The Mechanism of the Decomposition of Peroxides and Hydroperoxides by Mineral Fillers

D. H. Solomon[a]; Jean D. Swift[a]; G. O'leary[a]; I. G. Treeby[a]

[a] Division of Applied Chemistry C.S.I.R.O., Melbourne, Australia

PLEASE SCROLL DOWN FOR ARTICLE

The Mechanism of the Decomposition of Peroxides and Hydroperoxides by Mineral Fillers

D. H. SOLOMON, JEAN D. SWIFT, G. O'LEARY, and
I. G. TREEBY

Division of Applied Chemistry
C.S.I.R.O.
Melbourne, Australia

SUMMARY

The interaction of fillers and pigments with free radical initiators has been studied. Clay minerals have a marked influence on both the rate and the mechanism of the decomposition of peroxides and hydroperoxides. Kaolinite is a particularly effective catalyst and causes rapid decomposition even at room temperature. The reaction of cumene hydroperoxide with kaolinite is first-order in peroxide and the rate constant is proportional to the ratio of clay to hydroperoxide. From a study of the products of the reaction and the influence of solvent on the decomposition, a mechanism involving an intramolecular rearrangement or closely associated ion pairs has been proposed. The application of these results to polymer filler composites is discussed.

INTRODUCTION

The modification of an organic polymer system by the addition of pigments and fillers is practised widely in the formulation of plastics,

elastomers, and surface coatings for industrial use. Pigments or fillers are added for a variety of reasons. For example, to reduce damage to the organic polymer when exposed to various environments, to provide filling properties in coating compositions used for surface preparation, to perform a decorative function, or to influence and modify the mechanical properties of the system.

Changes in the mechanical properties of the composites have generally been attributed solely to the physical characteristics, such as particle size, particle size distribution, and morphology, of the filler [1]. However, recently we have shown that clay fillers develop significant surface acidity when the free surface moisture and the polarity of the system as a whole are low [2]. This situation would be expected in polymer composites such as elastomers and filled thermoplastics. Consequently, it is desirable to establish if there is any chemical effect of the clay fillers in these systems.

This paper, one of a series in which we will discuss chemical interactions in filled polymer systems, is primarily concerned with the interactions between pigments and fillers and free radical initiators, and with the application of these results to the formulation of filled polymer systems.

DISCUSSION

The study of chemical reactions in polymeric composites is complicated by the initial viscosity of the medium and by the change in solubility which accompanies any cross-linking reactions. It is therefore more convenient to study the reactions between free radical initiators and fillers or pigments in a low viscosity nonreactive organic solvent first and then to apply these results to systems in which polymer has replaced the solvent. Benzene and hexane were chosen as the initial solvents because their polarities are similar to those of many elastomers and hydrocarbon-type polymers (e.g., polyethylene).

A marked increase in the rate of decomposition of peroxides and hydroperoxides was caused by clay fillers that belong to the aluminosilicate class (e.g., kaolinite, montmorillonite, attapulgite), by those titanias that have an aluminum-silicate coating, and by zinc oxide. The zinc oxide-promoted breakdown is different in character from that shown by the clays and will be discussed in a subsequent publication. Other typical fillers or white pigments have little, if any, effect on the stability of peroxides at room temperature. The relative effect of fillers on the breakdown rate

Table 1. The Effect of Fillers on the Breakdown Rates of
Peroxides and Hydroperoxides

Filler[a]	% Initiator remaining after 24 hr			
	CHP[b]	TBHP[b]	BP[b]	DCP[b]
Rodda 37	0[c]	0	41	0
Hydrite 10	0[d]	0[d]	43	0[d]
Gelwhite L	0[c]		54	
Talc	91	95	100	92
Zinc oxide	72			
Attapulgite	0[c]	0		0
Rutile titania coated with aluminum silicate	80	85	98	84
Uncoated rutile titania	100	100	100	100
Polyphosphate treated Rodda 37	14	85	99	26
Hydrite 10S	31	87	99	43
Kaophobe 5	100	100	100	100
Sodium kaolinite (ex. Rodda 37)			97	0

[a] Dried at 110°C for 2 hr.

[b] CHP = cumene hydroperoxide, TBHP = t-butyl hydroperoxide, BP = benzoyl peroxide, DCP = dicumyl peroxide.

[c] After 2 min, 6% remained with Rodda 37, 22% remained with Gelwhite L, and 9% remained with Attapulgite.

[d] See Table 4 for half life-times.

is shown in Table 1. Some indication of the magnitude of the catalytic effect is given by the decomposition of cumene hydroperoxide by a commercially used kaolinite filler–Hydrite 10–which contained 0.6% surface moisture (the % moisture is defined as the weight loss after drying at 110°C for 2 hr); 99% is decomposed in 2 hr (Table 2) at a clay/peroxide ratio similar to those used in commercial formulations.

A number of observations suggest that the surface acidity of the minerals is responsible for promoting the peroxide or hydroperoxide breakdown. First, the relative effectiveness of the minerals in promoting these decompositions is kaolinite > attapulgite > montmorillonite. This

Table 2. The Effect of Moisture Content of Kaolinite (Hydrite 10) on
the Rate of Breakdown of CHP and DCP

% Moisture	% CHP remaining after 2 hr	% DCP remaining after 2 hr
0.6	1	45
1.5	9	71
3	97	87
6	99	90

Table 3. The Effect of Solvents on the Rate of
CHP Decomposition in the Presence of
Kaolinite (Hydrite 10)[a]

Solvent	% CHP remaining after 2 hr
Hexane	0
Ethyl acetate	98
Ethanol	99
Butanol	97
Acetone	0

[a]Concentration used = 0.4 mmole initiator/g kao-
lin (dried 110°C, 2 hr) in 10 ml solvent.

is the order of decreasing acid strength of the mineral surfaces as measured
by Hammett indicators [2]. Second, the effect of water (Table 2) and of
organic solvents (Table 3) on the reaction rate is similar to their effect on
the surface acidity [2]. For example, the reaction rate is slower at higher
surface moisture contents where the surface acidity has been shown to be
reduced [2]. Third, the order of decreasing decomposition rate for the
peroxides and hydroperoxides is cumene hydroperoxide (CHP) > dicumyl
peroxide (DCP) > t-butyl hydroperoxide (TBHP) > benzoyl peroxide
(BP) (Table 4); this is the predicted order for nucleophilic attack and is
similar to the results of Kharasch and Burt [3] for perchloric acid
catalyzed breakdown.

   Substantiating evidence for the ionic nature of the clay catalyzed per-
oxide decompositions is given by the quantitative formation of phenol

Table 4. The Effect of Kaolinite[a] on the
Rate of Breakdown of Initiators

Initiators	Time of half reaction
CHP	30 sec
DCP	60 sec
TBHP	$5\frac{1}{2}$ min
BP	19 hr

[a] Kaolinite Hydrite 10 dried at $110°C$
for 2 hr. Concentration used = 0.4 mmole
initiator/g kaolin.

and acetone from CHP, and phenol, acetone, and α-methylstyrene dimers
from DCP. Kharasch et al. [4] have previously shown that these products
result from the acid-induced breakdown whereas acetophenone is the major
product from radical or homolytic decomposition.

A more detailed insight into the mechanism of the reaction has been
gained by the use of polymerizable solvents for the reaction. When styrene/
methyl methacrylate (1/1), tetroxane, or trioxane were used in place of
benzene as the solvent, no polymers or low molecular weight components
resulting from the monomers were found. These results suggest that no
free active species are formed. Under similar conditions experiments with
perchloric acid/acetic acid/hydroperoxide mixtures also failed to yield
polymeric or low molecular weight products derived from monomers used
as solvents even where complete decomposition of the peroxide occurred.
Thus, the results with perchloric acid and kaolinite suggest that the per-
oxide and hydroperoxide decompositions proceed by an intromolecular
rearrangement or via a closely associated ion pair.

This conclusion is in agreement with those of Shushunov and Yablokov
[5] who have recently shown that ionic chain reactions are not involved
in the acid catalyzed breakdown of CHP.

It should be noted that in these reactions clay is functioning in a
similar manner to acidic carbon blacks and acidic silicas. Both of these
decompose DCP to phenol, acetone, and styrene dimers [4] by acid-
induced reactions.

Kinetic studies of the kaolinite/CHP reaction show that the rate is
first-order in peroxide (Fig. 1) and that the rate constant is proportional
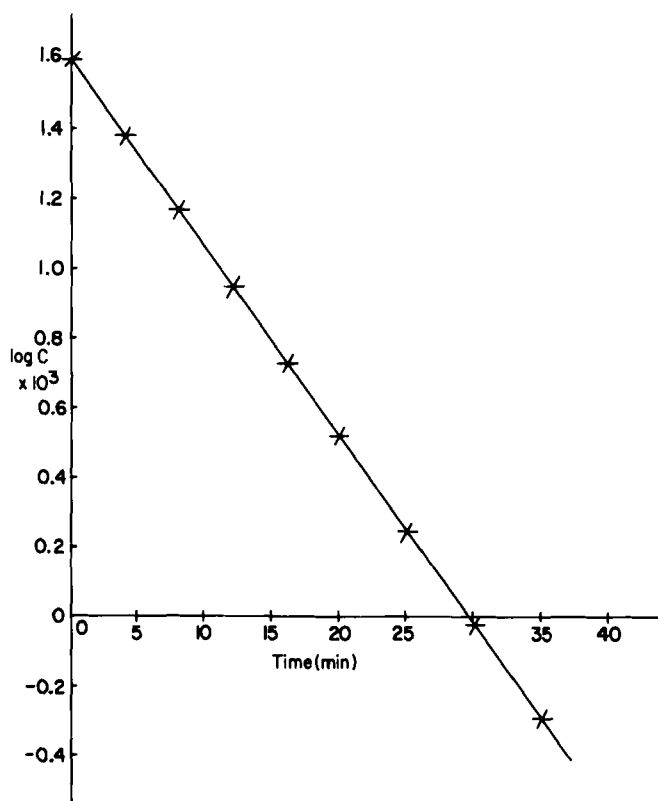to the ratio of clay to peroxide (Table 5). These findings are similar to

Fig. 1. First-order plot of the decomposition of CHP in the presence of kaolinite (2 g Hydrite 10, dried at 110°C for 2 hr) in 200 ml of 0.040 M solution of CHP in benzene. Rate constant $k = 2.06 \times 10^{-3}$ sec^{-1}.

Table 5. The Effect of Kaolinite[a] Concentration on the Rate Constant of CHP Decomposition

Amount of clay (g)	Rate constant (sec^{-1})
0.09	5×10^{-4}
0.23	12×10^{-4}

[a] Kaolinite Hydrite 10 dried at 130°C for 2 hr.

those of Seubold and Vaughan [6] for the p-toluene sulfonic acid degradation of CHP.

It should be noted that reproducible kinetics require careful standardization of the procedure used to dry the clay. Residual moisture has a significant effect on acidity which is reflected by the rate constants obtained after drying the clay at 110 and 130°C (Fig. 1 and Table 5).

Some indication of the potency of the clay can be gleaned from the comparison of the rate constants obtained by us with those obtained by Seubold and Vaughan [6] who used p-toluene sulfonic acid as catalyst. To obtain equivalent rate constants, the amount of p-toluene sulfonic acid required is 120 times the amount of kaolin. This gives some idea of the acid strength of the kaolinite in this system.

A reaction mechanism consistent with the observed kinetics and products of the decomposition is shown as Fig. 2.
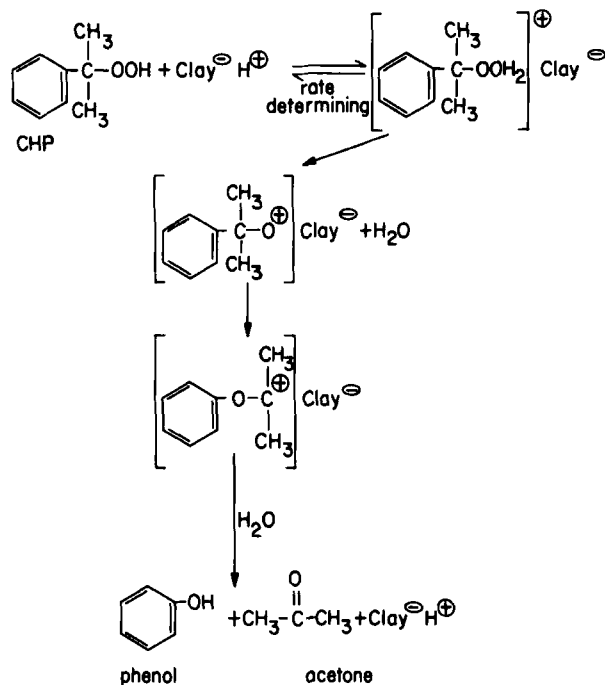

Fig. 2. Reaction mechanism of cumene hydroperoxide with kaolinite.

In marked contrast to the peroxides, the decomposition at room tempera-
ture of azo compounds such as azodiisobutyronitrile (AIBN) is not pro-
moted by the clay fillers. At elevated temperatures decomposition appears
to be by the normal homolytic process, but an accurate count of the radi-
cals formed is complicated by the presence of the clay.

This observation has important practical consequences and suggests the
use of azo initiators for the generation of free radicals in the presence of
acidic particulate matter (e.g., in elastomers and unsaturated polyesters).
Alternatively, if peroxides are to be used in the presence of clays, control
of the surface acidity is desirable. The fillers can be neutralized before use,
either by inorganic salts (e.g., sodium hexametaphosphate) or by organic
bases (usually amines). Fillers treated in this manner cause less acid-induced
peroxide breakdown than untreated fillers (Table 1). The other approach
widely used to neutralize the clay surface is the use of "additives" or
solvents sufficiently basic to reduce the acidity of the clay. An example
is the use of magnesium oxide with triethanolamine or ethylene glycol in
elastomer compositions.

In elastomers a further impelling reason for minimizing the heterolytic
breakdown of DCP and CHP is the need to avoid the formation of phenol
and acetone, both of which degrade the mechanical properties of the
Vulcanizate. It is noteworthy that recent developments of clays as pig-
ments in white-walled tires have concentrated on a neutralized grade of
pigment because of the improved vulcanization rate [7].

In some polymer systems the ionic decomposition of peroxides is desir-
able. For example, in the weathering of polyethylene, one of the degrada-
tion reactions is oxidation to form peroxides and hydroperoxides. These
can decompose homolytically and the resultant radicals cause cross-linking
and embrittlement of the polymer. The results in Table 6 show that the
addition of an acidic filler reduces cross-linking, as measured by the change
in yield stress, presumably by favoring the ionic breakdown of the
peroxides.

Therefore the possibility now exists for the selection of fillers for their
chemical as well as their physical properties. The acidity of clay surfaces
can be used to advantage in the promotion of the nonradical breakdown
of peroxides or the acidity can be controlled by neutralization where
radical reactions are required.

Table 6. The Effect of Fillers on
Weathering of Polyethylene Compound[a]

Filler	Increase in yield stress during weathering $(lb/in.^2)$
TiO$_2$	200
Talc	220
Attapulgite	170
Montmorillonite	100
Kaolinite	120

[a]Composition: 90% polyethylene, 9%
TiO$_2$, 1% filler.

EXPERIMENTAL AND RESULTS

All solvents were purified by standard techniques and were thoroughly dried. Styrene and methyl methacrylate were washed free of inhibitor, dried, and distilled under nitrogen at reduced pressure.

BP was purified by the method of Augood et al. [8] and assayed at 99.7% by iodometric titration. TBHP was fractionally distilled under nitrogen at reduced pressure. Iodometric titration showed the purity to be >96%.

CHP (approx 70%) was treated as follows: to 10 ml of CHP was added cold aqueous sodium hydroxide solution (30 ml, 25%) and the mixture allowed to stand for 2 hr. The precipitate which formed was filtered off, washed first with sodium hydroxide solution, and then with a little acetone. The precipitate was dissolved in water (100 ml) and this solution was neutralized with HCl, acidified with carbon dioxide, and extracted with petroleum ether (3 × 30 ml of bp 30-40°C, aromatic free). To remove any acid present the petrol extract was washed with bicarbonate solution. After the extract was dried overnight (anhydrous Na$_2$CO$_3$), it was distilled under reduced pressure in an inert atmosphere and gave cumene hydroperoxide, bp 61-63°C at 0.1 mm. The purity estimated by iodometric titration was 99.8%.

DCP (99% by iodometric titration) and AIBN (Fluka-premium grade) were used without further purification.

The kaolinites used were from the following sources: 1) Hydrite 10—
a commercial grade, supplied by the Georgia Kaolin Co., with a particle
size of approximately 0.55 μ and a water content as received of 0.6% when
measured by drying for 2 hr at 110°C; 2) a natural kaolinite—Rodda 37, a
Mt. Egerton, Australia, kaolinite supplied by Rodda Pty. Ltd. This was
used as an example of a clay not subjected to a beneficiating process. In
general no significant differences were observed between the results for
Hydrite 10 and Rodda 37 kaolinites.

Homoionic sodium kaolinite and polyphosphate (Calgon) treated kao-
linite were prepared by the method of Solomon and Rosser [9]. Hydrite—
10 has aluminum and possibly some hydrogen cations.

The other fillers and pigments used were from the following sources:
Hydrite 10S (a polyphosphate treated Hydrite 10), Kaophobe 5 (a neutral
organophilic kaolinite), and Gelwhite L (a Texas calcium montmorillonite)
from Georgia Kaolin Co.; Attapulgus Attasorb RVM (an attapulgite) from
MCP Chemical Distributors; Sierra talc from U.S.A.; zinc oxide from
Durham Chemicals.

Identification of Reaction Products

(I) From CHP/Kaolin Reaction. Kaolin (3.0 g, dried 2 hr at 110°C)
was added to a solution of CHP (0.7609 g, 0.0050 mole) in toluene
(20.00 ml). The mixture was shaken at 30°C for 4 hr. GLC of an aliquot
of the solution showed that it contained acetone (0.0049 mole) and phenol
(0.0050 mole). No other products were detected. Acetone was isolated as
the 2,4-dinitrophenyl hydrazone (mp and mixed mp 126.5-127.5°C), and
phenol was isolated and identified by the formation of 2,4,6-tribromophenol
(mp and mixed mp 94-95°C).

(II) From DCP/Kaolin Reaction. Kaolinite (3.0 g, dried 2 hr at 110°C)
was added to a solution of DCP (1.3520 g, 0.0050 mole) in toluene (20.00
ml). By GLC the product was shown to contain acetone (0.0045 mole),
phenol (0.0044 mole), α-methylstyrene dimers (0.0027 mole), and α-
methylstyrene (0.0004 mole).

Kinetic Studies

Two techniques were used to follow the kinetics of the clay/initiator
reactions. In Method A, which was used where the ratio of clay to initiator
and solvent is small, the clay, initiator, and solvent were stirred under a
nitrogen atmosphere in a 250-ml flask thermostatted at 30°C. Samples

were withdrawn at intervals and the residual peroxide or hydroperoxide measured by iodometric titration. In Method B, used for the higher clay loadings, the clay, initiator, and solvent were weighed into ampoules. These were tumbled in a water-bath and the reaction followed as in Method A. AIBN was measured on a Unicam SP300 Spectrophotometer by the optical density measurement of the 360 mμ adsorption. The results of the kinetic runs are shown in Fig. 1 and Tables 1-5.

Monomers as Polymerizable Solvent

A mixture of CHP (0.0628 g, 0.0004 mole), dry kaolin (1.000 g), and styrene/methyl methacrylate/benzene 25/25/50 (10.0 ml) was reacted for 2 hr; no CHP remained. Phenol (0.0360 g, 0.0004 mole) and acetone (0.0230 g, 0.0004 mole) were identified and measured by GLC on an aliquot of solution. No methanol insoluble polymer and no monomer derived low molecular weight products were present.

Effect of Kaolinite on AIBN Decomposition

A solution of AIBN (0.0657 g) in benzene (10 ml) with kaolin (1.00 g, dried 110° for 2 hr) after 24 hr at 30°C still contained 0.0655 g (99.7% of original) AIBN.

REFERENCES

[1] C. Y. Haas and H. A. Smith, *Paint Varn. Prod.*, **57**(3), 36 (1967).

[2] D. H. Solomon, J. D. Swift, and A. J. Murphy, *J. Macromol. Sci.– Chem.*, **A5**, 587 (1971).

[3] M. S. Kharasch and J. G. Burt, *J. Org. Chem.*, **16**, 150 (1951).

[4] M. S. Kharasch, A. Fono, and W. Nudenberg, *J. Org. Chem.*, **15**, 748, 753 (1950).

[5] V. A. Shushunov and V. A. Yablokov, *Dokl. Akad. Nauk. Chem. (Eng. Trans.)*, **151**, 613 (1963).

[6] F. H. Seubold and W. E. Vaughan, *J. Amer. Chem. Soc.*, **75**, 3790 (1953).

[7] Georgia Kaolin Co., Product Information on Struex 95S.

[8] D. R. Augood, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, **1952**, 2094.

[9] D. H. Solomon and M. J. Rosser, *J. Appl. Polym. Sci.*, **9**, 1261 (1965).