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Properties of Closed-Cell Butyl and Nitrile Materials

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INTRODUCTION

Closed-cell materials differ from open-cell materials in that the cells are not interconnected. Three types of processes—chemical, physical or mechanical—are used to generate cellular structures. Closed-cell elastomeric materials may be made by incorporating into a solid-phase formulation a chemical blowing agent, which can be either an organic or inorganic powder, that decomposes at processing temperatures with the release of nitrogen or carbon dioxide [1,2]. One of the most important criteria in the selection of the blowing agent is its decomposition temperature, which must be matched to the processing temperature of the elastomer being used. A careful balance between the amount of curing and blowing agents is required to assure that the compound will expand to the required degree and, then, crosslink rapidly before the cellular structure has a chance to collapse or shrink [3]. In addition, a close control of a compound's viscosity is of extreme importance in the successful production of stable cell structures. Fillers are customarily added to elastomeric materials to improve their physical properties and lower the cost. The nonreinforcing fillers, such as clays and talcs, produce compounds that are easier to expand than those made with reinforcing carbon blacks or silicas [4].

This paper discusses the properties of closed-cell materials made from two types of thermosetting elastomers: carboxyacrylonitrile-butadiene

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copolymer (nitrile) and isobutylene-isoprene copolymer (butyl). The nitrile and butyl elastomers were chosen for the study because of the resistance to petroleum-type solvents and oils of the former and to oxygenated solvents of the latter, as evidenced by the solubility parameters of the respective polymers [5].

EXPERIMENTAL

Materials and Process

The ingredients [6] of the formulations given in Table 1 were blended into the solid-phase thermosetting nitrile and butyl elastomers on an unheated, two-roll mill in the order listed. In the case of the nitrile formulation, dioctyl phthalate was added for the purpose of plasticizing the nitrile elastomer, which in an uncured state has a rather high glass transition temperature (T_g) of -45°C versus T_g of -71°C for an uncured butyl elastomer, and, thus, to facilitate the cell formation. A medium-reinforcing-type carbon black, N339, which had an average particle size range of 26 to 30 nanometers, was selected as the filler. Zinc 2-mercaptotoluimidazole (Vanox ZMTI) and octylated diphenylamines (AgeRite Stalite S) were used as antioxidants. The nitrile and butyl polymers were crosslinked with sulfur and zinc oxide. Zinc stearate and stearic acid activated the crosslinking reaction and, in addition, served as lubricants. Tellurium dieth-

Table 1. Formulations yielding cellular nitrile and butyl materials.

Ingredient	Formulation (parts by weight)	
	Nitrile	Butyl
Nitrile, Nipol 1072 EP	100	0
Butyl, Exxon 268	0	100
AgeRite Stalite S	1	0
Vanox ZMTI	1	0
Carbon black, N339	30	40
Dioctyl phthalate	7	0
Stearic acid	1	0
Zinc oxide	5	5
Zinc stearate	0	1
Ethyl tellurac	0	1.5
MBTS	0	1
Sulfur	5	1
OBSH	3	2
Total	153	151.5

ylthiocarbamate (Ethyl Tellurac) and benzothiazyl disulfide (MBTS) were used for accelerating crosslinking and, thus, to shorten the cure time. The chemical blowing agent, *p,p'*-oxybis(benzenesulfonyl hydrazide), or OBSH for short, a crystalline powder which decomposes liberating nitrogen, was added last. It consisted of very fine particles, less than 0.1% of the particles were retained by a 325-mesh-sieve, which assure a uniform dispersion of the powder throughout the uncured elastomer and a formation of small cells. The OBSH decomposes rapidly between 153° and 160°C and, typically, generates 120 cc of nitrogen per gram. This temperature is sufficiently high to allow the chemical blowing agent to be milled directly into the elastomer without causing its decomposition. The cellular materials were made in a sheet form, up to 1.27 cm thick, by compression molding at 160°C for 30 minutes. The mold was only partially filled with the elastomeric compound to allow the expanding elastomer to fill the cavity. The clamping pressure on the mold was held at 1.0 MPa. For comparison purposes, noncellular materials analogous to the cellular ones were also made. They were prepared from formulations given in Table 1 from which the OBSH blowing chemical was withheld. The process conditions were those used for the cellular materials; however, in this case the mold cavity was completely filled with the compound.

Characterization of Materials

The physical properties of materials were determined according to the following ASTM Test Methods [7]: density D792; hardness D2240; tensile strength and elongation D412; tear strength D624, die C; resistance to abrasion D1630; and compression set D395, method B, 25% deflection. The curing behavior of compounds was determined with a Monsanto Oscillating Disk Rheometer, Model R-100 according to D2084. The viscoelastic properties of cured materials were studied with a TA Instruments Dynamic Mechanical Analyzer, Model 983, in accordance with D4065. The specimens, which were 50.84 by 12.30 by 6.12 mm in size, were tested in flexure between -90° and 80°C, at 2°C per minute heating rate and a frequency of 1.0 Hz.

RESULTS AND DISCUSSION

The butyl and nitrile formulations given in Table 1 were designed to yield closed-cell structures. As shown by the torque versus time cure curves in Figure 1, the torque of the compound drops at first as the compound is heated at a constant temperature of 160°C. The minimum torque value is proportional to the viscosity of the uncured compound.

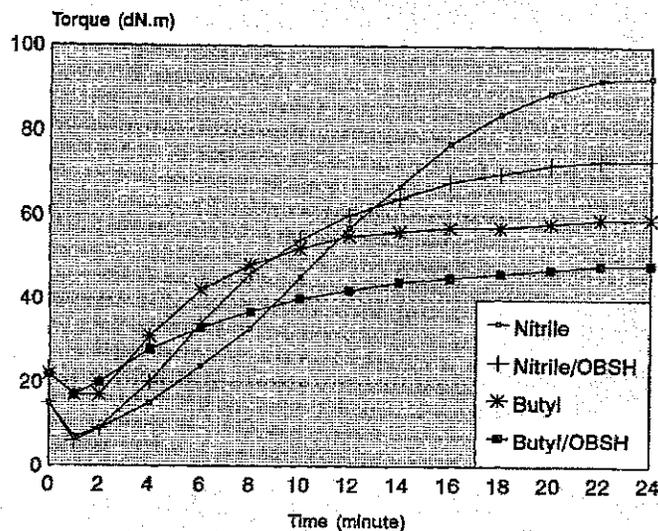


Figure 1. Cure curves of butyl and nitrile compounds, with and without OBSH blowing agent, obtained at 160°C and 3° disk oscillation.

Then, as the crosslinking progresses over time, the stiffness or torque values of the compound rise until a maximum crosslinking density is reached. The cure system was synchronized with the release of the blowing agent to achieve proper timing of gas generation and the development of structural strength. The compounds containing the OBSH blowing agent had lower maximum torque values than the compounds prepared without the blowing agent. By using a ratio of blowing-agent-to-elastomer of 3 to 100 parts by weight for the nitrile and of 2 to 100 for the butyl elastomer, and by varying the quantity of the compound placed in the mold, cellular materials with densities ranging between 0.66 and 0.84 g/cc were obtained. The cells were uniformly dispersed throughout the elastomeric matrix. The materials had an average cell diameter ranging from 30 to 64 micrometers. Figure 2 is a scanning electron microscope micrograph of a cellular nitrile material having a density of 0.76 g/cc and an average cell diameter of 46.9 micrometers with a standard deviation of 29.6.

Figure 3 shows dynamic mechanical properties of cellular and noncellular nitrile materials having densities of 0.76 and 1.13 g/cc, respectively, and Figure 4 of cellular and noncellular butyl materials having densities of 0.74 and 1.09 g/cc, respectively. The spectra provide flexural storage modulus, E' , loss modulus, E'' , and tangent delta values over a tempera-

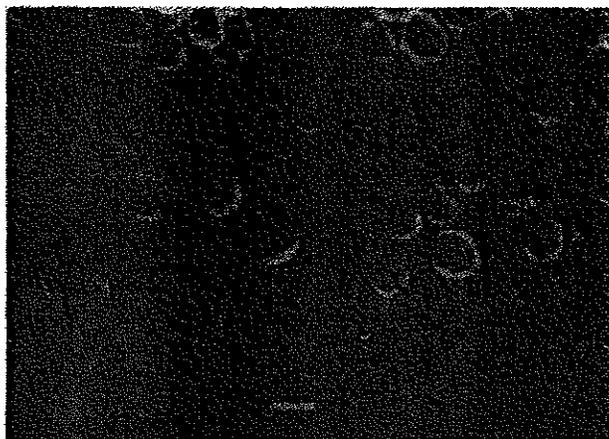


Figure 2. A micrograph of cellular nitrile material having density of 0.76 g/cc.

ture range of -90° to 80°C . They illustrate a profile of the sample's stiffness and energy dissipation capabilities as a function of temperature. In these scans, the E' curves (solid lines) show that initially the modulus decays at a constant rate, but then drops rapidly while passing through the sample's T_g region. The T_g region for the cellular and noncellular nitrile materials was between -20° and 20°C , and between -60° and -20°C for the butyl materials. The E'' and tangent delta curves reach maxima while passing through the T_g region. The higher the tangent delta value, which is defined as the ratio of the E'' modulus to the E' modulus, the greater the energy damping or dissipation of the material. The energy dissipation capabilities of the butyl materials surpass those of the nitrile materials. Overall, the E' scans indicate that the butyl materials are less rigid than the nitrile materials, furthermore, that the cellular materials are less rigid than their noncellular counterparts. The broadening of the E'' peak area of the cellular and noncellular nitrile materials is attributed to the presence of the dioctyl phthalate plasticizer in the formulation.

The ratio of the blowing agent to the elastomer matrix determines the density, and thereby affects the physical properties of these materials. Tables 2 and 3 provide comparison between some of the physical properties of the cellular and noncellular nitrile and butyl materials. The physical properties of the cellular materials approach a straight-line relationship, when plotted against density, indicating that the physical properties are a function of volume-percent-elastomer in the material. The excellent abrasive resistance of the flexible, cellular nitrile materials was further improved by forming a two-layered structure. The process involved compression molding a sandwich structure which had a thick cellular core

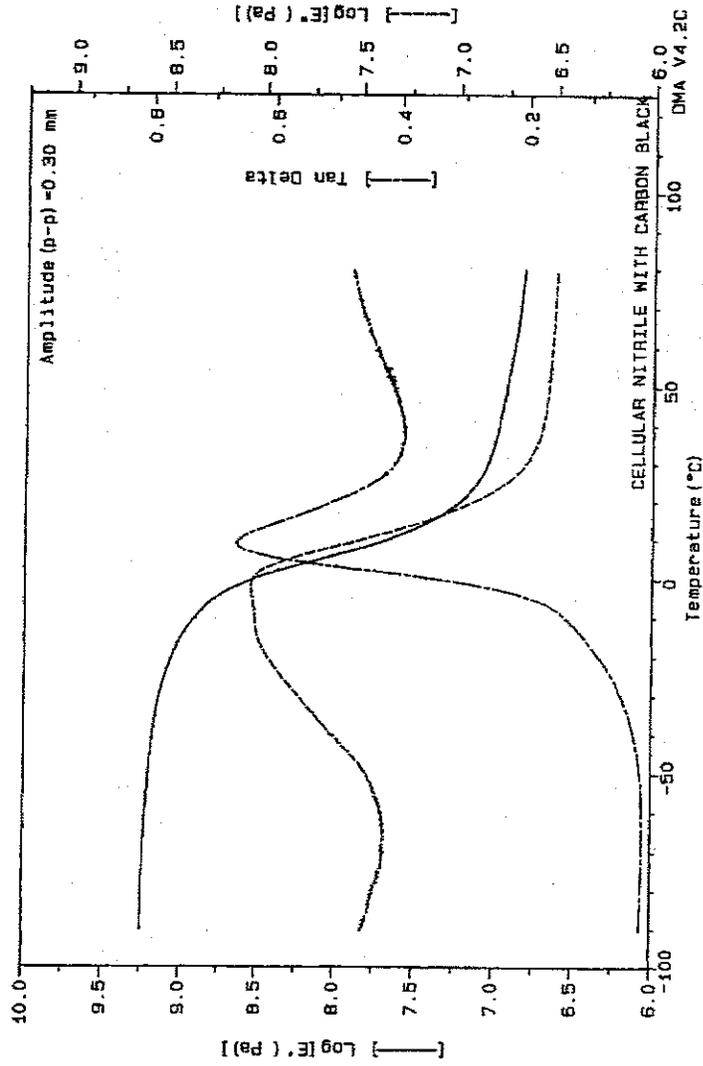


Figure 8. Spectra of dynamic mechanical properties of nitrile materials: cellular, having density of 0.76 g/cc.

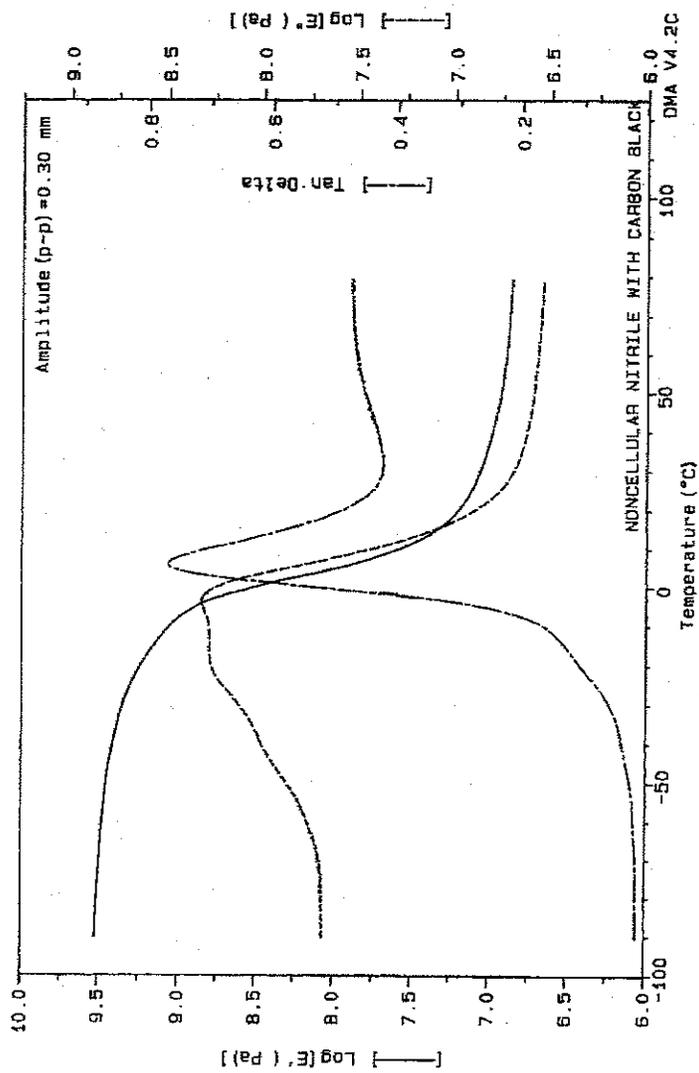


Figure 3 (continued). Spectra of dynamic mechanical properties of nitrile materials: noncellular, having density of 1.19 g/cc.

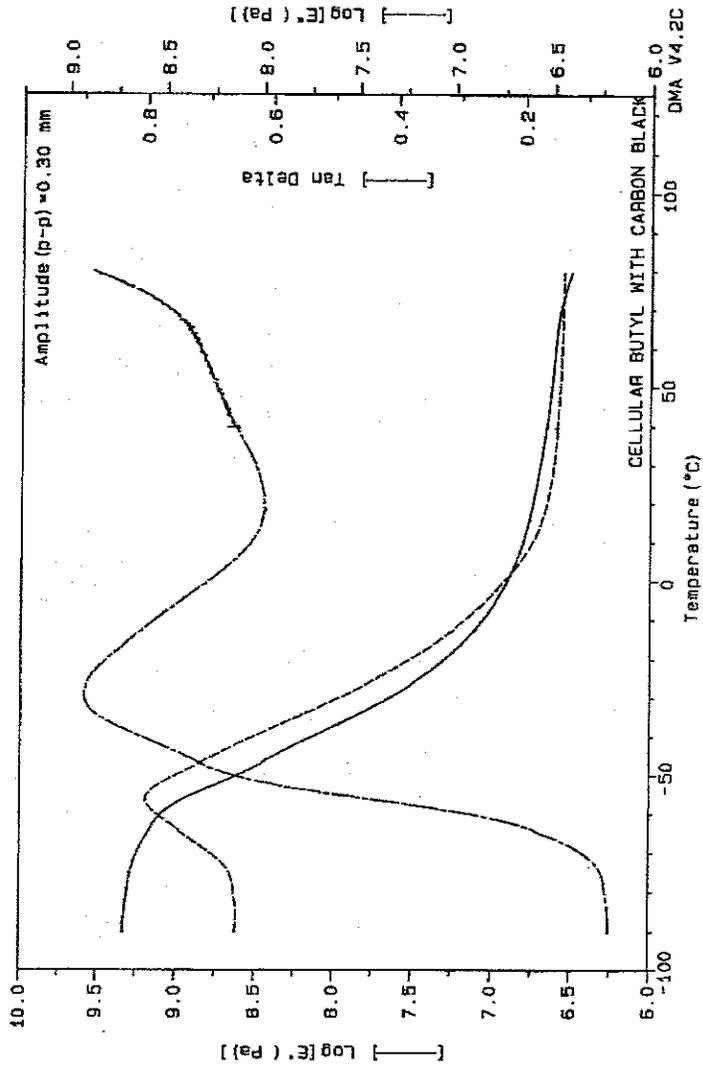


Figure 4. Spectra of dynamic mechanical properties of butyl materials: cellular, having density of 0.74 g/cc.

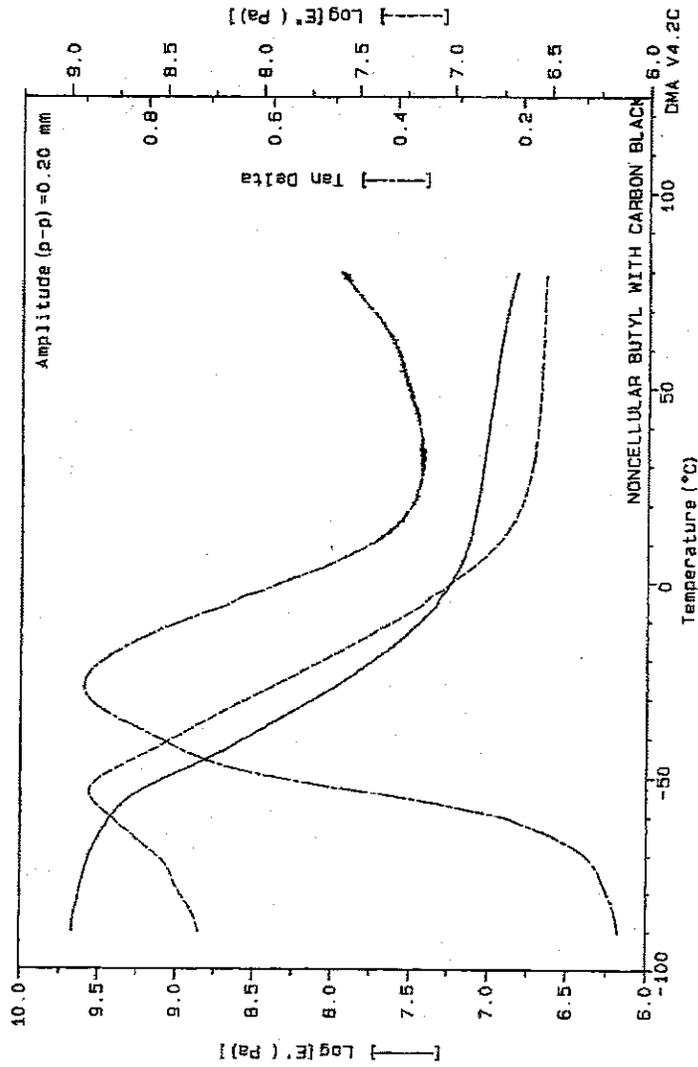


Figure 4 (continued). Spectra of dynamic mechanical properties of butyl materials: noncellular, having density of 1.09 g/cc.

Table 2. Physical properties of cellular and a noncellular, 1.13 g/cc, nitrile materials.

Property	Material Density (g/cc)			
	0.69	0.76	0.84	1.13
Hardness (Shore A)	59	63	68	78
Tensile strength (MPa)	9.1	10	11.5	17.1
Elongation at break (%)	170	210	245	325
Tear strength (kN/m)	20.7	23.5	27.5	43.8
Compression set, 22 hrs @ 70°C (%)	16	16	18	24
Abrasive index	121	388	500	660

and a thin, approximately 0.2 cm thick, noncellular skin. The nitrile formulation shown in Table 1 was used for the cellular layer, and the same formulation, less the OBSH blowing agent, was used for the skin layer. The two compounds were placed in the mold cavity, where a predetermined amount of space was provided to allow the layer containing OBSH to expand and to simultaneously bond the layers together during the curing stage. The skin layer of the resulting material had an abrasive index of 630, that is, the value closely corresponds to the abrasive index of 660 shown in Table 2 for the noncellular nitrile material having a density of 1.13 g/cc.

CONCLUSIONS

When compared with cellular butyl materials, the closed-cell nitrile materials investigated in this study show superior resistance to abrasion. Both carbon black filled and unfilled cellular nitrile offered good resistance to compression set, which is needed in applications such as cushioning, impact shock absorption, and gasketing. Moreover, butyl's excellent

Table 3. Physical properties of cellular and a noncellular, 1.09 g/cc, butyl materials.

Property	Material Density (g/cc)			
	0.66	0.74	0.84	1.09
Hardness (Shore A)	35	39	45	58
Tensile strength (MPa)	8.5	10.3	12	16.9
Elongation at break (%)	330	380	450	583
Tear strength (kN/m)	18.7	24.2	31.2	45.9
Compression set, 22 hrs @ 70°C (%)	15	15	17	20
Abrasive index	26	32	37	49

energy dissipation and flexibility at low temperatures especially warrant consideration of its cellular structures for these applications.

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