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# Effect of Hydrated Silica on the Permeation Resistance and Mechanical Properties of Nitrile Butadiene Rubber†

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The permeation of toluene in nitrile butadiene rubber was investigated. It was found that the incorporation of a reinforcing filler, hydrated silica, has a favorable impact on both the chemical resistance and the mechanical properties of the elastomer.

## INTRODUCTION

The chemical resistance of elastomers and plastics has always been of great significance in polymer science. The present work was undertaken to study the *permeation* of toluene in nitrile butadiene rubber (NBR) by measuring the so-called *breakthrough time*. The

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† Abstracted in part from A. R. Md. Ghouse's M.S. thesis, Western Illinois University, 1987.

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influence of filler content on the chemical resistance and the mechanical properties of NBR was of special interest to us.

Permeation of a chemical (liquid or gas) in a polymeric material occurs on the molecular level. Permeation consists of three basic processes: 1, sorption of the chemical onto the outside surface of the material; 2, diffusion of the molecules within the material; 3, desorption of the chemical from the inside surface of the material. (*Penetration*, on the other hand, is an entirely different phenomenon taking place nonmolecularly: It involves the flow of a chemical through seams, closures, pinholes and other imperfections in the material).

The breakthrough time is the elapsed time between the initial contact at the outside surface and the time of detection of the chemical at the inside surface of the material. Therefore the breakthrough time is a measure of the unsteady state diffusion time combined with sorption and desorption effects. The American Society for Testing and Materials (ASTM) Committee on Protective Clothing (F-23) has established the appropriate standards (ASTM F739-85), and throughout this study we used the suggested apparatus and methods.

## THEORETICAL BACKGROUND

The recent models of permeation phenomena are based on the *free volume theory*.<sup>1,2</sup> The free volume is the empty space in the material, i.e., the space which is not occupied by molecules. In polymers the free volume is essentially constant below the *glass transition temperature* ( $T_g$ ).<sup>3-5</sup> The *fractional free volume*,  $V_f$ , is given by the ratio of the free volume and the total volume.  $V_f$  of a polymer increases with increasing temperature and decreases with increasing  $T_g$ . Since permeants have more  $V_f$  than polymers, higher permeant concentration corresponds to an increase in  $V_f$  of the system. For every permeant-polymer pair the amount of local free volume,  $V^*$ , necessary for diffusion can be determined.  $V^*$  depends on the size of the permeating molecules, since the bigger the molecules the more local free volume is needed for random molecular motion. The overall expression for the diffusion

coefficient is given by

$$D = RTA \exp(-V^*/V_f)$$

where  $R$  is the gas constant,  $T$  is the absolute temperature, and  $A$  is a proportionality factor.

In the presence of another solid material the resulting heterogeneous system can be described as a *disperse phase* in a *continuous phase*.<sup>2,6</sup> The disperse phase, the filler in our case, generally has a much lower affinity with the permeant than the polymer, so the diffusion coefficient and the solubility of the filler with respect to the permeant can be considered zero for all practical purposes. Thus the filler, if it is present in a large enough concentration, may substantially reduce the permeability of the system, proportionately to its volume fraction.

## EXPERIMENTAL SECTION

All the materials were obtained via Servus Rubber Company; they were of industrial grade. NBR was compounded with a reinforcing filler (hydrated silica), a plasticizer, an antioxidant, accelerators, sulfur, etc. (Table I), in a Farrel 6"-13" two-roll mill. The polymer had 30% acrylonitrile content (ACN%), and 55 Mooney viscosity. The hydrated silica had a surface area of 150 m<sup>2</sup>/g, an average particle size of 0.022 microns, and the particles were nearly spherical.

TABLE I

Compounded materials, in parts per hundred parts NBR. (\*The brand names are proprietary.)

Hydrated silica	0-70 phr
ZnO	5 phr
Stearic acid*	3 phr
Antioxidant*	1 phr
Accelerator*	2 phr
Plasticizer*	5 phr
Sulfur	1.75 phr

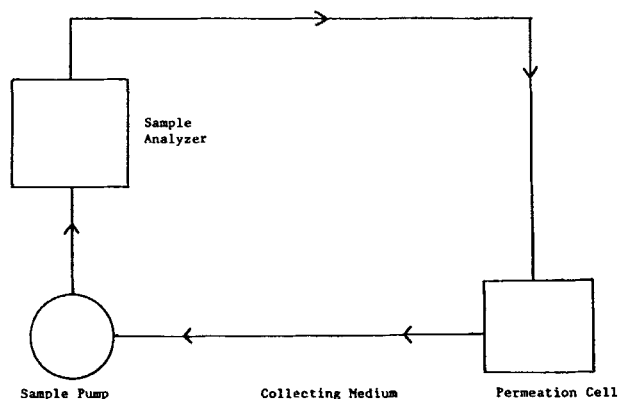


FIGURE 1 Experimental setup for permeation measurements.

The NBR compound was molded in a Wabash handpump press at 150°C for 15 minutes under 400 bar pressure. Before each run the thickness of the specimen was measured with a micrometer to the nearest 0.05 mm.

A standard procedure (ASTM F739-85) was followed for the determination of the permeation resistance of the NBR samples. A closed circulating setup was employed with continuous sample analysis (Figure 1). The specimen was inserted between the two chambers of a permeation cell, one of which contained the test chemical, toluene, and the other, connected to the circulating system, was filled with the collecting medium, 10% ethanol. The exposed area of the specimen had a diameter of 7.5 cm. Initially we did use the recommended glass permeation cell (Pesce Laboratories), but replaced it later with an aluminum cell having the same internal structure and dimensions. The collecting medium was circulated using an FMI lab pump (Fluid Metering) with a flow rate of 390 ml/min. The concentration was monitored with a Perkin-Elmer 552 UV/vis spectrophotometer at 206 nm.

Furthermore, *tensile strength* and *elongation at break* were also measured (ASTM D412-83) at different filler contents.

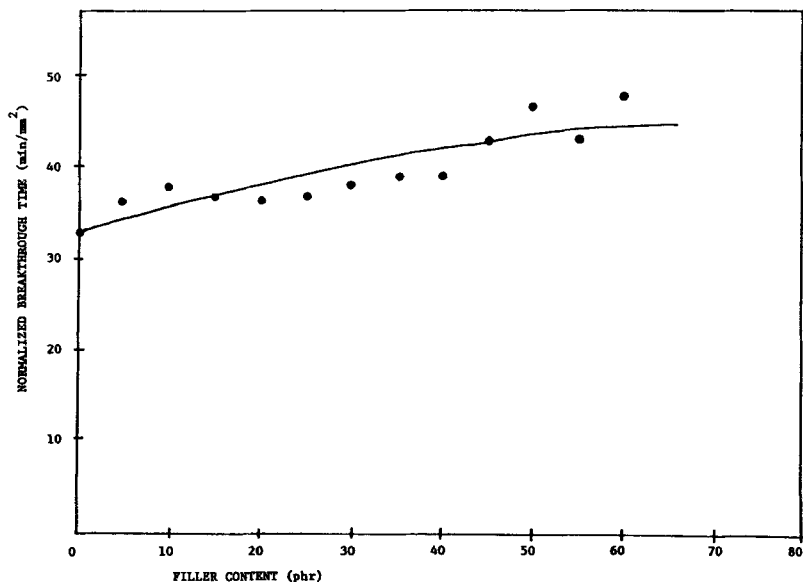


FIGURE 2 Average normalized breakthrough time vs. filler content in the NBR-(hydrated silica)-toluene system.

## RESULTS AND DISCUSSION

Toluene was chosen for test chemical because it has a substantially lower breakthrough time in NBR than aniline, dimethyl formamide, methyl isobutyl ketone, hexane, etc. Data analysis of the permeation measurements shows that the breakthrough time increases with increasing filler content up to a limit (50 phr), beyond which a plateau appears (typical example, Figure 2). The decrease in permeability proves that the *wettability*, i.e., binding between the filler particles and the polymer molecules, is satisfactory. In case of incomplete wetting, the permeability would actually increase with increasing filler content due to the presence of air vacuoles.

The influence of hydrated silica on the mechanical properties was also determined. The results of tensile strength vs. filler content (Figure 3) and elongation at break vs. filler content (Figure 4)

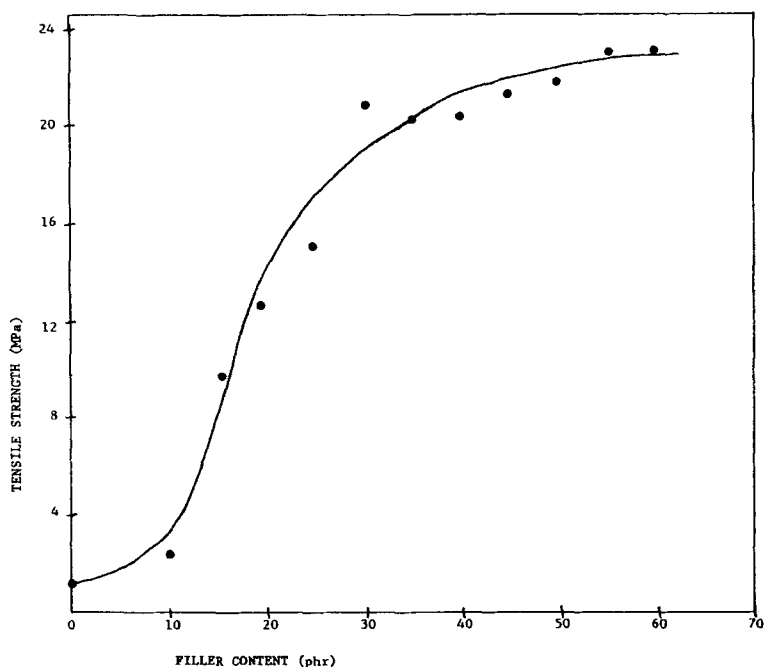


FIGURE 3 Tensile strength vs. hydrated silica content for nitrile butadiene rubber.

experiments prove that hydrated silica has a strong reinforcing effect on NBR. The filler particles act as retarders of crack propagation by lengthening the path of crack, which must move around the particles dissipating more energy. (In case of incomplete wetting, similarly to permeation resistance, the mechanical properties would deteriorate with increasing filler content). One should note, that below 10 phr there is not much improvement, due, probably, to the too wide separation between the filler particles.

The effect of ACN% has also been of interest to us. Using 50 phr hydrated silica and an NBR with 40 ACN% instead of 30 ACN%, there is an improvement of almost 100% in the normalized breakthrough time; carboxy-modified NBR with 27 ACN%, which is also more polar than the original NBR, exhibits an 80% better chemical resistance. While the elongation at break seems to be

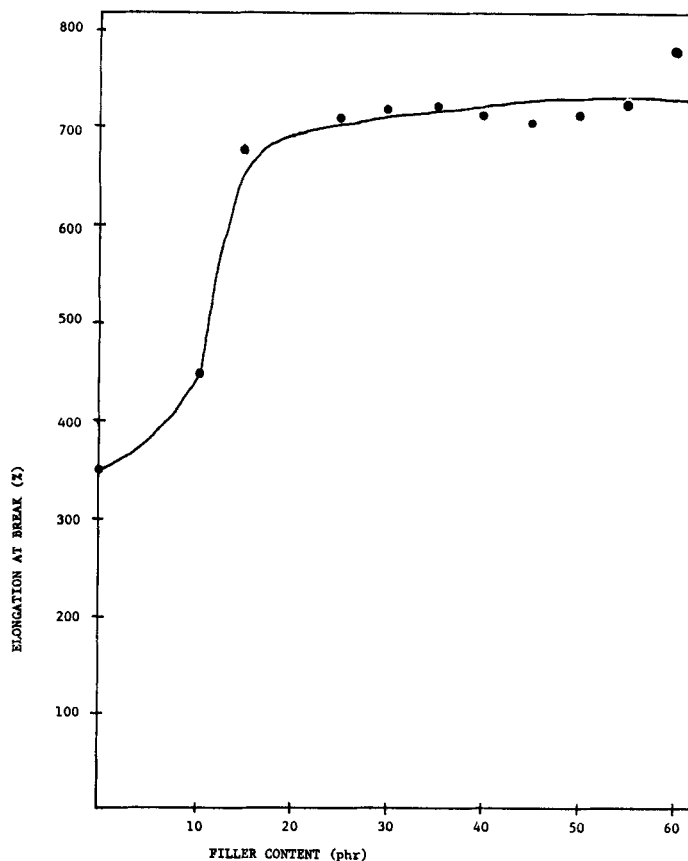


FIGURE 4 Elongation at break vs. hydrated silica content for nitrile butadiene rubber.

largely unaffected by polarity, the tensile strength of the compounded NBR was found to increase due to greater intermolecular attraction (25% and 50% with 40 ACN% NBR and carboxy-modified NBR, respectively). Higher ACN% or having carboxyl groups in the polymer results in stronger contacts between the molecules. Thus the sum of the forces holding each molecule to its neighbors is greater, leading to higher tensile strength. The main disadvantage in commercial applications, however, is that the more



polar NBR have limited low-temperature flexibility due to an increase in  $T_g$ .

## CONCLUSION

The incorporation of hydrated silica improves the chemical resistance of nitrile butadiene rubber. The filler has an effective wettability with NBR. The tensile strength and the elongation of the compounded elastomer are also favorably influenced by hydrated silica, which has a large surface area. Hydrated silica is relatively inexpensive and colorless, the latter property being advantageous over other fillers, like carbon black, in many applications. Both the chemical resistance and the tensile strength exhibit even greater improvements if NBR with high ACN% or carboxy-modified NBR is used. The latter two, however, do not meet all the specifications at lower temperatures.

In another paper, we have described the effect of hydrated silica on the foam stability and apparent viscosity of NBR.<sup>7</sup> In a related study, application of NBR for flexible, chemically protective coating has been investigated.<sup>8</sup>

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