

Bound Rubber in Chlorobutyl Compounds: Influence of Filler Type and Storage Time

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ABSTRACT: Bound rubber (BdR) is considered as a measure of the filler–polymer interaction in rubber compounds. The variation of the BdR content with storage time was studied in chlorobutyl compounds filled with fillers like carbon black, carbon–silica dual phase filler (CSDPf), silica, and nanoclays. The effect of the addition of a silane coupling agent on the BdR in carbon black and silica filled compounds was also studied. The BdR content increased with

storage time in all compounds. The increase in BdR was higher during the initial 15 days of storage. Thereafter there was only a marginal increase. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 715–720, 2006

Key words: bound rubber; chlorobutyl compounds; carbon–silica dual phase filler; filler; storage

INTRODUCTION

One of the consequences of the incorporation of fillers into a polymer is the creation of an interface between a rigid phase and a soft solid phase. Because of the interaction between the rubber and filler, the polymer molecules can be adsorbed onto the filler surface either physically or chemically. This adsorption leads to two phenomena, which are well documented: the formation of bound rubber (BdR) and a rubber shell on the filler surface. The phenomenon of BdR in rubber compounds has been studied extensively and is considered a typical feature of surface activity. BdR can be defined as the rubber portion of an uncured compound, which cannot be extracted by a good solvent because of the adsorption of rubber molecules onto the filler surface. Many studies have dealt with the mechanisms and factors affecting the formation of BdR.^{1–7} BdR depends on filler characteristics like the surface area, structure or morphology, and surface activity. With regard to the polymer, the chemical nature (saturated or unsaturated, polar or nonpolar) and the microstructure of the polymer chains (configuration, molecular weight, and molecular weight distribution) influence the level of BdR content.

Generally, the BdR content is measured by extracting the unbound rubber with solvents. Other techniques include IR,⁸ microcalorimetry,⁹ electron spin

resonance,¹⁰ and NMR.^{11–13} Factors affecting the BdR content during the measurement are the nature of the solvent and its interaction with the rubber compound. The interaction between the solvent and rubber compound depends on the solvent characteristics such as the cohesive energy density and the chemical interactions (if any) that are generated.

In the present work, the variation of the BdR content of filled chlorobutyl rubber compounds with the storage time was studied for five types of carbon blacks [superabrasion furnace (SAF), high abrasion furnace (HAF), general purpose furnace (GPF), semireinforcing furnace (SRF), and medium thermal (MT)], carbon–silica dual phase filler (CSDPf), and organically modified nanoclay. Three solvents (cyclohexane, trichloroethylene, and chloroform) were used for extraction of unbound rubber in carbon black filled compounds.

EXPERIMENTAL

Materials

Bayer chlorobutyl 1240 (1.25% chlorine content, Mooney viscosity ML_{1+8} at 100°C = 38) was procured from Bayer AG. The plasticizer was highly saturated pharmaceutical grade processing oil with a specific gravity of 0.82 as supplied by C.D. Pharmaceuticals (Calcutta, India). Zinc oxide was chemically pure grade and had a specific gravity of 5.4. TMTD was supplied by ICI Ltd., Rishra (Hooghly, India) with a specific gravity of 1.42. Other compounding ingredients were chemically pure grade and procured from standard suppliers.

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Fillers

All the furnace blacks were supplied by Phillips Carbon Black Ltd. (Durgapur, India). The designation and properties of the carbon blacks, silica, CSDPf, and nanoclay were as follows:

1. SAF (N-110): mean particle diameter = 85 nm, surface area = 133 m²/g, dibenzoyl peroxide (DBP) absorption = 115 mL/100 g, pH 7.8.
2. HAF (low structure, N-330): mean particle diameter = 133 nm, surface area = 83 m²/g, DBP absorption = 100 mL/100 g, pH 7.6.
3. GPF (N-660): mean particle diameter = 283 nm, surface area = 36 m²/g, DBP absorption = 91 mL/100 g, pH 7.6.
4. SRF (N-774): mean particle diameter = 261 nm, surface area = 32 m²/g, DBP absorption = 72 mL/100 g, pH 7.7.
5. MT (N-990): mean particle diameter = 436 nm, surface area = 9 m²/g, DBP absorption = 35 mL/100 g, pH 7.7.
6. silica: Ultrasil VN3, manufactured by Degussa, surface area = 234 m²/g, oil adsorption = 240 g/100 g, pH 6.0.
7. CSDPf F variety: trade name CRX-2002, manufactured by Cabot Corporation, silica content = 3.2%, surface area = 102.6 m²/g.
8. nanoclay: organically modified montmorillonite-type nanoclay (Cloisite 15), obtained commercially; modified by methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium (~65% C18, ~30% C16, ~5% C14) with chloride anion; modifier concentration = 125 meq/100 g clay.

Sample preparation technique

The compounds were mixed in a laboratory size (325 × 150 mm) mixing mill at a friction ratio of 1:1.25 according to ASTM D 3182 standards while carefully controlling the temperature, nip gap, time of mixing, and uniform cutting operation. The temperature range for mixing was 65–70°C.

The contents of BdR were determined by extracting the unbound materials such as the ingredients and free rubber with three solvents for 7 days followed by drying for 2 days at room temperature. The weights of the samples before and after the extraction were measured, and the BdR contents were calculated using the following expression:

$$\text{BdR} = 100 \times \frac{W_{\text{fg}} - W_1 \left[\frac{m_1}{m_1 + m_r} \right]}{W_1 \left[\frac{m_1}{m_1 + m_r} \right]}$$

where BdR is the BdR content, W_{fg} is the weight of filler and gel, W_1 is the weight of the sample, m_1 is the

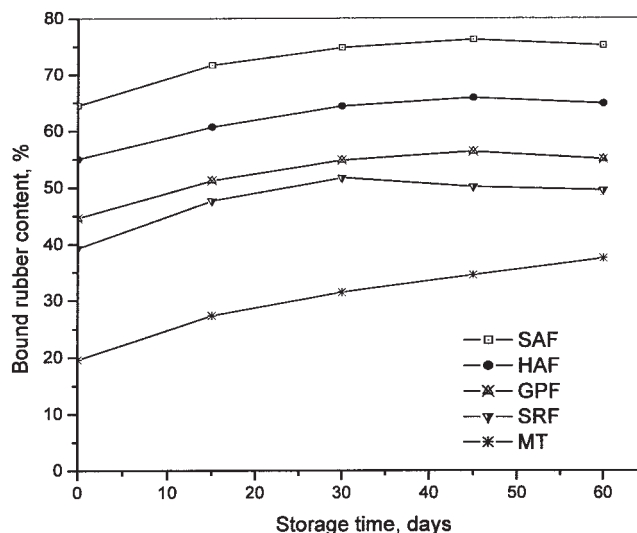


Figure 1 The variation of the bound rubber content for different carbon black filled chlorobutyl compounds as a function of the storage time in cyclohexane.

fraction of filler in the compound, and m_r is the fraction of rubber in the compound. In order to investigate the influence of the storage time the samples were aged for 60 days and the BdR content was measured at intervals of 15 days.

RESULTS AND DISCUSSION

Effect of types of carbon black

Figures 1–3 show the variation of the BdR content with the storage time for chlorobutyl compounds filled with 40 phr of SAF, HAF, GPF, SRF, and MT carbon blacks extracted with cyclohexane, chloroform, and trichloroethylene. In all the solvents it is evident that SAF loaded CIIR has the highest BdR values and that of MT black filled has the lowest. The high reinforcement and the high percentage of BdR content of SAF is attributed to the small size, high surface area, and high structure whereas MT is weakest because of its comparatively large size, low surface area, and low structure. With increasing structure of carbon black, the breakdown of the aggregates during mixing is greater which results in an increase in filler–polymer interface. Besides there is higher surface activity of freshly built surface of carbon blacks which results in instantaneous interactions between carbon black and the rubber chain ends.

Gessler¹⁴ conducted in depth research on the BdR properties of isobutylene-based elastomers and obtained exceptionally high BdR values in sulfur added compounds. He postulated that free radicals are generated by mechanical breakdown during milling of rubber and carbon black, which is responsible for the higher BdR content. For chlorobutyl compounds, he

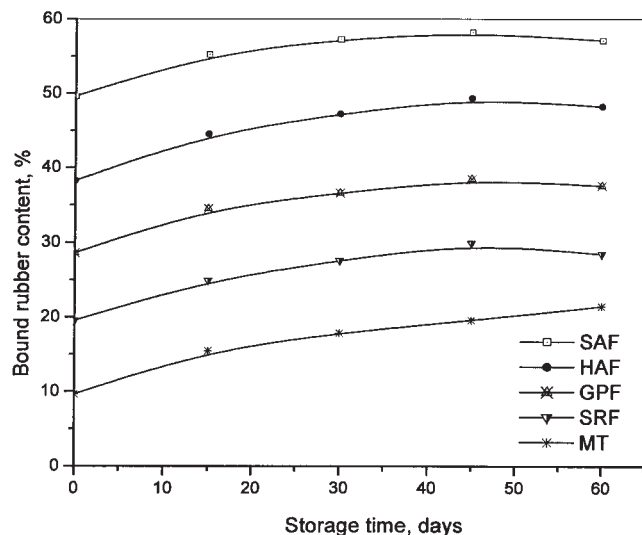


Figure 2 The variation of the bound rubber content for different carbon black filled chlorobutyl compounds as a function of the storage time in chloroform.

explained this phenomenon as a two-step theory: the reaction of sulfur with black and the reaction of this sulfur modified black with the polymer. The surface groups on carbon black react with sulfur and cure accelerators so that $\equiv\text{CS}\cdot$ radicals or $\equiv\text{CX}$ (X is SH or residues of a cure accelerator) are formed.

Hess et al.¹⁵ and Serizawa et al.¹⁶ studied the BdR phenomenon in saturated or nearly saturated elastomers like butyl rubber and found that the oxygen functionality of the carbon blacks has a profound effect in BdR formation. In case of high structured and high surface area carbon blacks like SAF and HAF, Ban et al.¹⁷ demonstrated the existence of physical adsorption that results in BdR formation. Dannenberg¹⁸ showed a decrease in BdR per unit surface with decreasing particle size of carbon blacks for styrene-butadiene rubber (SBR) compounds filled with 50 phr of carbon black. Wolff and Wang¹⁹ proposed that the rubber chains may repeatedly attach onto the carbon black surface at different sites, reducing the effectiveness of the surface because only a single attachment would render the whole molecule inextractable in a solvent. Therefore, with decreasing particle size of the carbon blacks the probability of multiattachment of rubber chains increases, thereby showing more BdR values.

It is widely accepted that the formation of BdR in a compound involves physical adsorption, chemisorption, and mechanical interaction, of which chemisorption is considered as the crucial one. The physico-chemical characteristic of the filler surface and filler morphology has a profound effect on the BdR content in a compound. Donnet et al.⁷ assumed that the unpaired spin electrons on the carbon black surface as free radicals interact with the polymer free radicals

generated by chain scission during processing, which are stabilized by the grafting of polymer molecules on the carbon black surfaces by the formation of covalent carbon-carbon bonds.

The primary carbon black parameters influencing elastomer reinforcement are the particle size or specific surface area, structure, and surface activity. The surface activity dominates polymer-filler interactions, filler aggregate interactions, as well as filler-ingredient interactions. This factor can be related to different chemical groups on the black surface such as carboxyl, quinonic, phenol, and lactonic groups. In a physical sense, variations in surface energy determine the adsorptive capacity of the filler and its energy of adsorption. In high structured carbon blacks like SAF, during the milling operation there is breakdown of the structure, resulting in more interaction between the carbon black and polymer chains, thus increasing the BdR content. The rate of increase of BdR with storage time is more in the SAF filled compounds than in other blacks. However, in all the blacks the rate of increase is more prominent in the first 45 days, after which there is a slight decrease in intensity of growth of the BdR, except in MT black filled compounds in which there is a continuous increase throughout the storage time.

Effect of silane coupling agent in carbon black filled compounds

Figure 4 show the variation in BdR with storage time in 6% silane coupling agent added chlorobutyl compounds filled with 40 phr of various types of carbon blacks extracted with chloroform. In all the compounds there is a tremendous increase in BdR values

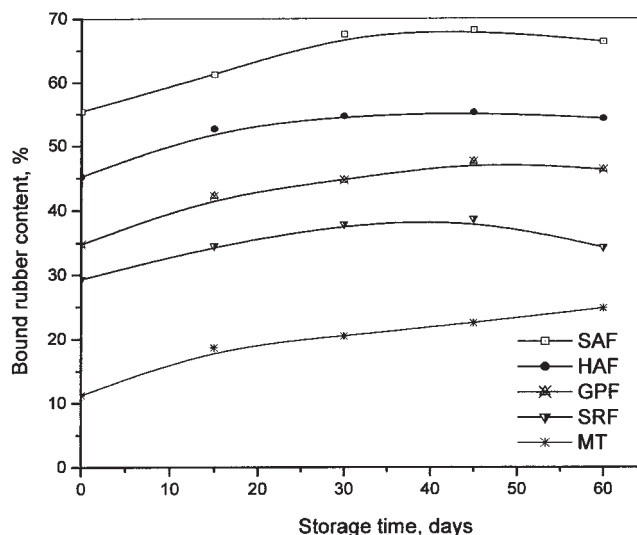


Figure 3 The variation of the bound rubber content for different carbon black filled chlorobutyl compounds as a function of the storage time in trichloroethylene.

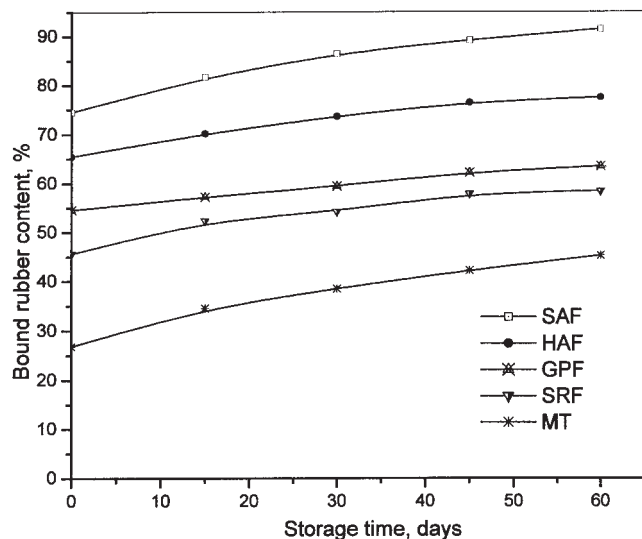


Figure 4 The variation of the bound rubber content for 40 phr of different types of carbon black filled chlorobutyl compounds as a function of the storage time and silane coupling agent loading extracted with cyclohexane.

with storage time, especially in SAF filled compounds, which have BdR values as high as 90%. The surfaces of carbon blacks have functional groups like carboxyl, ethoxy, aldehyde, and hydroxyl groups. The ethoxy group of the silane coupling agent reacts with these surface groups on the carbon blacks to form siloxane bonds. Choi²⁰ proposed a mechanism for the formation of chemical bonds between filler and rubber through silane coupling agents. He proposed that the polysulfidic links that are formed disassociate even at low temperatures if the storage times are long enough to form free radicals, which react with the rubber chains through the silane coupling agent.

Silica filled compounds

Silica is a major reinforcing agent in the rubber industry. Figure 5 shows the variation in BdR values of CIIR-silica compounds as a function of storage time and silane coupling agent. The compounds in which no silane coupling agent was added showed lower BdR values. This can be explained by the poor dispersion of silica in the CIIR matrix. The observed BdR values are consistent with the observations of Wagner and Sellers,²¹ who explained BdR formation in silica filled polyisobutylene elastomers. On the basis of the activation energy and the effect of free radical inhibitors they concluded that the mechanism of BdR formation is similar to carbon black. The surface of silica has a number of hydroxyl groups, which results in strong filler-filler interactions. These strong filler-filler interactions of silica can cause poor dispersion of silica in rubber compounds. Thus, silane coupling agents such as bis-[3-(triethoxysilyl)-propyl]-tetrasul-

fide (TESPT or Si-69) are used to improve filler dispersion and to prevent adsorption of curatives on the silica surface. The silane coupling agent reacts with the silanol groups on the surface of the silica filler to form a siloxane bond. Figure 5 shows the variation in BdR content with storage time at a constant silica loading of 40 phr with 0, 3, 6, or 9% filler loading. The BdR content in compounds with silane coupling agent show higher values when compared to compounds without it. This is due to the formation of chemical bonds between the silica and rubber through the silane. Si-69 has a sulfide linkage between triethoxysilyl propyl groups. The silica filler has numerous silanol groups on its surface. The ethoxy groups of the coupling agent react with the silanol groups of the silica to form siloxane bonds. With storage time, there is an increase in BdR content in all compounds, the highest being in the compound containing 9% coupling agent. Even in compounds with no coupling agent, there is an increase in BdR with storage time. This is contrary to the results obtained by Choi,²⁰ who found a slight decrease in BdR values with storage time in silica filled SBR compounds without silane coupling agent. Because the silica surface and chlorobutyl rubber are both polar, there may be interactions between them during stabilization of the rubber chain during storage, thereby increasing the BdR content. For the silica filled compounds containing silane coupling agent, the initial increment in BdR content with storage time is remarkable. This implies that during the initial storage period most of the chemical bonds between the silica and rubber are formed. TESPT is very reactive even at room temperature, and the reaction between silica and TESPT has been well documented.²²

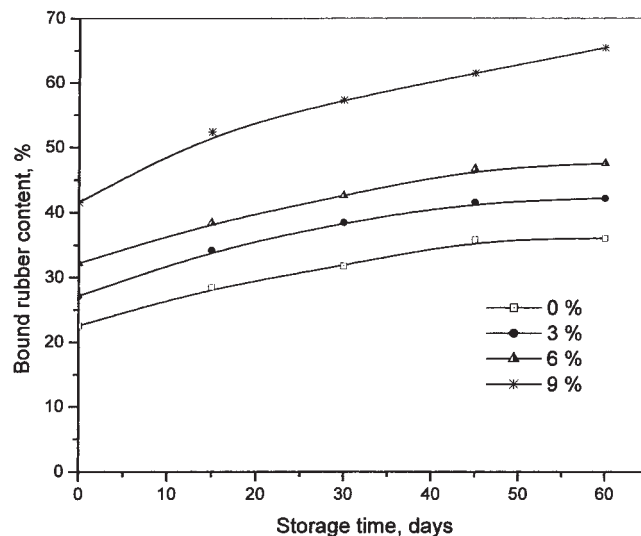


Figure 5 The variation of the bound rubber content for 40 phr silica filled chlorobutyl compounds as a function of the storage time and silane coupling agent loading extracted with cyclohexane.

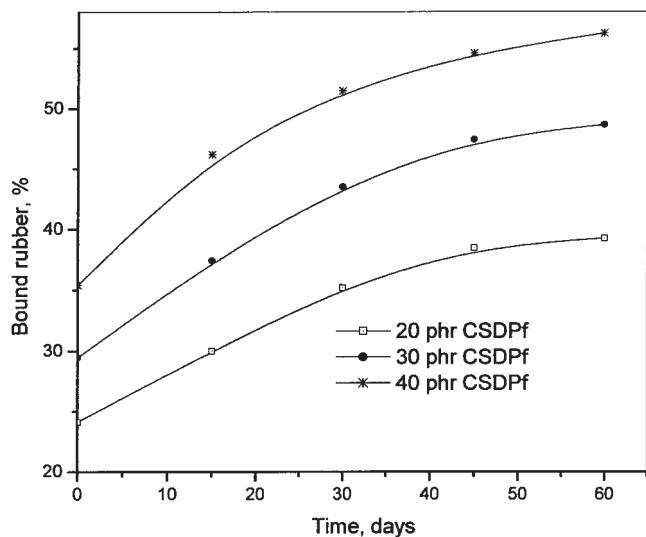


Figure 6 The variation of the bound rubber content for CSDPf filled chlorobutyl compounds as a function of the storage time extracted with chloroform.

CSDPfs

CSDPf is a new generation filler that shows excellent dynamical mechanical properties. It has a silica phase that is finely distributed in the carbon phase along with 90–99% of elemental carbon, oxygen, and nitrogen as in traditional carbon blacks. The BdR of CSDPf added chlorobutyl compounds as a function of storage time is provided in Figure 6. From the plots it is evident that the BdR is increasing with storage time. However, when we compare the BdR of CSDPf filled chlorobutyl compounds with conventional black filled systems like HAF, SAF, GPF, and SRF, the degree of BdR is considerably less. This is contrary to the findings of higher BdR in natural rubber–CSDPf systems by Wolff et al.,²³ who attributed higher values in CSDPf systems to the higher surface activity of CSDPf when compared to conventional carbon black and silica. The lower BdR values in CIIR–CSDPf compounds can be explained on the basis of a specific component of CSDPf. It has higher surface activity when compared to traditional blacks, but they have low specific components,^{24,25} in a polar polymer matrix like chlorobutyl the specific component plays a crucial role in the interaction of the polymer matrix and the filler. This phenomenon was also reflected in the physico-mechanical and dynamic mechanical properties of CSDPf systems.²⁶

Nanoclay fillers

Montmorillonite-type nanoclay fillers are being increasingly investigated as a replacement for traditional rubber fillers like carbon black and silica in rubber compounding because of the potential for the

tailoring of unique lightweight materials with distinctly superior mechanical, thermal, and barrier properties. CIIR–nanoclay composites were prepared by the solution method, the details of which are reported elsewhere.²⁷ There are no reports about the effect of the addition of nanoclay on BdR in any elastomers. The variation of the BdR in CIIR–Cloisite 15 compounds as a function of filler loading and storage time is shown in Figure 7. Note from the plot that there is an increase in BdR values with storage time, but the rate of increase in BdR values with time is not as high as observed in carbon blacks and CSDPf. Even at low nanoclay loadings of 10 phr the BdR is comparable to 40 phr carbon black loaded compounds. This can be explained by the concept of increased availability of the surface area nanoclays for the polymers to interact. The dry surface area of the nanoclay determined by Brunauer–Emmett–Teller nitrogen adsorption and the wet surface area in aqueous solution by methylene blue adsorption²⁸ are 71 and 1100 m²/g, respectively. This increased available surface of the filler may lead to increased polymer–filler interactions. Generally, the BdR in the filled compound is formed by physical adsorption and chemisorption between the rubber and the filler.

Beuche proposed that the addition of filler particles into the polymer matrix causes an increase in the number of entanglements in filled systems.²⁹ These chain entanglements can affect the particle diffusivity in a polymer matrix.³⁰ Many researchers suggested that polymer films (nanoscale) confined between adsorbing surfaces show enhanced entanglement interactions between polymer chains due to geometrical confinements even in scenarios of weak adsorp-

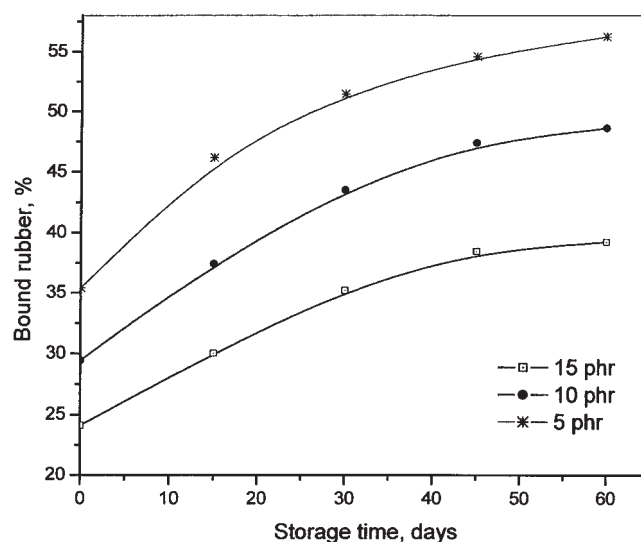


Figure 7 The variation of the bound rubber with storage time in fully exfoliated, organically modified, montmorillonite nanoclay reinforced chlorobutyl compounds extracted with cyclohexane.

tion.³¹⁻³³ These increased entanglements may also be a reason for the good BdR values in nanoclay reinforced CIIR compounds.

CONCLUSIONS

The variation in the BdR content with storage time in chlorobutyl compounds filled with 40 phr of different types of carbon blacks was studied in three different solvents. Regardless of the solvent used, the BdR increases with increasing structure of carbon black in the order SAF > HAF > GPF > SRF > MT. Solvents with more interaction with the polymer tend to show lower BdR values. The effect of a silane coupling agent in both silica and carbon black filled chlorobutyl compounds was investigated. The initial increase in BdR values in the first 15 days of storage was remarkable, after which there was only a slight increase. With an increase in silane coupling agent there was an increase in the BdR value due to an increase in the formation of chemical bonds between the filler and polymer chains. CSDPf was also used in this study. CSDPf filled chlorobutyl compounds showed lower BdR when compared to traditional black filled systems. Finally, the effect of the addition of fully exfoliated organically modified clay on BdR was studied. It was observed that nanoclay reinforced CIIR compounds showed lower BdR when compared to traditional filler systems. However, the rate of increase of BdR with storage time was found to be less than conventional fillers.

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