

# Polymer-Filler Interactions in Hydroxy-Terminated Polybutadiene-Ammonium Perchlorate System in the Presence of a Bonding Agent

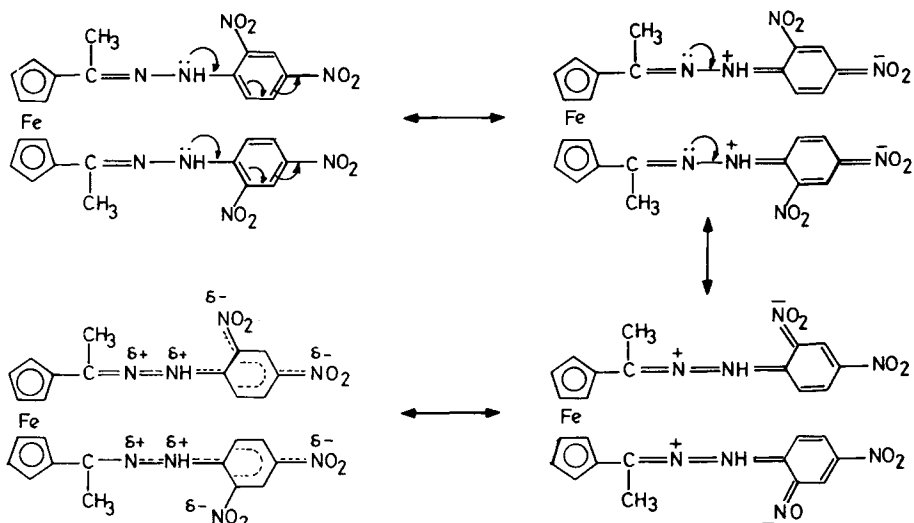
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## Synopsis

Bonding between ammonium perchlorate (AP) and hydroxy-terminated polybutadiene (HTPB), constituting a nonreinforcing filler system, has been studied in the presence of a unique bonding agent (BA)—a zwitter ion molecule, 2,4-dinitrophenylhydrazone derivative of 1,1'-bisacetylferrocene (DNPHD AF). Extensive conjugation and a permanent ionic character makes the DNPHD AF to bond strongly with the ionic oxidizer AP. Through its terminal —OH group, HTPB bonds with the NO<sub>2</sub> groups of DNPHD AF. Bonding sites in the molecules have been located from IR studies and from the first-order rate constant measurements of the bonding of DNPHD AF and other model BAs with HTPB and AP. The bonding ability of DNPHD AF is further evidenced from SEM micrographs.

## INTRODUCTION

In polymer composites two kinds of fillers are employed, (a) reinforcing type and (b) nonreinforcing type. Glass-fiber-filled resins are well-known examples of reinforced systems. Composite solid propellants, where oxidizer like ammonium perchlorate (AP) in particulate form is distributed in a polymer matrix, could be considered as a nonreinforcing system. Improvement in the mechanical properties in such non-reinforcing systems is generally achieved by the use of bonding agents (BA). Though a number of compounds<sup>1-14</sup> have been used as BA in nonreinforcing systems, the choice it appears is mostly based on trial and error basis. An ideal bonding agent would be the one which is not only compatible with organic binders but should have sufficient ionic character to bond with the inorganic compounds like AP. For this purpose, it was thought to use "zwitter ion" type molecule as a bonding agent; the choice and application of such molecules as a BA is hitherto unknown. In the present work, we have investigated a zwitter ion molecule, 2,4-dinitrophenylhydrazone derivative of 1,1'-bisacetylferrocene (DNPHD AF), as a potential BA in a model nonreinforcing system consisting of AP and hydroxy-terminated polybutadiene (HTPB). DNPHD AF has permanent ionic character due to



Scheme 1. Resonance structure of DNPHD AF.

extensive conjugation as shown in Scheme 1. Efforts are directed, in the present investigation, to locate the bonding site and examine the bonding mechanism of DNPHD AF with AP and HTPB.

### EXPERIMENTAL

HTPB (hycar HTBN) from B. F. Goodrich was vacuum-dried and used. AP was recrystallized, powdered, and sieved to a particle size of 150–200  $\mu\text{m}$ .

The 2,4-dinitrophenylhydrazone derivatives of mono- and 1,1'-bisacetylferrocene were prepared by the procedure described elsewhere.<sup>15</sup>

1,1'-Bis(phenylazomethine) ferrocene (a new compound) was prepared as follows. 1,1'-Bisacetylferrocene (0.001 mol), 0.002 mol of aniline, 3–5 drops of pyridine in 100 mL of dry benzene were refluxed for 10–12 h using a Dean and Stark trap to remove water. After the completion of the reaction, the solvent was evaporated to about 5 mL; it yielded red crystals (88% yield) of the title compound (mp 44–45°C) on cooling. The product was characterized by IR and <sup>1</sup>H-NMR spectra.

IR (mull): 1675 (s), 1510 (w), 1460 (s), 1390 (s), 1290 (s), 1110 (m), 870 (m), 520 (m)  $\text{cm}^{-1}$ .

<sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>): 2.40  $\delta$  (s, 6H), 4.60  $\delta$  (m, 2H), 4.87  $\delta$  (m, 2H), 7.17  $\delta$  (s, 10H).

Kinetic measurements were done as follows: HTPB (3 g) in 50 mL of dry *n*-hexane and various concentrations of the bonding agent in DMF (50 mL) were taken in a 150-mL stoppered conical flask; *n*-hexane and DMF layers were immiscible. The mixture (kept at  $28 \pm 0.5^\circ\text{C}$ ) was stirred at a constant speed; the decrease in the concentration of the BA in DMF layer was determined at different intervals of time using a Beckman Model-25 UV-VIS

TABLE I  
Rate of Decrease in Concentration of Bonding Agent in DMF Layer at 28°C

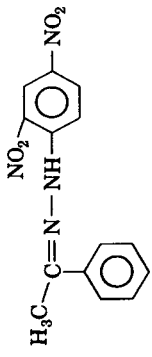
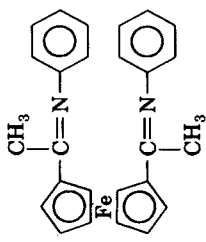
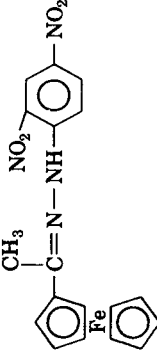
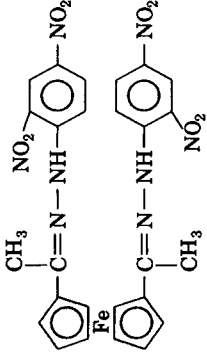
Bonding agent	Concn of bonding agent in DMF (mol L <sup>-1</sup> )	$\lambda_{\max}$ (nm)	Rate constant of the bonding agent	
			With HTPB (3 g) alone (min <sup>-1</sup> )	With HTPB (3 g) + AP (2 g) (min <sup>-1</sup> )
(1) 	$5 \times 10^{-5}$	380	$4.00 \times 10^{-3}$	$2.86 \times 10^{-2}$
(2) 	$2.5 \times 10^{-5}$	365	$1.01 \times 10^{-4}$	$8.06 \times 10^{-4}$
(3) 	$5.0 \times 10^{-5}$	375	$3.89 \times 10^{-3}$	$2.88 \times 10^{-2}$
(4) 	$2.5 \times 10^{-5}$	375	$3.85 \times 10^{-3}$	$3.06 \times 10^{-2}$

TABLE II  
Variation of First-Order Rate Constant  
with Various Inorganic Salts<sup>a</sup>

Inorganic salt	Rate constant (min <sup>-1</sup> )
NH <sub>4</sub> ClO <sub>4</sub>	3.06 × 10 <sup>-2</sup>
KClO <sub>4</sub>	3.01 × 10 <sup>-2</sup>
NaClO <sub>4</sub>	3.15 × 10 <sup>-2</sup>
NH <sub>4</sub> Cl	0.92 × 10 <sup>-2</sup>
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	2.65 × 10 <sup>-2</sup>

<sup>a</sup>DNPHD AF = 2.5 × 10<sup>-5</sup>M, HTPB = 3 g, temperature 28°C, and λ-max = 375 nm.

spectrophotometer. The first-order rate constants were obtained from the plot of log (optical density) vs. time; the optical density directly corresponded to the BA concentration. The above experiments were repeated with AP + HTPB system also; AP particles were first coated with BA and subsequently mixed with HTPB. The semisolid viscous lump was placed at the bottom of the conical flask under *n*-hexane and DMF layers. The solution was stirred and the dissolution of BA was monitored against time, as discussed above. At equilibrium BA was partitioned in DMF and *n*-hexane layers, HTPB went to *n*-hexane layer, and AP powder remained at the bottom of the flask. The first-order rate constants of different systems are presented in Tables I and II. Since the rate constants will depend upon stir speed, interfacial surface area, and AP particle size, these parameters were maintained constant. The rate constants in Tables I and II are for internal comparison only.

Infrared (IR) spectra were recorded on a Perkin-Elmer Model 597 spectrophotometer using KBr pellets.

Scanning electron microscope (SEM) photographs were taken on a Cambridge Stereoscan 150 instrument. Since AP undergoes sublimation and decomposition in the presence of electron beam, we used ammonium sulphate crystals (30 μm size) as a good substitute in the study. The BA-coated ammonium sulfate was prepared by dispersing the ammonium sulfate crystals over acetone solution of BA; evaporation of acetone gave the BA coated crystals of ammonium sulfate. Few crystals of BA coated ammonium sulfate and also uncoated ammonium sulfate were then mixed with HTPB separately and photographed. All the samples were coated with thin electrically conducting layer of gold for SEM recording.

## RESULTS AND DISCUSSION

From the UV experiments, the decrease in the concentrations of BAs (DNPHD AF) and other model compounds (Table I) as a function of time were measured with HTPB and AP + HTPB. In HTPB + BA experiments, the decrease in the concentration of BA in the DMF layer is a measure of the interaction of the BA with HTPB. In the experiments with HTPB + AP system, the extent of decrease in BA concentration in DMF is expected to be more if BA interacts with both HTPB and AP. The rate constants for HTPB and HTPB + AP systems are shown in columns 4 and 5 (Table I), respectively; the first-order rate constants in column 5 are about 7–8 times higher

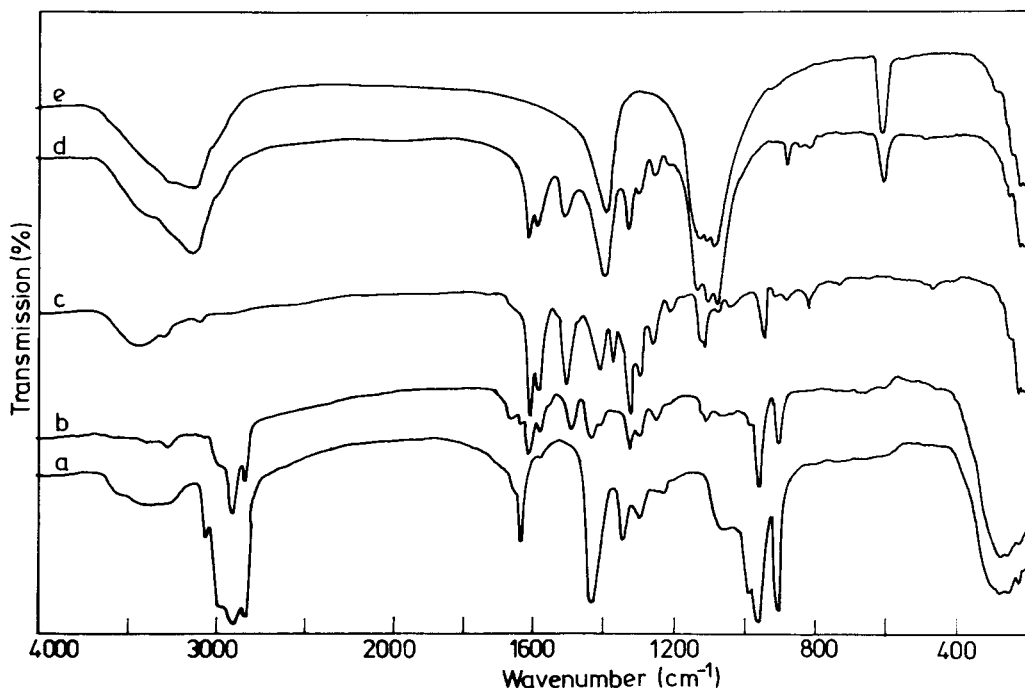


Fig. 1. IR spectra of (a) HTPB, (b) HTPB + DNPHD AF, (c) DNPHD AF, (d) AP + DNPHD AF, and (e) AP.

than in column 4 suggesting that BA interacts with HTPB and AP both; the extent of bonding with AP being much higher. The concentrations of the models BA 1 and 3 were taken twice compared to the BA 2 and 4 (Table I) because the former compounds have only one side chain in the molecule. BA 1,3, and 4 have identical rate constants in both HTPB and AP + HTPB systems, suggesting that they have similar active bonding sites present in the molecules. Since BA 1 has no ferrocene center, it is not involved in the bonding for different rate constants of the compound 1 with respect to 3 and 4 would have been observed. An insight into the bonding site can be obtained by comparing BA's 2 and 4. The rate constants of compound 4, in HTPB or in AP + HTPB systems, is about 38 times higher compared to compound 2, which shows that the active bonding center lies only in the side chain, for the ferrocene center is not involved in the bonding. The side groups which are present in compound 4 (DNPHD AF) and absent in compound 2 are  $-\text{NH}-$ ,  $-\text{NO}_2$ ; it is obvious that  $-\text{NH}-$  and  $-\text{NO}_2$  are involved in bonding with AP and HTPB. Further confirmation was obtained from IR studies.

IR spectra of HTPB, DNPHD AF, and HTPB + DNPHD AF (1:1 by weight) are shown in Figure 1. The  $-\text{OH}$  bending vibration in HTPB ( $1340\text{ cm}^{-1}$ ) completely shifted in the mixture, indicating that the  $-\text{OH}$  group in HTPB is involved in bonding with DNPHD AF. There is no change in the

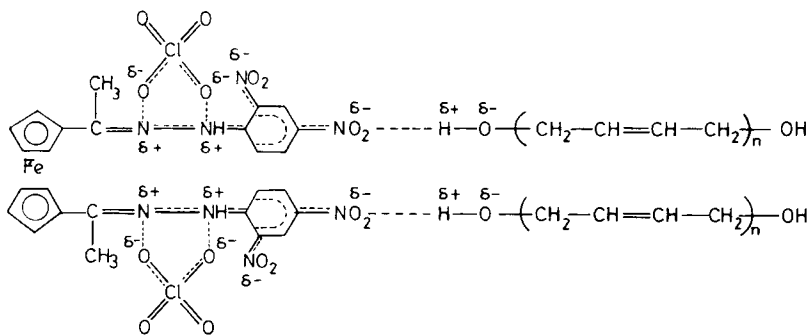
vinyl  $\begin{array}{c} \diagup \\ \text{C}=\text{C} \\ \diagdown \end{array}$  stretching ( $1635\text{ cm}^{-1}$ ) and vinyl  $=\text{C}\begin{array}{c} \text{H} \\ \diagup \\ \text{H} \\ \diagdown \end{array}$  bending ( $905$  and

$960\text{ cm}^{-1}$ ), indicating that the bonding of HTPB with DNPHD AF does not occur through these groups. The asymmetric stretching vibration of the  $-\text{NO}_2$  group in DNPHD AF in the HTPB + DAPHD AF mixture shifts from  $1510$  to  $1495\text{ cm}^{-1}$  indicating that the  $-\text{NO}_2$  group is involved in bonding. This type of interaction may be of hydrogen bonding type; however, it could not be seen in IR because of the broad adsorption in the region  $3100\text{--}3600\text{ cm}^{-1}$ .

The bonding between AP and DNPHDF was also examined by IR (Fig. 1). The  $\text{ClO}_4^-$  bending band ( $620\text{ cm}^{-1}$ ) shifts to  $605\text{ cm}^{-1}$ , indicating that  $\text{ClO}_4^-$  in AP is involved in bonding. The  $\text{N}-\text{N}$  stretching frequency ( $960\text{ cm}^{-1}$ ) in DNPHD AF completely shifts to  $945\text{ cm}^{-1}$  in the AP + DNPHD AF mixture, indicating that the bonding occurs through  $\text{N}-\text{N}$  bonds in DNPHD AF. Though the  $\text{N}-\text{H}$  stretching in AP and  $\text{N}-\text{H}$  stretching in DNPHD AF are in the same region, there is no shift in the  $\text{N}-\text{H}$  stretching peak, suggesting that bonding does not occur through  $\text{NH}_4^+$ .

Further confirmation for the bonding site in AP is obtained from Table II. The rate constants are presented in the presence of various inorganic salts wherein the cations and anions are varied. If the anion ( $\text{ClO}_4^-$ ) is involved in bonding, then the variation of cations should not change the rate constants. Similarly, if the cation ( $\text{NH}_4^+$ ) is involved in bonding, then one should not observe any difference in the rate constants when the anion is varied. Table II shows that cations do not change the rate constant but anions drastically affect it, which unequivocally confirm that, in the inorganic salts, it is the anions which are involved in the bonding with DNPHD AF. Taking into account the above observations, the bonding of AP and HTPB with DNPHD AF could be schematically represented as shown in Scheme 2.

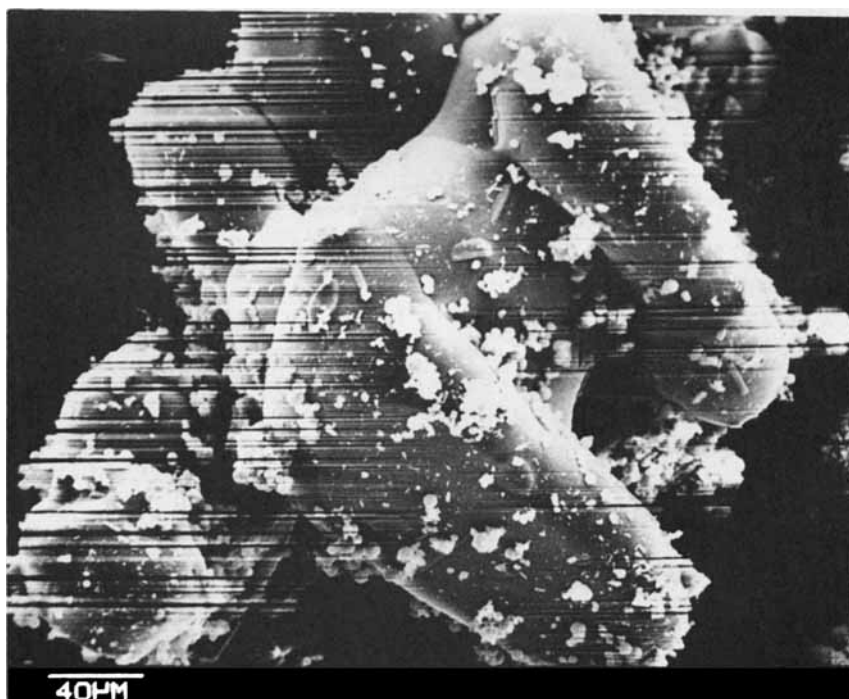
SEM was used to have a visual evidence for the bonding of inorganic salt and the binder in the presence of DNPHD AF; this is shown in Figure 2. Micrograph A shows big crystals of ammonium sulfate; some small crystals of ammonium sulfate are also seen adhering the bigger crystals. When ammonium sulfate crystals are mixed with DNPHD AF, it adheres on the surface of the crystals due to the bonding between the two; this is shown in micrograph



Scheme 2. Schematic representation of the bonding of DNPHD AF with HTPB and AP.



(a)



(b)

Fig. 2. SEM micrographs of (A) ammonium sulfate, (B) ammonium sulfate + DNPHD AF, (C) ammonium sulfate + HTPB, and (D) ammonium sulfate + HTPB + DNPHD AF.



(c)



(d)

Fig. 2. (Continued from the previous page.)



B. Ammonium sulfate particles are mixed with HTPB; this is shown in micrograph C. The black-shaded portions represents the dispersion of binder in the mixture. In the presence of DNPHD AF, the bonding between ammonium sulfate particles and HTPB is so strong that it shows a lump structure (micrograph D), this is because the solid particles are strongly held by the binder in presence of DNPHD AF. SEM results clearly show that the bonding agent DNPHD AF brings about an excellent adhesion between the inorganic particles and the organic binder. It may be noted that micrographs C and D are not as clear as A and B because of the presence of amorphous HTPB.

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