ORGANOCLAYS BONDED TO POLYETHYLENE BY IONIZING RADIATION*

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ABSTRACT

EXPLORATORY experiments on irradiation of mixtures of polyethylene and organo-montmorillonites with gamma rays indicated that the polyethylene became crosslinked to the organoclays. Subsequently, 264 samples of 1 : 1 clay–polyethylene compositions were irradiated with 2 MeV electrons and tested for tensile strength and weight fraction extractable in toluene at 110°C. From statistical analysis of the variables of clay lattice, clay surface, polyethylene type and radiation dose it is concluded that: (1) polyethylene can be bonded directly to the clay surface by ionizing radiation, and (2) at least one organoclay bearing a " polyethylenelike " chain, polyvinyl alcohol, is more effective than wholly inorganic clay for the purpose of radiatively linking polyethylene to clay surface. The data below show the markedly increased solvent resistance of polyethylene radiatively bonded to clay over that of equivalently irradiated pure polyethylene.

Clay	Clay surface	Type of polyethylene	Electron dose, Mrad	Weight % of sample not dissolved*
(Pure polyethylene)	None	Linear	55	12.8
Montmorillonite	4-Vinyl pyridinium	Linear	55	94.8
(Pure polyethylene)	None	Linear	100	24.4
Montmorillonite	Hexamethylene-diammonium	Linear	100	96.6
Montmorillonite	Polyvinyl alcohol	Linear	100	98.2
(Pure polyethylene)	None	Branched	100	37.4
Kaolinite	Proton	Branched	100	97.1
Montmorillonite	Polyvinyl alcohol	Branched	100	99.2

* After 7 weeks.

INTRODUCTION

IT IS well-known that clays can be usefully modified by reaction with organic materials through ion exchange, acid-base neutralization or adsorption. A number of such organoclay complexes have attracted commercial interest

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(Jordan, 1963; Murray, 1963, pp. 296–7; Nahin, 1963a and b; Nahin and Backlund, 1963). This is because these materials have properties that reflect the presence of both the organic and inorganic parts and, so, behave as " hybrids ".

In the case of clay-polymer combinations, the desired complex could be made chemically by copolymerizing an organic monomer with a clay bearing active organic groups or by treating an active organoclay with a functionally active organic polymer. The reaction of styrene with 4-vinyl pyridinium montmorillonite is an example of the first type and the reaction of 4-vinyl pyridinium montmorillonite with isoprene-terminated polyisobutylene is an example of the second type. A third type of clay-polymer combination is that between a relatively unreactive polymer and a clay that may or may not carry active organic functional groups, e.g. the combination of ethylpolysiloxane and kaolinite (Kukharskaya, Skorik and Boiko, 1963) or of polyethylene and montmorillonite.

Synthesis of such compositions by ordinary chemical reactions involves complex problems of polymerization catalysts, polymerization regulators, temperature control, separation of homopolymer from desired product, etc. Irradiation* with gamma rays or electrons to induce crosslinking between an organic polymer and a suitably modified clay seemed to be an experimentally simpler way of making organosilicate graft-type interpolymers: organoclay and polymer are dispersed homogeneously in the absence of any added chemicals and irradiated. If the irradiated mixtures proved to have superior properties, an effort to prepare similar materials by possibly more economical copolymerization reactions would be justified.

Polyethylene, a polymer derived from petroleum, is known to become crosslinked by ionizing radiation. The basic concept of the work reported here was to prime the clay surface with " polyethylenelike " tails and bridges, such as would be afforded by reaction of hydrogen-clays with polyvinyl alcohol or hexamethylene diamine, and then crosslink them to the much longer real polyethylene chains by means of gamma rays or fast electrons. If the chains of methylene groups ($-CH_2-$) between or on the clay surfaces were long enough, the crosslinking reaction would proceed between the polyethylene chains and the clay-surface chains as readily or nearly so as between contiguous polyethylene chains. The result would be a three-dimensional polymer in which the organic chains become firmly anchored to large silicate sheets of great strength, excellent thermal stability and immunity to organic solvents.

In the first experiment to test this concept solid dispersions containing equal weights of organoclay and polyethylene were irradiated in a pure gamma field generated by nuclear-reactor spent fuel elements. The results indicated that the polyethylene became crosslinked to the clay. Therefore, a second more extensive experiment was conducted based on the statistical

* Studies of a similar nature have recently been reported (Egorov, Novikov, Razgon and Tsetlin, 1962; Glavati, Polak and Shchekin, 1963).

method of "factorial design" and using the more easily controllable fast electrons as ionizing agent. The details follow.

EXPERIMENTAL

Materials

The chemicals and methods used to prepared the various clay surfaces are given in Appendices 1 and 2. The clays were research-grade kaolinite from the Georgia Kaolin Company and Wyoming montmorillonite from the Baroid Division of the National Lead Company. The two polyethylenes used were the conventional branched low-density (0.932 g per cc) Union Carbide Corporation DYNK grade of 24,000 molecular weight and the relatively linear high-density (0.958 g per cc) Hercules Powder Company HIFAX of over 50,000 molecular weight.

Gamma Irradiation of Clay-Polyethylene

Thirty-five grams of each of the following clays:
As-received montmorillonite
Hydrogen montmorillonite
Oleyl ammonium montmorillonite
Bentone-18 (octadecyl ammonium montmorillonite)
Bentone-34 (dioctadecyl ammonium montmorillonite)
Hexamethylene diammonium montmorillonite

was dispersed in 35 g of DYNK polyethylene on a small heated rubber mill. The milling procedure was the same for all samples: the polyethylene was preheated until tacky, banded on the rollers at a surface temperature of 106°C using 33 psig steam and then loaded with clay. The total time of mixing to a homogeneous sheet was 15 min. Four samples, 3 × 3 × 1/10 in., of each composition were compression-molded at 150°C and 3300 psi for 10 min in an electrically heated hydraulic press and cut into halves. The four samples of each composition were committed as follows: one-half of each was retained as a non-irradiated control; the remaining halves of Samples 1 and 2 were irradiated in the low-level gamma field at 28 megarads (Mrad)* as duplicates and the remaining halves of Samples 3 and 4 were irradiated in the high-level field at 146 Mrad as duplicates. The samples were placed in standard irradiation urns, one for the low-level, the other for the high-level field and sent to Argonne National Laboratory. The low-level irradiation of 28 Mrad was a 24-hr exposure in a matrix of spent fuel elements; the 146-Mrad exposure was acquired over a weekend. Upon return, the samples were tested qualitatively for softening and quantitatively for tensile strength.

Softening test and results.—The softening test was used as a qualitative criterion of the degree of radiation bonding achieved. A strip of 16-gauge

* One megarad (Mrad) is 10^8 ergs ionizing energy absorbed per gram of sample.

stainless steel was formed into a U-shaped holder 2 in. wide, 2 in. high and 4 in. in length. Strips, $3 \times 1/4$ in., were cut from the samples and laid across the open part of the holder. A ruler was taped to one end of the holder to measure the inches of dip in air as the temperature was increased in a small temperature-controlled oven. The data obtained established the ability of the test to distinguish measurable differences among the various samples and indicated that all of the irradiated samples were thermally more stable than the non-irradiated samples. Therefore, a few selected samples were subjected to a more prolonged and severe test of the same general nature. Samples of pure milled DYNK polyethylene, as-received montmorillonite–DYNK, hydrogen montmorillonite–DYNK, oleyl ammonium montmorillonite–DYNK and hexamethylene diammonium montmorillonite–DYNK, which had been irradiated with 0, 28 and 146 Mrad of gamma rays were kept on the holder in air at 122°C for four days. *All of the non-irradiated samples collapsed in less than an hour*, and *none of the irradiated samples was collapsed even after* 4 *days*. The relative degrees of droop, best to worst, were: oleyl, hexamethylene, hydrogen, pure DYNK. The 146-Mrad samples remained very nearly horizontal; the 28 Mrad samples showed moderate droop of about 1/4 in. over the 2-in. bridge. All of the non-irradiated control samples became hard and brittle and were severely charred; all of the irradiated samples remained flexible and almost unchanged in external appearance.

Tensile test and results.—Stress-strain curves were run on $2\frac{1}{2}$-in. specimens using an Instron Tensile Testing Instrument Type TT-C. Conditions of operation were: load scale, 0–20 lb; magnification ratio, 2 : 1; gauge length, 1 in.; head, 2.0 in. per min; chart, 4 in. per min. The data are given in Table 1.

TABLE 1.—Effect of Gamma Irradiation on Tensile Strength of 1:1 Organo-Montmorillonite-Polyethylene Compositions

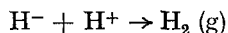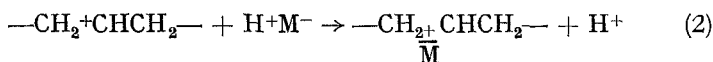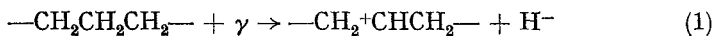|	Tensile, psi before irradiation	Tensile, psi, after	
Organoclay		28 Mrad	146 Mrad
Polyethylene (milled)	2923(6)*	2542(3)	2240(2)
As-received bentonite (Na–Mg form)	1800(5)	1983(2)	2033(2)
Hydrogen montmorillonite	1904(4)	2083(2)	2208(2)
Hexamethylene diammonium montmorillonite	2228(4)	2450(2)	2640(2)
Oleylammonium montmorillonite	2058(5)	2340(2)	2705(2)
Bentone-18	1800(5)	2050(2)	2532(2)
Bentone-34	941(6)	1199(3)	1070(3)

* Number in parenthesis designates number of tensile tests.

The significantly increased tensile strengths of the exposed samples indicate that the polyethylene became crosslinked to the clay, the more so at the higher dose. (The elongations were correspondingly decreased.)

Thus, the tensile strength of the oleyl ammonium montmorillonite-polyethylene increased 31.5 per cent in the high field; the pure polyethylene lost 23.3 per cent. Hexamethylene diammonium montmorillonite–DYNK gained 18.5 per cent. Bentone-18–DYNK was improved by 40.7 per cent but to a lower final tensile strength than was obtained with either the oleyl or hexamethylene derivatives. Since Bentone-18 has a higher organic content than these derivatives, this result may be considered as indicative of the tensile-improving effect of crosslinking polyethylene to organic-surfaced clay.

In no case was tensile strength impaired by irradiating the organoclay–polyethylene compositions. The sodium montmorillonite and hydrogen montmorillonite control samples, although providing less improvement, appeared to protect the polyethylene against radiation damage; the sodium montmorillonite gave a 12.4 per cent increase in tensile strength, and the hydrogen montmorillonite gave a 16.0 per cent improvement in the high gamma field.

The latter result may mean that reinforcement occurred through gamma-catalyzed ion exchange of the clay lattice with the momentarily positively charged " hot " polyethylene radical according to the reactions:

$$—CH_2CH_2CH_2— + \gamma \rightarrow —CH_2{}^+CHCH_2— + H^- \tag{1}$$

$$—CH_2{}^+CHCH_2— + H^+M^- \rightarrow —CH_{\underset{\overline{M}}{2+}}CHCH_2— + H^+ \tag{2}$$

$$H^- + H^+ \rightarrow H_2 \text{ (g)}$$

where γ = gamma quantum, M^- = negatively charged montmorillonite lattice and $—CH_{\underset{\overline{M}}{2+}}CHCH_2—$ = polyethylene montmorillonite ion-exchange complex.

These experiments suggested the possibility that clay surface chains even longer than the C-18 oleyl might be more effective in binding polyethylene to clay. Accordingly, montmorillonite and kaolinite complexes of polyvinyl alcohol, poly-(ethylene oxide) and poly-(vinyl siloxane) were prepared and added to the group of organoclays investigated in the second phase of this study.

Electron Irradiation of Polyethylene–Clay

The encouraging results of the gamma ray experiment led to a more comprehensive study of the effect of irradiation on tensile strength and solvent resistance of the system 1 : 1 organoclay–polyethylene. For this second phase, high-energy electrons produced by a General Electric resonant transformer were employed. The main reasons for changing to accelerated electrons were: the energy and dosage are easily controllable, this type of machine is in current commercial use and the method would be less time consuming for the large number of samples needed. The following variables were investigated:

clay lattice: montmorillonite and kaolinite
clay surface: 3 inorganic and 7 organic
polyethylene type: branched and linear
electron dosage: 0, 10, 55 and 100 Mrad

The statistical experimental method of " factorial design " (Davies, 1956) was used in conjunction with an IBM-650 computer to circumvent the need for the large number of samples and correspondingly much larger number of tests required for a complete single-factor-at-a-time type of experiment. Thus, in a single-factor-at-a-time experiment, the number of possible combinations of the 10 surfaces, 2 clays, 2 polyethylenes, 4 dosages plus blanks on the 2 pure polyethylenes is $10 \times 2 \times 2 \times 4 + 4 \times 2 = 168$. The factorial design required only 88 different compound-treatment combinations from which the analogous properties of the 80 combinations not run could be calculated with a relatively high degree of certainty. Selection of a much smaller number of samples for more thorough evaluation was then made.

The samples, consisting of 50.0 g each of organoclay and polyethylene, were prepared for the electron irradiation in essentially the same way as for the gamma irradiation except that both the DYNK and HIFAX samples were banded on the rollers at 80 psig (300°F) steam pressure. The cooled strip was cut to fit a 6-in.^{2} mold and treated according to the procedure described in Appendix 3.

Two hundred and sixty-four samples, $6 \times 2\frac{3}{4} \times 0.1$ in., were sent to the General Electric Company for the irradiation service. The conditions were 7.5 Mrad per pass at a conveyor speed of 40 in. per minute at 2 MeV, and 2-mA beam-out current. The samples were sufficiently thin to warrant irradiation from one side only. The one-side-only treatment would not appreciably affect the validity of the solubility test, since this test is an indirect measure only of the number of clay-to-polyethylene bonds formed; however, the tensile results could conceivably be adversely affected because the degree of crosslinking will vary with sample thickness owing to decrease in electron intensity with sample depth.

Another fact having direct bearing on the interpretation of the tensile results is that the rate of irradiation was too high in some cases and resulted in visible gas bubbles with consequent physical injury to the samples. The wide variation in gas bubble evolution can be taken as an indication of the differences in radiation sensitivity of some of the organic surfaces on the clay derivatives. For example, oleyl is much more productive of bubbles than is hexamethylene when attached to the same clay. This behavior can be avoided by lowering the dose rate and/or by using longer cooling periods between passes.

Tensile test and results.—Stress-strain curves were run on standard-size 6-in. specimens using an Instron Tensile Tester in accordance with ASTM Test D 412-51T. The results are tabulated in Appendix 4.

The factorial design tensile coefficients show conclusively that certain of

the clay surfaces are more effective than others for radiative crosslinking with polyethylene, the best being 4-vinyl pyridinium, ammonium and polyvinyl alcohol. Thus, as much as 1514 ± 330 (or 22 per cent) psi more tensile strength can be realized *on the average for this particular design* by changing the organosurface from oleyl ammonium to 4-vinyl pyridinium. This may well result from vinyl addition to polyethylene unsaturation near the clay surface. Alternatively, this addition to tensile strength may originate in part during the milling operation and not be due primarily to radiation (see beta dosage coefficients). The most significant factor affecting tensile strength is polyethylene type for which a tensile increase of 1044 ± 49 (4.7 per cent) psi, on the average, is realized by changing from DYNK to HIFAX. This may be due to a closer approach of the much higher molecular weight HIFAX linear chains to the clay surface than is true for DYNK; the latter has a more irregular configuration because of its protruding side branches that may result in a larger average distance from the clay surface of the $—CH_2—CH_2—$ linear portions and their pendant vinyl groups. This would tend to decrease the type of addition reaction that may be required for higher tensile strength. Moreover, the observed tensile increase was obtained under mild conditions of mill mixing and appears not to be sharply dependent on radiation dosage.

The remaining factors of clay lattice type and beta dosage, while not insignificant, are definitely less important than the nature of the clay surface modifier and type of polyethylene. Thus, changing from montmorillonite to kaolinite produces, on the average, a tensile increase of 381 ± 49 (13 per cent) psi; the beta-dose effect from zero to 100 Mrad decreases the tensile strength by 409 ± 66 (16 per cent) psi, on the average, for this particular factorial design.

Solubility in toluene.—Although the tensile tests showed conclusively that polyethylene-to-clay bonds were formed even in the absence of radiation, it appeared desirable to verify this by at least one different test. In work with high polymers, the decrease in solubility of a polymer in a solvent in which it is normally soluble is taken as a measure of the degree to which the polymer has become crosslinked. Polyethylene, normally soluble in toluene, when linked to toluene-insoluble clay by primary chemical bonds would not be expected to dissolve. Therefore, the per cent loss in weight (sol fraction) of the samples upon extraction in toluene at 110°C for periods ranging from 24 hr to 7 weeks was determined.

It should be pointed out that the solubility test is a better indicator of chemical bonding, in this case, than is the tensile test, because the sol-fraction data are not seriously affected by such sample artifacts as microscopic inhomogeneities, cracks, cuts and flex history; the tensile data are very seriously affected by such artifacts.

The test procedure consisted of the following steps: the samples, weighing from 2–3 g, were dried to constant weight under nitrogen in a vacuum oven at 70°C, placed in stainless steel cylindrical 16 mesh, $2 \times 1\frac{5}{16}$ (diam.)-in. wire baskets and extracted in a 20-place stainless steel electrically heated Soxhlet

extractor, using Baker & Adamson reagent grade (A.C.S.) toluene (b.p. 110.6° ± 1.0°C). All samples were finally dried to constant weight.

Solubility test results

One-day experiment.—All irradiated and non-irradiated control samples were extracted for 24 hr to obtain a preliminary ranking of the various compositions for the factorial design analysis. *All unirradiated polyethylenes and their organoclay co-mixtures dissolved or disintegrated completely under this test.* The factorial design coefficients are given in Appendix 4. The fact that the oleyl montmorillonite ranked high by tensile strength in the gamma ray series but lowest in both tensile and sol fraction tests in the electron experiment is explained as follows: The ionization produced by the gamma rays is much more uniform throughout the sample than is the case with the electrons (samples irradiated from one side only) because of the difference in penetrating powers of the two forms of radiation.

One-week experiment.—The selected group of 55-Mrad and 100-Mrad samples was extracted repeatedly for an initial period of 24 hr and then for successive 48-hr periods until a total of 7 days had been accumulated. The results are given in Table 2.

TABLE 2.—SOL FRACTIONS OF ELECTRON-IRRADIATED CLAY–POLYETHYLENE 1:1 MIXTURES AFTER EXTRACTION IN TOLUENE AT 110°C FOR ONE WEEK

DYNK Samples	Sol Fraction	HIFAX Samples	Sol Fraction
	55 MRAD		
DYNK (100%)	36.6	HIFAX (100%)	39.4
VSA-Montmorillonite	9.86	OA-Montmorillonite	12.1
OA-Montmorillonite	8.85	HMD-Kaolinite	10.7
PVA-Kaolinite	5.48	VSA-Montmorillonite	9.48
HM-Kaolinite	5.00	PVA-Kaolinite	8.70
H-Montmorillonite	4.69	H-Montmorillonite	4.76
		4VP-Montmorillonite	4.20
	100 MRAD		
DYNK (100%)	24.7	HIFAX (100%)	23.3
VSA-Kaolinite	3.93	OA-Kaolinite	5.69
PVA-Montmorillonite	3.71	VSA-Kaolinite	4.61
HMD-Montmorillonite	3.51	H-Kaolinite	3.76
OA-Kaolinite	3.51	HMD-Montmorillonite	2.93
H-Kaolinite	2.58	PVA-Montmorillonite	2.53

Table 2 shows clearly that the irradiated clay-polyethylene compositions contain considerably smaller sol fractions than the pure polyethylenes. Moreover, after the first day, the rate of extractive weight loss observed was markedly less for the clay-containing samples than for the pure polyethylenes. This may be interpreted as insolubilization of the previously toluene-soluble polyethylene either by radiatively induced primary bonding of polyethylene to the organic part of the clay surface or to the clay lattice directly,

or, alternatively, by " clathration " or total nonbonded inclusion of the clay by a spatial network of radiatively induced polyethylene crosslinks. This latter possibility seems less likely because, unless the clay behaves in some unknown way as a crosslinking catalyst or interferes substantially with the dislinking reaction (which occurs simultaneously with the crosslinking reaction, although to a lesser net extent), the rate of increase in the sol fraction would be expected to be even greater than for the pure polyethylene. This latter would be true because the density of the clay lattice (2.65) is much greater than that of polyethylene and, therefore, the dissolution of equal amounts of polyethylene in the two cases would result in greater sol fractions for the clay-containing samples—a circumstance that was not observed.

These speculations about a possible mechanism of the radiative insolubilization or " bonding " reaction made it seem worth while to extend the extraction periods from a scale of days to a scale of weeks. The objective was to determine quantitatively, in terms of sol fractions, whether the rate of weight loss of the clay–polyethylene samples continued to decrease with respect to the rate of weight loss of the pure irradiated polyethylenes.

Table 3.—Sol Fractions of Electron-Irradiated Clay-Polyethylene 1:1 Mixtures after Extraction in Toluene at 110°C for Seven Weeks

DYNK samples	Sol fraction	HIFAX samples	Sol fraction
	55 Mrad		
—	—	HIFAX (100%)	87.2
—	—	4VP-Montmorillonite	5.15
	100 Mrad		
DYNK (100%)	62.6	HIFAX (100%)	75.6
HMD-Montmorillonite	22.2	H-Kaolinite	4.77
H-Kaolinite	2.89	HMD-Montmorillonite	3.40
PVA-Montmorillonite	0.79	PVA-Montmorillonite	1.84

Accordingly, a selected series of samples in quadruplicate (Table 3) was subjected to three successive extractions of 1, 2 and 4 weeks for a cumulative total of 7 weeks. Meticulous care was taken to assure validity of the sol-fraction data, viz. before beginning the run all samples were dried at 70°C in a vacuum oven with repeated purging with nitrogen for a total of 91 hr until constant weight was obtained using an automatic (Fischer Gramatic) balance. The samples were extracted for one week and then dried 120 hr to constant weight. An additional 2-week extraction followed, and this time it was found necessary to dry 120 hr at 80°C.

Seven-week experiment.—After 7 weeks of extraction, the 100-Mrad pure DYNK had lost 62.6 per cent of its weight, whereas hydrogen kaolinite–DYNK lost 2.89 per cent and polyvinyl alcohol montmorillonite–DYNK lost only 0.79 per cent. The reason for the progressively lower sol fractions in the latter is unknown. Oxidation may be the cause, although it seems unlikely

this would occur in a closed system containing boiling toluene and one atmosphere pressure of toluene vapor.

The 100-Mrad pure HIFAX lost 75.6 per cent of its weight, whereas hexamethylene diammonium montmorillonite–HIFAX lost 3.40 per cent and polyvinyl alcohol montmorillonite–HIFAX lost only 1.84 per cent.

The influence of radiation dose is increasingly evident from the data for 4-vinyl pyridinium montmorillonite–HIFAX at 55-Mrad; after 7 weeks, the pure HIFAX had lost 87.2 per cent of its original weight, whereas the organoclay–HIFAX lost only 5.15 per cent.

These results tend to confirm the first mechanism, namely, direct bonding of polyethylene to clay and resultant insolubilization. The sol fractions of the clay–polyethylenes showed little increase with extraction time, whereas the pure polyethylenes indicated eventual complete solubility. The pure polyethylenes were reduced to brittle, yellowed shapeless masses; the clay–polyethylenes, for the most part, remained flexible and retained essentially their original shapes and colors. The appearance of a typical group of samples is shown in Plate 1.

CONCLUSION

It is concluded that (1) polyethylene can be bonded directly to a clay surface by means of ionizing radiation, and (2) at least one organoclay bearing a " polyethylenelike " chain, polyvinyl alcohol montmorillonite, is more effective than wholly inorganic clay for the purpose of radiatively linking polyethylene to clay surface.

The resultant general classes of new materials are visualized as polyorganosilicate graft-type polymers. It should prove feasible to obtain similar results with monomers and other polymers by wholly chemical means when suitable organo-functional groups are attached to the clay surface.

ACKNOWLEDGMENTS

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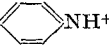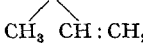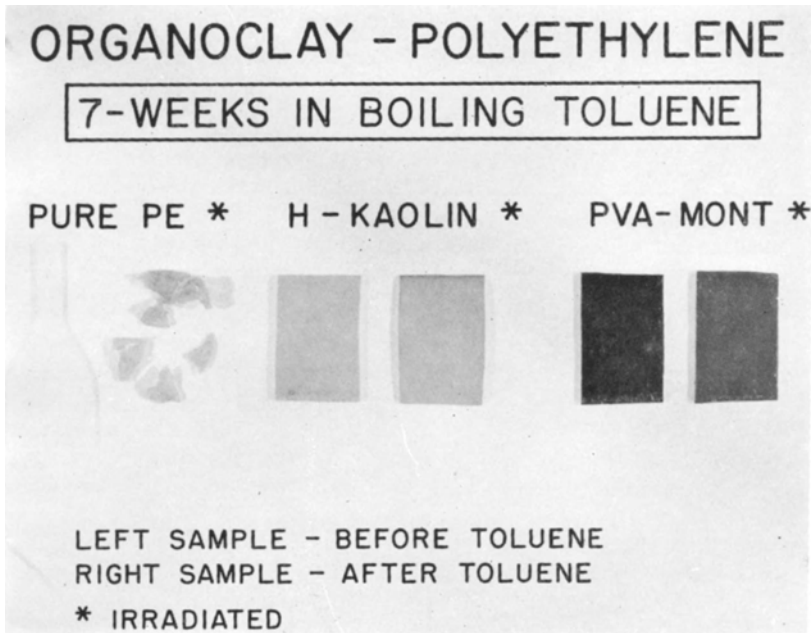
ORGANOCLAY – POLYETHYLENE

7-WEEKS IN BOILING TOLUENE

PURE PE *   H – KAOLIN *   PVA – MONT *

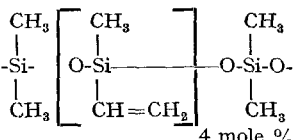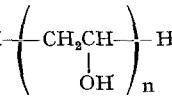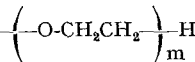LEFT SAMPLE – BEFORE TOLUENE
RIGHT SAMPLE – AFTER TOLUENE
* IRRADIATED

PLATE 1

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Appendix 1. Table of Clay Surfaces

Derivative	Symbol	Chemical Structure	Supplier of Organic Intermediate
Calcium Ion	Ca	Ca^{++}	
Proton	H	H^+	
Ammonium	NH_4	NH_4^+	
Oleyl ammonium	OA	$CH_3(CH_2)_7CH:CH(CH_2)_8NH_3^+$	Armour & Company
Hexamethylene diammonium	HMD	$^+H_3N(CH_2)_6NH_3^+$	E. I. du Pont de Nemours & Co (Inc.)
4-Vinyl pyridinium	4VP	$CH_2:CH$—⟨ ⟩—NH^+	Reilly Tar & Chemical Corp.
Vinyl silicone ammonium	VSA	$(CH_3O)_3Si\text{-}O\text{-}Si(O\text{-}Si)_?\text{-}O\text{-}(CH_2)_{5-10}\text{-}NH_3^{+*}$ CH_3 $CH:CH_2$	Dow Chemical Company
Poly-(vinyl silicone) ("Silastic S-2054")	PVS	$-Si-[O-Si]-O-Si-O-$ (CH_3) (CH_3, $CH=CH_2$) (CH_3) 4 mole %	Dow Chemical Company
Polyvinyl alcohol ("Elvanol 72-60")	PVA	$H\left(CH_2CH\atop OH\right)_n H$	E. I. du Pont de Nemours & Co. (Inc.)
Poly-(ethylene oxide) ("Polyox WSR-701")	PO	$H\left(O\text{-}CH_2CH_2\right)_m H$	Union Carbide Corp.

* Postulated structure based on correspondence with supplier.

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APPENDIX 2. PREPARATION OF SURFACE-MODIFIED CLAYS

The hydrogen, calcium and ammonium forms of the clays were prepared by ion exchange on Amberlite IR-120 resin columns. Organic ammonium clays were prepared by neutralization of hydrogen clays to pH 7.00 ± 0.05 with the appropriate amine. The poly-(vinyl silicone), polyvinyl alcohol and poly-(ethylene oxide) complexes were prepared by simple adsorption from solution. Analytical data for most of the preparations are given below.

Analytical Data[1]

Clay[2]	Total CEC[3] meq/100 g	Hydrogen Ion Exch. Cap., meq/100 g	Nitrogen[4] %	Carbon[5] %	Hydrogen %	CaO %
H-M	67.8	29.3	0.432			0.08
H-K	3.0	2.0	0.022			0.065
Ca-M	66.6	<0.1	0.050			1.30
Ca-K			0.026			
NH₄-M	73.1	0.2	1.02			
NH₄-K			0.044			
4VP-M	28.3	0.2	0.565	4.9	1.4	
4VP-K		0.4	0.050	([6])	1.7	
HMD-M	24.5	2.6	1.01			
HMD-K	2.3	0.3	0.024			
OA-M	44.8	0.5	0.890			
OA-K	6.2	0.7				
PVA-M	69.3	27.2	0.362	1.5	1.4	
PVA-K		1.5		1.1	1.9	
PO-M	69.3	32.2		1.4	1.4	
PO-K		8.2		1.3	1.9	

[1] No data available for VSA and PVS derivatives.

[2] See Appendix 1 for definition of symbols; M = montmorillonite, K = kaolinite.

[3] Cation exchange capacity.

[4] Kjeldahl.

[5] By combustion—micro method.

[6] Not detected.

APPENDIX 3. PREPARATION AND LABELLING OF SAMPLES FOR ELECTRON IRRADIATION

Four $6 \times 6 \times 1/10$-inch individually compounded samples were made for each composition by blending 50-g modified clay with 50-g preheated polyethylene on a two-roll steamheated mill. The samples were molded in a standard $7\frac{1}{2} \times 7\frac{1}{2}$ in. overall ASTM mold between standard ferroplates in a single-place electrically heated Wabash 7 in.-stroke hydraulic press. The molding cycle was: 2-min preheat, at no applied pressure, 5 min at 982 psig, and, finally, for 10 min at 1339 psig. Mold release agent was silicone diluted with benzene.

The following diagram shows how the four samples of a given composition were stamp-labelled for the treatments at 10 and 100 Mrad.

34A-10	34A-100		34B-10	34B-100		34C-10	34C-100		34D-10	34D-100
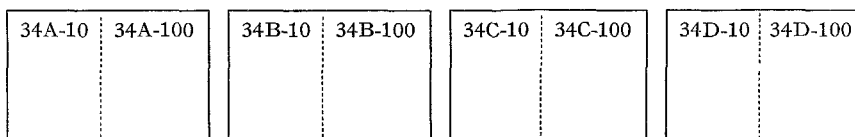
It is to be especially noted that each of the 10-Mrad and 100-Mrad slabs is an individually compounded, individually molded, and individually irradiated specimen. It should also be noted that, because of the factorial design of this experiment, there are no 0-Mrad or 55-Mrad analogues; similarly, the 0-Mrad and 55-Mrad samples have no 10-Mrad or 100-Mrad analogues.

Appendix 4. Electron Irradiated 1:1 Clay-Polyethylene Factorial Design Coefficients (Weighting Factors) for the Tensile Strength and 24-Hour Sol Fractions

	$\bar{G}_t = 2585 \pm 25$ psi*		$\bar{G}_s = 21.44 \pm 0.18$ %†	
Variable	Tensile coefficient psi	Tensile ranking	Sol fraction coefficient, %	Sol fraction ranking
H	-110 ± 74	8	0.03 ± 1.04	6
NH$_4$	214 ± 70	2	0.62 ± 1.04	8
Ca	146 ± 71	4	0.55 ± 1.08	7
OA	-935 ± 67	10	2.20 ± 1.10	10
HMD	85 ± 71	6	-1.79 ± 1.10	1
4VP	579 ± 72	1	-0.16 ± 1.14	4
PVA	193 ± 70	3	-0.51 ± 1.10	3
PO	103 ± 71	5	0.82 ± 1.10	9
PVS	-48 ± 78	7	-0.04 ± 1.08	5
VSA	-149 ± 77	9	-1.17 ± 0.99	2
Kaolinite	191 ± 25	1	0.17 ± 0.36	2
Montmorillonite	-190 ± 26	2	-0.18 ± 0.38	1
HIFAX PE	578 ± 27	1	0.74 ± 0.39	2
DYNK PE	-466 ± 22	2	-0.65 ± 0.34	1
0-Mrad	154 ± 35	1	28.02 ± 0.55	4
10-Mrad	49 ± 44	2	-4.03 ± 0.64	3
55-Mrad	-8.4 ± 46	3	-16.40 ± 0.66	2
100-Mrad	-255 ± 44	4	-18.63 ± 0.68	1

* $\bar{G}_t$ = mean value of the tensile strengths for the samples tested.

† $\bar{G}_s$ = mean value of the sol fractions for the samples tested.