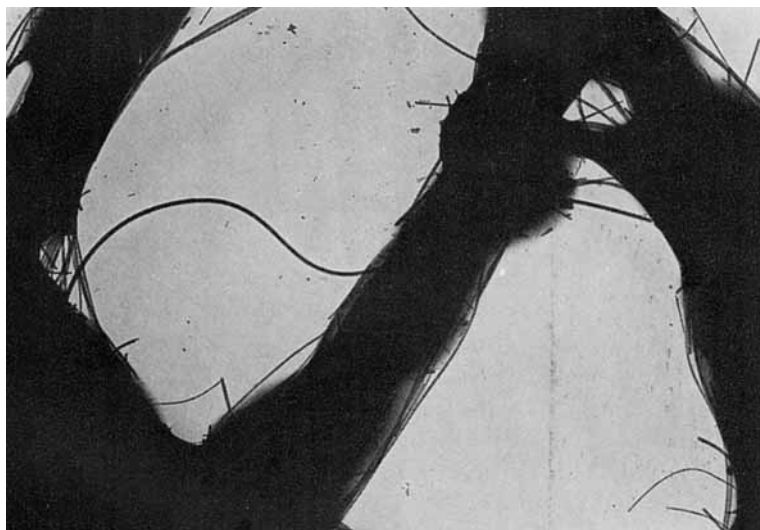

Fig. 7. Fibers coated with poly(ethyl acrylate).   Polymerization in the presence of asbestos dispersed with basic aluminum formate (AIBN as initiator).   5,010 ×.

In the case of an oil-soluble initiator (AIBN), suspension polymerization is usually observed whenever poly(acrylic acid) or inorganic salts are used as dispersing agents, the polyelectrolyte or the dispersed asbestos functioning as suspending agents.   When a more efficient emulsifier is employed (a more favorable HLB), such as a copolymer of acrylic acid and styrene, stable emulsions tend to form with much smaller particles, as shown in Figure 4.

The degree of coverage is controlled mainly by the aqueous solubility of the monomer (Figs. 5, 6, and 7) and is independent of the nature of the initiator, provided that the monomer concentration is at or below its solubility limit.   The aqueous solution polymerization of MMA has been extensively studied by Fitch and Chen.[24]   A probable polymerization mechanism as suggested by these authors in the presence of asbestos may involve: (a) initiation in the aqueous phase; (b) growing of oligomeric polyMMA chains to a critical size and subsequent precipitation onto the asbestos surface, and/or coalescence with preexisting polymer particles, which eventually precipitate onto the substrate; (c) diffusion of the monomer from the aqueous phase into the adsorbed polymer–monomer coating and continued polymerization to completion.

The fate of the excess insoluble monomer droplets depends upon the initiator solubility, since oil-soluble and water-soluble initiators favor emulsion and suspension polymerization, respectively.

For the water-soluble acrylonitrile and ethyl acrylate, two other factors affect their polymerization behavior: the insolubility of the acrylonitrile in its own polymer and the low T_g of poly(ethyl acrylate) ($-22°C$).   The locus of the polymerization, in the first case, resides mainly in the aqueous phase.   Continuous formation of new particles throughout the bulk of the solution causes finally precipitation of fibers almost completely coated with polymer (Fig. 6).   The low T_g of PEA, combined with the high polymerization temperature and the absence of efficient stabilization, increases the tackiness of the formed particles, resulting in coalescence (Fig. 7) and coprecipitation of asbestos–polymer.

Copolymerization

From Table IV, it can be seen that by using a basic comonomer, such as dimethylaminoethyl methacrylate, monomers such as styrene or methyl methacrylate could be forcibly grown on the surface of the asbestos, presumably as a result of the strong attachment of the basic comonomer for the polyelectrolyte dispersing agent (Figs. 8 and 9).   The increased solubility of the comonomer mixture and the ionic attractions between the negatively charged asbestos surface (due to the polyacrylate anions) and the cationic oligomeric or polymeric particles lead to quantitative coating of the colloidal substrate.   Neutralization of poly(acrylic acid) by dimethylaminoethyl methacrylate produces a highly polyfunctional dispersing agent which can participate in subsequent copolymerization reactions, thereby leading to a high degree of ionic grafting.[27]   The formation of an ordered polyelec-

trolyte complex by polymerization of monomeric amines in the presence of polyacrylate anions has been observed,[28] resulting in strong polar interactions.

Generally for encapsulation with ionomers, the monomer concentration ratios were critical for best results. For complete encapsulation (1%
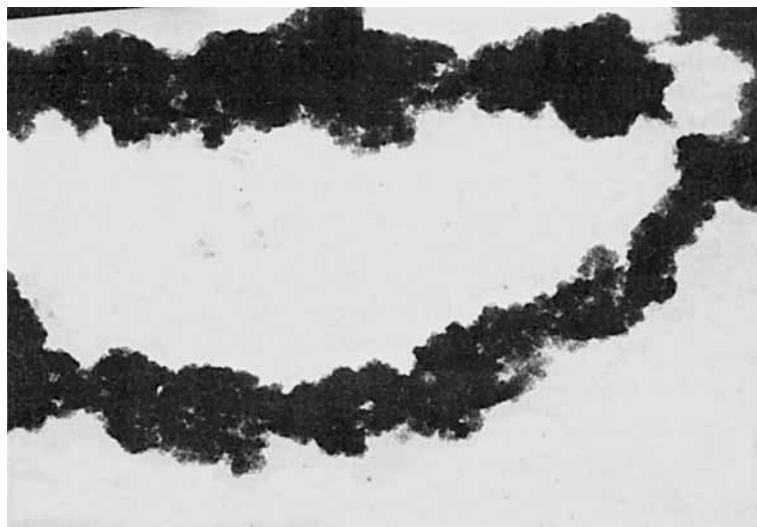

Fig. 8. Electron micrograph showing completely coated chrysotile fibers. Copolymerization of styrene/DMAEMA (3/1) in the presence of PAA (AIBN as initiator). 6,340×.

Fig. 9. Electron micrograph showing completely coated chrysotile fibers. Copolymerization of styrene 1 DMAEMA (3/1) in the presence of PAA (AIBN as initator). 5,010×.

asbestos dispersion), the optimum ratios were 1/3 for DMAEMA/monomer, with the poly(acrylic acid) concentration at least 0.15% by weight. Oil-soluble initiators were preferable, especially in the case of oil-soluble monomers, since the formation of free polymer was minimized.

Evaluation of Composites

Composites prepared by encapsulation have flexural properties similar to those prepared by latex compounding techniques.[10]   The main advantages resulting from the use of encapsulated asbestos are improved processability, ease of molding, and high heat distortion temperature due to the large surface area of the fibrils.

The formation of three-component systems (asbestos–polystyrene–poly(ethyl acrylate)) illustrated the advantage of locating an energy absorbing layer at the fiber–matrix interface rather than at random in the matrix.   A considerable increase in toughness (ASTM Izod impact strength) was observed when the rubbery phase was concentrated at the interface, whereas little or no improvement was found when the poly(ethyl acrylate) was randomly dispersed in the matrix or was completely isolated from the interface (Fig. 10).   The introduction of the weak rubbery layer acting as interfacial stress concentrator and crack arrestor affects the stiffness and strength of the composite.   Increase in impact strength by a factor of 2.5 (PEA $V_f = 0.08$) corresponds to a drop in flexural modulus and strength of nearly 30%.
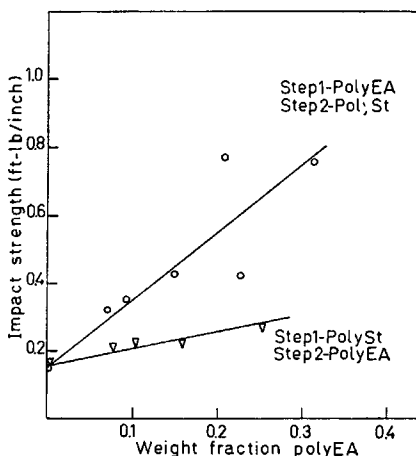

Fig. 10. Impact strength vs. weight fraction of poly(ethyl acrylate) for asbestos–poly(ethyl acrylate)–polystyrene composite of constant asbestos volume loading: (O) fibers coated with poly(ethyl acrylate); (∇) fibers coated with polystyrene.

CONCLUSIONS

Carboxylic polyelectrolytes were found to be excellent dispersing agents for chrysotile asbestos in neutral or slightly alkaline aqueous solutions.

Previous methods for encapsulating inorganic materials in aqueous suspensions were found to be inefficient when applied to colloidal asbestos dispersion. This process, for colloidal substrates, is generally favored by increased monomer solubility and by the presence of comonomers possessing a charge opposite to that of the surface. In the absence of the above comonomers, polyelectrolytes do not promote complete and uniform polymer deposition on the substrate, contributing, on the contrary, to the formation of excessive free polymer (either stabilized in dispersion or homoprecipitated). Quantitative coverage of the substrate's surface can be achieved by the use of polymeric dispersing agents which interact (through ionic substituents) with the encapsulating polymer. Hence, a polymer containing basic substituents (dimethylaminoethyl ester groups) will interact strongly with a polyacrylate dispersing agent and promote a more uniform coating.

Composites of controlled interfacial properties and improved processability and molding characteristics can be designed by using coated reinforcing agents. Increase in toughness may be achieved by introducing an energy-absorbing polymeric layer at the matrix–filler interface. While in the case of polyEA the impact strength is significantly improved, there is a corresponding loss of modulus and strength. Therefore, the use of interfacial coatings having a somewhat higher modulus but capable of high energy absorption is indicated, that is, ductile plastics which are responsive to high strain rates.

References

1. C. Brynko, U.S. Pat. 2,969,330 (1961).
2. J. A. Orsino and C. E. Mandel, U.S. Pat. 3,121,658 (1964).
3. D. F. Herman and A. L. Resnick, U.S. Pat. 3,272,897 (1966).
4. J. W. Adams and H. W. Hoftiezer, U.S. Pat. 3,370,935 (1968).
5. D. J. Bridgeford, U.S. Pat. 3,318,826 (1967).
6. D. F. Herman et al., U.S. Pat. 3,265,644 (1966).
7. Encyclopedia of Polymer Science and Technology, Vol. 8, Interscience, New York, 1968.
8. Uskov et al., Vysokomol. Soedin, 8 (1), 26, (1966).
9. S. A. Michaels, U.S. Pat. 3,519,594 (1970).
10. E. A. Noga and R. T. Woodhams, SPE J., 26 (9), 23 (1970).
11. A. M. Schwartz and C. A. Rader, papers presented at the 12th National SAMPE Symposium A.C.-1, Calif., 1967.
12. I. J. Novak, U.S. Pat. 2,626,213 (1953).
13. G. D. Barbaras, U.S. Pat. 2,661,287 (1953).
14. A. W. Naumann and W. H. Dresher, U.S. Pat. 3,297,516 (1967).
15. W. H. Dresher and A. W. Naumann, U.S. Pat. 3,409,499 (1968).
16. O. A. Battista, U.S. Pat. 3,410,751 (1968).
17. R. W. Hausslein and H. J. Bixler, ACS Organic Coating and Plastic Chemistry, Vol. 29, No. 2, Sept. 1969.
18. R. F. House, Can. Pat. 857,779 (1970).
19. H. R. Dittmar and E. D. Strain, U.S. Pat. 2,289,540 (1942).

20. H. P. Brown and C. F. Gibbs, *Ind. Eng. Chem.*, **47**, 1006 (1955).

21. W. Heller and T. C. Pugh, *J. Chem. Phys.*, **24**, 1107 (1956).

22. G. D. Parfitt, *Dispersions of Powders in Liquids*, Elsevier, Amsterdam, 1969.

23. W. D. Harkins, *J. Amer. Chem. Soc.*, **69**, 1428 (1947).

24. R. M. Fitch and T. Chen, *Polymer Preprints*, **10** (No. 1), (April 1969).

25. D. H. Napper and A. G. Parts, *J. Polym. Sci.*, **61**, 113 (1962).

26. C. P. Roe, *Ind. Eng. Chem.*, **60** (9), 20 (1968).

27. R. Davidson and M. Sitting, Eds., *Water-Soluble Resins*, Reinhold, New York, 1968.

28. V. A. Kabanov, *Polymer Preprints*, **11** (No. 2), (February 1970).