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INTERACTIONS OF CLAY MINERALS WITH ORGANIC POLYMERS. SOME PRACTICAL APPLICATIONS

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Abstract—An account is given of the interactions between clay minerals and organic polymers with particular reference to their applications in agriculture, foundation engineering and industry.

INTRODUCTION

THE INTERACTION of clay minerals with organic polymers have received a considerable amount of attention because of their great agricultural and industrial potential. It has not been possible, nor was it deemed desirable, to include all of the methods of formation and the properties of clay-polymer derivatives. Rather, in this article, an attempt is made to draw together examples from those areas in which the clay-polymer interaction has found practical applications.

The beneficial effect of organic matter on soil physical conditions has been recognized for a very long time. In recent years, it has become clear that the water-stability of natural soil/clay aggregates is related to the presence of polysaccharides in the soil (Greenland *et al.*, 1962; Harris *et al.*, 1963; Clapp and Emerson, 1965). Aided by the rapid advances in polymer technology, this observation has stimulated research into the use of synthetic organic polymers as conditioning and stabilizing agents in agricultural and foundation engineering applications (Hedrick and Mowry, 1952; Lamb and Michaels, 1954; Emerson, 1956; Mussell and Roth, 1957).

Of the many industrial processes in which raw or modified clays have been used (Jordan, 1961; Murray, 1961; Nahin, 1961; Cook, 1966), only those relating to their functions as fillers or reinforcing materials in elastomer and plastic compositions are included in this review. The term "filler" is used here in the sense of a finely divided solid which is incorporated into the polymer matrix in order to modify its properties and to meet specific industrial or commercial requirements. Because of this abundance, availability, low cost, and surface properties, the clay minerals are admirably suited for this purpose.

DISCUSSION

Effect of clay-polymer interactions on soil/clay properties

The addition of small quantities of charged and uncharged linear polymers to soil and clay systems has a profound effect on their physical and colloidal properties. The literature on this subject has been summarized by van Olphen (1963) and more recently by Greenland (1965) whilst Ingles (1968) has brought together information on the use of simple and polymeric organic compounds as soil stabilizing agents. Only the salient features will therefore be discussed in this instance.

Improvements observed in the structure and stability of soils after treatment with synthetic organic polymers are basically due to increases in aggregation and water-stability of the aggregates formed. Of a wide variety of organic polymers employed, polyanions and uncharged hydroxylated polymers have been most successful. At first sight, it might appear that positively charged polymers would be effective aggregate stabilizers but this does not accord with practice. Apparently, the rate of collapse of the polycation onto the negatively charged clay surface is so great that only very limited interparticle bridging by the polycation can be achieved.

Polyanions are known to be effective flocculants when added to dilute clay suspensions (Michaels, 1954; Bergmann and Fiedler, 1955; Beutelspracher, 1955; Michaels and Morelos, 1955; Packter, 1957; Warkentin and Miller, 1958; LaMer and Smellie, 1960; LaMer and Healy, 1963). Flocculation involves adsorption of the polyanion as well as formation of interparticle bonds. The mode of action of the polyanions has therefore been likened to the formation of a "string of beads" (Greenland, 1963). Unlike polycations and uncharged polymers of the polyvinyl alcohol type, polyanions do not appear to penetrate the interlayer space of the expanding layer-lattice minerals (Ruehrwein and Ward, 1952; Hagin and Bodman, 1954; Holmes and Toth, 1957; Ahlrichs, 1962) but are attached mainly to the edges of the crystals to form "peripheral" complexes (Emerson, 1955). However, under conditions in which the polyanion molecule is present in an undissociated or slightly dissociated form, some interlayer adsorption may occur. Thus, at a pH of 2·5, a considerable amount

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of a low molecular weight soil fulvic acid is adsorbed in the interlayers of montmorillonite (Schnitzer and Kodama, 1967). Electrostatic attraction to positive charges at crystal edges, precipitation and coordination involving multivalent exchangeable cations and hydrogen bonding between the carboxyl groups of the polyanion and the oxygens of the clay lattice, have been invoked as bonding mechanisms (Ruehrwein and Ward, 1952; Michaels, 1954; Emerson, 1956, 1960; Packter, 1957; Warkentin and Miller, 1958; van der Watt and Bodman, 1960). Under the conditions of maximum chain extension and hence optimum flocculating efficiency, however, the polyanion is largely repelled by the negatively charged clay surfaces unless the zeta potential is lowered by addition of electrolytes (Ruehrwein and Ward, 1952; Mortensen, 1960). The number of polyanion segments involved in interparticle bonding is therefore not likely to be large. Further, individual segment-to-clay bond is not a strong one so that polyanions are generally not very effective aggregate stabilizers.

On the other hand, uncharged flexible linear polymers such as the polyvinyl alcohols, have been shown to be highly effective in increasing the mechanical strength and water-stability of natural soil/clay aggregates (Emerson, 1963; Williams *et al.*, 1967, 1968). In aqueous solutions, the polyvinyl alcohol molecule exists as a compact, randomly coiled chain seemingly unpromising as a flocculant for dilute clay suspensions. However, on contact with the clay the molecule rapidly uncoils and spreads, in Greenland's phrase, like a "coat of paint". This mode of action explains why the polymer is strongly and irreversibly adsorbed by clays (Greenland, 1963; Emerson and Raupach, 1964). Although individual segments of the polymer chain form only weak bonds with the clay surface (in the order of 4kT), the total energy of adsorption is largely due to the numerous points of contact (Silberberg, 1962). Furthermore, there will be a significant gain in entropy since the adsorption of one polymer molecule is accompanied by the desorption of many water molecules which will favor the adsorption process. The adsorption isotherm for polyvinyl alcohol on clays is accordingly of the "high-affinity" or H-type (Giles *et al.*, 1960). When polyvinyl alcohol is added to a system in which the clay crystals or domains are already in close proximity, interparticle bonding may also occur. Thus, the addition of small amounts (<0·02 per cent by weight) of polyvinyl alcohol to air-dry montmorillonite greatly reduces water uptake by the clay. However, swelling of the clay-polymer complex in water is not reduced much below half of the value of the untreated clay. This residual swelling probably takes place within domains which are presumably loosely uncapsulated by the polymer chains. Further entry of the polymer molecule to points within the domain would be difficult and hence, the effectiveness of subsequent additions of polymer in reducing swelling is also less (Theng *et al.*, 1967). The large increases in strength and water-stability of clay aggregates containing polyvinyl alcohol are ascribed by Williams *et al.*, 1967) to the lining of the pore surfaces by the polymer binding together the clay domains which constitute the walls of the large pores. On wetting, water moves in a controlled fashion from these pores to the remainder of the pore space. A similar mechanism has been proposed by Quirk and Panabokke (1962) to account for the stabilizing action of organic matter in natural soil aggregates.

Ingles (1968) has pointed out that in addition to lining of the aggregate pores by polymers of the polyvinyl alcohol type, bridging between aggregates may be necessary to achieve the kind of stability required by the foundation engineer. He indicated that the "ideal" polymer for this purpose would be one with positive or uncharged groups attached at the ends of a negatively charged chain or backbone. Such a molecule would not tend to collapse onto the clay surface and would be capable of tying aggregates together. To this end, a series of hydrolyzed polyethyl acrylates of different chain length and terminated at each end by polyethylene glycol units, has been prepared in C.S.I.R.O. (Melbourne) laboratories. Preliminary tests indicate that they are superior to the commercially available krilium-type soil conditioners in their ability to strengthen and reduce the swelling of clay aggregates in water (Theng *et al.*, 1969). It seems that close cooperation between soil engineer and polymer chemist is needed to bring about further advances in this direction.

Effect of clay–polymer interactions on polymer systems

Because clays cost much less than the polymer or resin to which they are added as fillers, they are frequently and commonly considered merely as extenders. The studies of Uskov (1960 b) and of Solomon (1968), however, have made it abundantly clear that clay minerals are not chemically inert but actively influence the polymerization of organic monomers (Theng and Walker, 1970). Clays may also interact chemically with preformed polymers as evidenced by the positive difference between the integral heat of solution-wetting of a mere mechanical mixture of polymethyl methacrylate-kaolinite and that of the polymer-clay composite (Uskov *et al.*, 1966). The extent of this interaction is influenced by the degree of dispersion, the size

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and shape, and the surface properties of the clay particles.

The efficiency of clays in the filling or reinforcement of polymer systems is dependent on their degree of dispersion in the organic medium since the more highly dispersed they are the greater is the surface area available for interaction with the polymer matrix. Apart from the use of conventional non-ionic dispersants to render the clay surface hydrophobic and hence, more compatible with the organic phase, dispersion may be greatly improved by replacing part or all of the inorganic cations with organic ions or polycations (Carter *et al.*, 1950; Gluesenkamp, 1957; Ruehrwein, 1957; Uskov, 1960 a; Nahin and Backlund, 1963; Carrett and Walker, 1967). Mechanical grinding or vibration milling has also been used to achieve a good dispersion and when carried out in the presence of organic monomers, may give rise to graft polymers showing substantial increases in hardness and flow temperature (Uskov, 1960 b; Uskov and Kusnitsyna, 1960).

The effect of clay particle size on the mechanical properties of rubber and amorphous polymers has been investigated by Cook and Pickering (1968) and by Uskov *et al.* (1964), respectively. In general, the efficiency of clay fillers in upgrading these properties may be considerably increased by reducing their average particle size. Likewise, the mechanical strength and stability of crystalline polymers, e.g. polycaproamide, can be increased by adding kaolinite to the polymer melt. On crystallization, the clay particles tend to become concentrated in the interspherulitic regions reducing the mobility of the polymer in these areas and preventing their regrouping in the crystalline phase. As a consequence, the average size of the spherulites is decreased, this reduction being greater as the size of the filler particles is decreased (Solomko *et al.*, 1966).

The shape of the filler particle has also a marked effect on its efficiency as a reinforcing agent of polymer systems. Thus, the plate-shaped kaolinite crystals have a greater stiffening effect on rubber than the spherical whiting particles of equivalent diameter. This is evident in the viscosity of an unvulcanized rubber compound and in the modulus of a vulcanizate. The stiffening effect of clay in the unvulcanized system gives better dimensional control and stability during processing (Cook and Pickering, 1968).

Clays, especially kaolinites, enjoy a substantial application for the filling and reinforcement of natural and synthetic rubber (Cook and Pickering, 1968; Smith, 1968). Infrared studies indicate that the interaction of kaolinite with rubber involves hydrogen bonding between the rubber molecule and the hydroxyl groups on the clay surface, particularly those located at crystal edges (Suito and Arawaka, 1964; Tarasenko *et al.*, 1964). A similar bonding mechanism has been postulated by Kiseley *et al.* (1968) for the interaction of polyvinyl acetate and polyalkyl methacrylates with silica surfaces. As was mentioned earlier, under certain conditions a considerable amount (20 per cent by weight) of polymethyl methacrylate may be grafted onto bentonite from which it could not be extracted by prolonged boiling in benzene (Uskov *et al.*, 1963). This observation was ascribed to hydrogen bond formation between the oxygens of the polymer molecule and the hydroxyls on the clay lattice since polystyrene which is incapable of being bonded in this way, could not be grafted. Their evidence, however, is not entirely convincing since only very few hydroxyl groups exposed at the edges of the montmorillonite lattice would be available for hydrogen bond formation. It seems more probable that the polymethyl methacrylate molecule penetrates the interlayer space of montmorillonite since its monomer does so whilst styrene is not intercalated (Blumstein, 1965; Solomon and Rosser, 1965; Solomon and Loft, 1968).

A highly effective method of reinforcing natural and synthetic elastomers has recently been claimed by Libby *et al.* (1967). It involves grafting of amino silane to kaolinite by attachment of the hydrolyzed silanol group to the clay surface leaving the pendent amino group free to react with the polymer molecule during vulcanization. The resulting cross-linked polymer-clay network shows significant improvements in modulus, abrasion resistance and compression-set properties as compared with the unfilled material.

Clay minerals have also been used in the filling of polyvinyl chloride and related thermoplastic compounds (Cook, 1966). As distinct from their application in elastomer systems, however, clays confer little or no reinforcement although they do increase the hardness and the rigidity of the product (Furter, 1964). A notable exception and one which may be regarded as a major advance in this direction has been reported by Fallick *et al.* (1968). Using a novel approach, they were able to develop a family of mineral (kaolinite and asbestos) reinforced linear polyethylene to which they gave the name of "Ceraplasts". Their method involves dispersing the filler particles in the polymer melt, encapsulating them with a thin sheath of resin and firmly binding this encapsulant to both the mineral and the polymer matrix. The substantial increases in tensile and impact strengths of "Ceraplasts" over conventionally filled polyethylene, are associated with the presence of a gradient in modulus between that of the mineral and the polymer matrix

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in the encapsulant. A later variant is the composite obtained by coating the clay particles with an ethylenically unsaturated compound and a free radical generator prior to blending the complex with polyethylene (Bixler and Fallick, 1969). A similar process has been claimed by Baum (1969) who coated his clays with high boiling point (>140° C) non-reactive, non-acidic, oxygen-containing organics and an organic peroxide which serves as a cross-linking agent between the modified clay and the polyethylene molecule. An important advantage of clay-filled over carbon black-filled polyethylene is that the former, besides displaying equal or superior mechanical properties to the latter material, are white and may be given any desired color by addition of an appropriate colorant.

Cross-linking of polyethylene and other thermoplastics to clay surfaces can also be achieved by irradiation techniques (Nahin and Backlund, 1963). The extent of this cross-linking may be greatly improved by priming the clay surface with organics having "polyethylene-like" chains, e.g., polyvinyl alcohol or hexamethylene diamine. When such modified clays are exposed to gamma rays or fast electrons in the presence of polyethylene, products of great strength, excellent thermal stability and resistance towards organic solvents, are obtained (Nahin, 1964).

Modified clays have also been successfully incorporated into polyurethane foams with the principal objective of lowering the cost of the product. Since a low density, open-celled material is desired, conventional inorganic additives such as silica, are not satisfactory in that they adversely affect the density and cell structure of the foam when used in appreciable quantities (10 per cent by weight or more). On the other hand, palygorskite ("attapulgite") coated with water-soluble polymers (polyvinyl pyrrolidone, polyvinyl alcohol, polyacrylamide) dispersed in the polyisocyanate–polyol system prior to its foaming, does not appear to cause an increase in density or a deterioration in texture (Ferrigno, 1962). The prime advantage in using coated clays of this nature, however, lies in the attendant increase in the volume of the foam produced by a given weight of reaction mixture so that the pigment may be considered as a true extender.

An extension and modification of the above process to include a wide range of modified clays and related alumino-silicate minerals, has been claimed by Showalter (1966).

CONCLUSION

In his review, Nahin (1961) has emphasized the importance of developing our concepts of clay-organic interactions in order for these to become practical. To a large measure, Nahin's perspective has been substantiated in that we have seen considerable progress being made in this area over the past few years. The development of synthetic organic polymers for soil stabilization purposes has, admittedly, not been dramatic. This is due partly to the high cost of organic soil conditioners as compared with that of conventional inorganic additives, and partly to the divergent requirements demanded from a soil stabilizing agent by the agriculturist and by the soil engineer. On the other hand, even this short appraisal has made it abundantly clear that clay minerals play an indispensable part in elastomer and plastic processing not to mention the applications they enjoy in the manufacture of paints, paper, insulation compounds, polyesters and epoxy resins.

One may, with confidence, expect to see an increasingly wider field of application of clay minerals in industry. Advances in clay-polymer technology will come about by a better understanding of the factors determining the interactions of organic polymers with clay surfaces and by the innovations and developments based on this understanding.

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Résumé – On donne un exposé des inter-réactions entre les minéraux argileux et les polymères organiques, en mentionnant en particulier leurs applications dans les domaines de l'agriculture, de la technique des fondations et de l'industrie.

Kurzreferat – Es wird über die Wechselwirkungen zwischen Tonmineralen und organischen Polymeren berichtet, und zwar unter besonderem Hinweis auf ihre Verwendungsbereiche in der Landwirtschaft, dem Ingenieurbau und der Industrie.

Резюме — Подробно рассмотрено взаимодействие глинистых минералов с органическими полимерами; особое внимание уделено их применению в сельском хозяйстве, для улучшения свойств грунтов и в промышленности.

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