

Using of Leather Fibers as an Additive in Elastomeric Compounds: Its Effect on Curing Behavior and Physico-Mechanical Properties

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ABSTRACT: In this study, leather fibers have been used as an additive in several elastomeric compounds based on nitril butadiene rubber (NBR), chloroprene rubber (CR), ethylene-propylene-diene monomer (EPDM), and chlorinated isobutylene-isoprene rubber (CIIR). The effects of employing fibers upon vulcanization characteristics, physico-mechanical and thermal properties of the compounds were studied. Measuring of vulcanization characteristics of the compounds exhibited that leather fibers has no considerable effect on initial viscosity, processability, and curing time of the compounds but increases cross-link density. Evaluation of mechanical properties of the vulcanized

compounds showed that using leather fibers leads to increase in tensile strength of NBR-based compound due to compatibility between NBR and leather fibers. Also hardness of all compounds increased drastically by employing leather fibers. The obtained results showed incorporation of leather fibers had no considerable effect on resilience, density, and thermal stability of compounds but enhanced liquid resistance. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1670–1675, 2009

Key words: elastomer; leather fibers; swelling behavior; mechanical properties; curing behavior

INTRODUCTION

Leather is a fibrillar protein consisting of collagen chains cross-linked by chromium ions into a network.¹ About 50% of raw hide is rejected as solid wastes which contain 2–6% Cr³⁺ ions.² These wastes have some environmental pollution hazards, because Cr³⁺ ions can be oxidized to the toxic Cr⁶⁺ which ends to ground water contamination.³ Most of these wastes are obtained during shaving process in the form of leather fibers.⁴ These leather fibers can be used as an ingredient of the polymeric compounds to modify some physical and mechanical properties and also reduce the cost of the compounds.⁵ Meanwhile, chromium ion acts as an oxidation agent and decreases degradation temperature of some polymers, so leather fibers can be used in rubber products which will be reclaimed after consumption. In addition using leather fibers in rubber compounds contain scrap rubber causes oxidation and degradation of some cross-links in scrap rubber, which increases interaction between scrap rubber and matrix and as a result, improves physical and mechanical properties of the compound. For example,

addition of leather fibers to natural rubber compounds which contain scrap rubber leads to higher tensile strength, modulus, hardness, and tear strength of the compounds.⁶ Investigations show that incorporation of leather fibers in polyvinyl chloride (PVC) compositions increases density, hardness, and abrasion resistance and decreases tensile properties. Also PVC sheets contain leather fibers show more flexibility and processability at high temperatures with lower cost.^{7,8} Using surface treated short leather fibers in polyurethane (PU) matrices has been led to more flexibility and thermal resistance of the films manufactured from PU. Acrylamide monomers have been used for surface modification of the short leather fibers.⁹

As the leather fibers have a lot of reactive functional groups and also contain Cr³⁺, so it is expected that using these fibers in elastomeric compounds affects the vulcanization characteristics and physico-mechanical properties of the compounds.

In this work, we used leather fibers as an ingredient of nitril butadiene rubber (NBR), ethylene-propylene-diene monomer (EPDM), chloroprene rubber (CR), and chlorinated isobutylene-isoprene rubber (CIIR) based compounds. Processability and curing behavior of the compounds were studied by using an oscillating disk rheometer. The effects of leather fibers upon thermal degradation and mechanical

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TABLE I
Specifications of the Leather Fibers used in this Study

| Properties | Values |
|--------------------------------|---------|
| Color | Grayish |
| Aspect ratio | 21.53 |
| Decomposition temperature (°C) | 280–350 |
| PH | 3.7 |

properties of the compounds were evaluated and variation of density and cross-link density were measured and reported. Also the effects of leather fibers on swelling behavior of the compounds in exposure to different liquids include toluene, water, oil, and ethanol was evaluated.

EXPERIMENTAL

Materials

Specifications of the used leather fibers and elastomers have been shown in Tables I and II, respectively. In this study, sulfur (S), carbon black (N330), zinc oxide (ZnO), paraffinic oil, and di octyl phthalate (DOP) were obtained from Iranian suppliers. Magnesium oxide (MgO), tetramethyl thiuram disulphide (TMTD), *N*-cyclohexyl-2-benzothiazol sulfenamide (CBS), mercaptobenzothiazole (MBT), and ethylene thiourea (ETU) from Bayer Company and stearic acid from Unichema have been used. Leather fibers were obtained from a local company and employed in the compounds after shredding with a cutter miller.

Samples preparation

The composition of the prepared compounds has been listed in Table III. In this table (N), (C), (CI),

TABLE II
Specifications of the Elastomers used in the Study

| Materials | Grade | Mooney viscosity | Manufacturer |
|-----------|------------------------------|------------------|---------------------|
| NBR | KOSYN KNB35L | 41 ^b | Kumho Petrochemical |
| EPDM | Herlen 521 | 45 ^b | Unimers India |
| CR | Butaclor DE 302 ^a | 50 ^b | Polimeri Europa |
| CIIR | CB 1240 | 38 ^c | Bayer |

^a This grade contains gelled (cross-linked) polymer.

^b Mooney viscosity (ML 1+4, 100°C).

^c Mooney viscosity (ML 1+8, 125°C).

and (E) represent compounds contained NBR, CR, CIIR, and EPDM rubbers, respectively, and (L) suffix denotes employing of leather fibers in the same corresponding compound. Mixing of the compounds was carried out on a Farrell laboratory 6-in. two roll mill.

To prepare specimens for measuring physical and mechanical properties of the vulcanizates, compression molding process was employed by using a hydraulic press at 150°C and 70 bar and compounds were cured into 2-mm thick sheets in a standard mold according to optimum cure time (t_{90}) obtained from an oscillating disc rheometer.

Characterization

Curing characteristics

Curing behavior of the compounds was measured according to ASTM D2084 by using ODR 100s Monsanto rheometer apparatus at $\pm 3^\circ$ oscillation angle. Maximum (MH) and minimum (ML) torques, scorch time (t_s), and optimum cure time (t_{90}) of the compounds were determined.

TABLE III
Composition of the Compounds Prepared in this Work

| Ingredients | N | N-L | C | C-L | E | E-L | CI | CI-L |
|--------------------|------------------|-----|------------------|-----|------------------|-----|------------------|------|
| NBR elastomer | 100 ^a | 100 | – | – | – | – | – | – |
| CR elastomer | – | – | 100 ^a | 100 | – | – | – | – |
| EPDM elastomer | – | – | – | – | 100 ^a | 100 | – | – |
| CIIR elastomer | – | – | – | – | – | – | 100 ^a | 100 |
| Carbon black(N330) | 70 | 70 | 30 | 30 | 50 | 50 | 15 | 15 |
| DOP oil | 15 | 15 | – | – | – | – | – | – |
| Paraffinic oil | – | – | – | – | 10 | 10 | – | – |
| Zinc oxide | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| Magnesium oxide | – | – | 3 | 3 | – | – | 2 | 2 |
| Stearic acid | 2 | 2 | – | – | 1 | 1 | – | – |
| CBS | 2 | 2 | – | – | – | – | – | – |
| MBT | – | – | – | – | 0.7 | 0.7 | 0.7 | 0.7 |
| TMTD | 2 | 2 | 1 | 1 | 1.5 | 1.5 | 1.5 | 1.5 |
| ETU | – | – | 0.5 | 0.5 | – | – | – | – |
| Sulfur | 0.3 | 0.3 | – | – | 1.5 | 1.5 | 1.5 | 1.5 |
| Leather fibers | 0 | 5 | 0 | 5 | 0 | 5 | 0 | 5 |

^a phr.

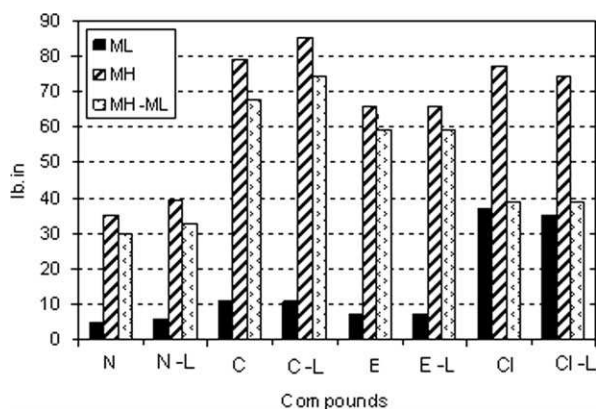


Figure 1 Comparison of torque of rheometry for prepared compounds.

Properties of the vulcanizates

Tensile properties of the vulcanizates were measured on specimens punched out from the molded sheets using ASTM Die-C by Instron 1026 equipment in accordance with ASTM D412, a standard test method for tensile properties of vulcanized rubber. Tensile tests were carried out at room temperature and cross-head speed of 500 mm/min. For each formulation, four specimens were tested and average values determined. Zwick hardness tester was employed according to ASTM D2240 for measuring hardness of the prepared samples. Density of the samples was determined with Wallace apparatus which is designed according to Archimedes rule. Also resilience of the vulcanizates measured according to DIN53512 standard with a Frank apparatus.

Thermal stability

Since thermogravimetric analysis (TGA) provides information about thermal degradation of polymers; a thermogravimetric analyzer (TGA Instrument, DuPont 951) was used to assess the influence of leather fibers on thermal degradation of the compounds. TGA tests were carried at a heating rate of 10°C/min with a thermal ramp over the temperature range of 30–600°C.

Swelling behavior

Swelling behavior of the compounds based on NBR and CR in exposure to toluene, water and ethanol, was evaluated according to ASTM D471 and weight variation of the specimens determined after 72 h at room temperature. Oil resistance of the compounds in exposure to ASTM No. 1 oil was measured after 650 h at room temperature with the same procedure.

RESULTS AND DISCUSSION

Vulcanization characteristics

Figure 1 shows the results obtained by rheometry test of the compounds. It can be seen that employing of leather fibers has no considerable effect on minimum torque of rheometry. It can be concluded that addition of 5 phr leather fibers had no remarkable effect on processability of the compounds.

Employing 5 phr leather fibers increases maximum torque and difference between maximum and minimum torque of rheometry for compounds based on CR and NBR compared with similar compounds without leather fibers, whereas there is no change in those parameters for compounds based on EPDM and CIIR (Fig. 1). Since using of leather fibers increased maximum torque and had no effect on minimum torque, it can be concluded that leather fibers are more compatible with polar rubbers such as CR and NBR compared with nonpolar elastomers like EPDM due to leather fibers polar structure. Exposing to high temperature conditions and formation of cross-links during vulcanization process reinforces interfacial adhesion between leather fibers and elastomer and causes to increase in torque of rheometry. On the other hand hydroxyl (OH) and carboxyl (COOH) groups of collagen chains affect the vulcanization process and increase its efficiency depending on the type of elastomer and curing agent of the compound. According to obtained results (Table IV), employing leather fibers has no considerable effect on scorch time and optimum cure time of EPDM-, NBR-, and CR-based compounds, but it increases these parameters in CIIR-based compound.

TABLE IV
The Results of Rheometric Tests and Physical-Mechanical Measuring of Compounds

| Properties | N | N-L | C | C-L | E | E-L | CI | CI-L |
|--|------|------|------|------|------|------|------|------|
| t_s (min) | 2.6 | 2.4 | 1.4 | 1.6 | 1.8 | 1.8 | 1.7 | 3.1 |
| t_{90} (min) | 5.6 | 5.7 | 11.2 | 9.8 | 6.2 | 6.6 | 10.5 | 17 |
| Tensile strength (Kg/cm ²) | 151 | 160 | 265 | 208 | 125 | 97 | 118 | 94 |
| Elongation at break (%) | 360 | 320 | 470 | 330 | 275 | 230 | 550 | 505 |
| Hardness (shore-A) | 66 | 77 | 62 | 72 | 62 | 68 | 43 | 48 |
| Density (g/cm ³) | 1.19 | 1.20 | 1.40 | 1.40 | 1.05 | 1.05 | 1.03 | 1.04 |
| Resilience (%) | 30 | 29 | 54 | 52 | 58 | 56 | 17 | 15 |

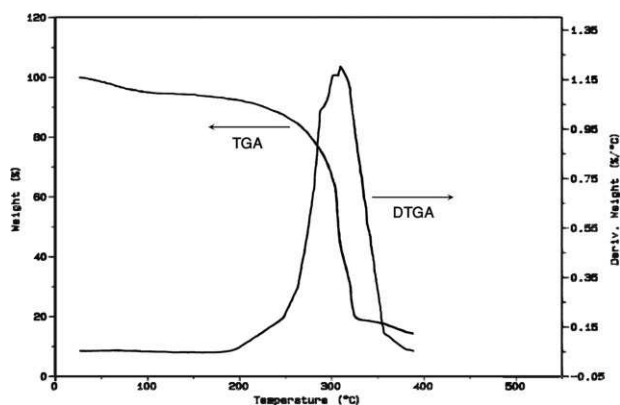


Figure 2 Thermogravimetric analysis of leather fiber used in this work.

Tensile properties

The obtained results of measuring tensile properties, hardness, density, and resilience of the vulcanizates have been shown in Table IV. As it can be seen in this Table, tensile strength of NBR-based compound improves by using leather fibers because of good compatibility between leather fibers and NBR due to their similar polarity which leads to a strong interfacial adhesion between leather fibers and NBR. Poor interfacial bonding ends to making voids at interfaces and growth of voids leads to crack formation and lower tensile strength of the compounds. Incorporation of leather fibers in CIIR, CR, and EPDM vulcanizates causes to decrease in tensile strength because of lower compatibility between fibers and these elastomers compared with NBR-based compound. On the other hand high difference between modulus of soft elastomeric matrices and hard fibers phase leads to difference between strain of these phases during applying tension, and making voids at interfaces. Growth of these voids finally ends to tear of samples and decreases elongations at break of all compounds contain leather fibers.

Hardness

Table IV shows that by employing of fibers, the hardness of all compounds has been increased. The incorporation of leather fibers has increased the hardness of NBR, CR, EPDM, and CIIR by 28%, 13%, 10%, and 11%, respectively, which can be attributed to the higher hardness of leather fibers compared with the elastomeric matrices and also to interfacial interaction between leather fibers and elastomer. It should be mentioned that in spite of increase in hardness, there are no considerable effect on minimum torque of rheometry (Fig. 1) and density (Table IV) of the compounds. Therefore, leather fibers can be used easily in the compounds to increase the hardness.

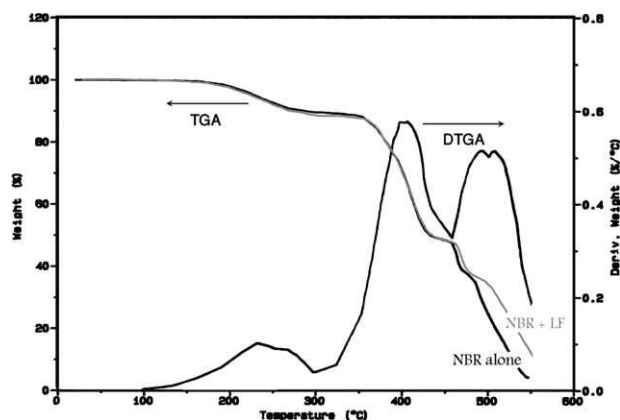


Figure 3 Thermogravimetric analysis of NBR-based compounds with and without leather fibers.

Rebound resilience

As presented in Table IV, the incorporation of leather fibers has no considerable effect on rebound resilience of vulcanizates and it was almost the same in compounds with and without leather fibers. It is known that resilience depends on viscoelastic properties of elastomeric material, therefore, it is expected that using leather fibers in an elastomeric compound does not lead to variation of viscoelastic properties.

Thermal stability

NBR- and CR-based vulcanizates were selected for evaluating their thermal properties due to their good performance in the case of using leather fibers as a component of the compound.

Thermograms (TGA and DTGA graph) obtained by TGA are shown in Figures 2–4. As it can be seen in Figure 2, degradation of pure leather fibers occurred at 280–350°C and indicates that compounds contain leather fibers can be cured safely and processed at high temperatures. As shown in the figures,

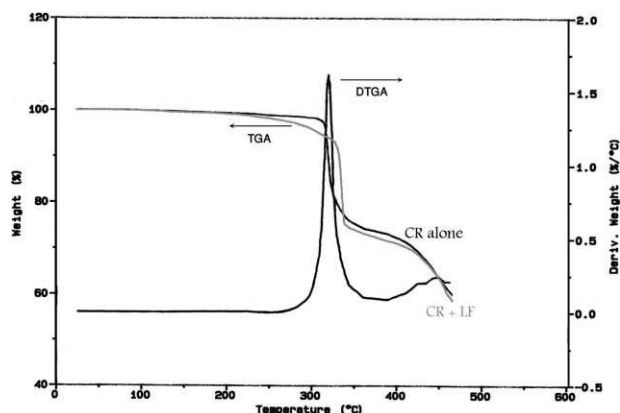


Figure 4 Thermogravimetric analysis of CR-based compounds with and without leather fibers.

TABLE V
Variation of the Vulcanizates in Exposure to Liquids and their Cross-Link Density

| Properties | N | N-L | C | C-L |
|--|--------|-------|--------|--------|
| Variation of compound in water (wt %) | 0.94 | 1.50 | 1.08 | 1.52 |
| Variation of compound in ethanol (wt %) | 5.38 | 4.93 | 0.98 | 0.71 |
| Variation of compound in oil No.1 (wt %) | -0.54 | -0.74 | 3.67 | 2.89 |
| Variation of compound in toluene (wt %) | 106.80 | 83.71 | 191.33 | 138.88 |
| Cross-link density (10^{-4} mol/cm ³) | 5.96 | 7.85 | 1.93 | 3.00 |

incorporation of a low level of leather fibers has no effect on start degradation temperature and degradation rate of NBR-based compound (Fig. 3) due to interaction between this elastomer and leather fibers. The amount of residual material of NBR compound at 550°C is about 5.5%, which is the residue of ingredients of the NBR compound, whereas that of the NBR compound with leather fibers is 10.5%, corresponding to the amount of fibers that has been added. Leather fibers in CR-based compound slightly decreases start point temperature of degradation (Fig. 4). However the presence of Cr³⁺ ion in tanned leather and its role as an oxidation agent may changes thermal stability of the compounds with high level contents of leather fibers.

Swelling behavior

The swelling behavior of the NBR- and CR-based compounds in exposure to different liquids was evaluated. The results obtained from swelling tests (Table V) showed that using leather fibers in NBR- and CR-based compounds increases water absorption of the compounds due to polarity of leather fibers and their tendency to water absorption. The same reason causes a slight reduction in diffusion of ethanol into the mentioned compounds.

As it can be seen in Table V, the weight of NBR-based compounds has been decreased a little in exposure to ASTM No. 1 oil, because of incidental extraction of aromatic oils which exist in the compounds, and incorporation of leather fibers in the compound has no considerable effect on oil resistance of the compound. In CR-based compounds using leather fibers ended to incidental improvement of compound oil resistance.

Table V shows a considerable reduction in toluene absorption for the compounds which contain leather fibers. Also Figures 5 and 6 indicate that the rate of toluene absorption is decreased by using leather fibers in the compound, these results can attribute to increasing of cross-link density.

Determination of cross-link density

The results obtained through swelling test of vulcanized samples by using toluene as a solvent

were employed to determine cross-link density of the compounds in accordance to Flory-Rehner equation:¹⁰

$$n = \frac{-[Ln(1 - v_2) + v_2 + \chi_1 v_2^2]}{V_1(v_2^{1/3} - v_2/2)}$$

where n is the cross-link density, V_1 is the molar volume of the solvent, v_2 is the volume fraction of polymer in the swollen sample, and χ_1 is the Flory-Huggins polymer-solvent interaction parameter which shows the enthalpy of mixing and can be determined by following equation:¹⁰

$$\chi_1 = \beta_1 + \frac{V_1(\delta_1 - \delta_2)^2}{RT}$$

where β_1 is lattice constant of entropic origin and often assumed equal to zero, T is media temperature, and δ_1 and δ_2 are solubility parameters for solvent (18.2 MPa^{0.5} for toluene) and polymer (20.26 MPa^{0.5} for NBR and 18.5 MPa^{0.5} for CIIR), respectively.¹¹

And v_2 can be calculated from equation:

$$v_2 = \frac{1}{1 + SR(\rho_2/\rho_1)}$$

where SR is the equilibrium swelling ratio of the samples, ρ_2 is the density of the vulcanizates, and ρ_1 is the density of the solvent (0.8669 g/cm³).

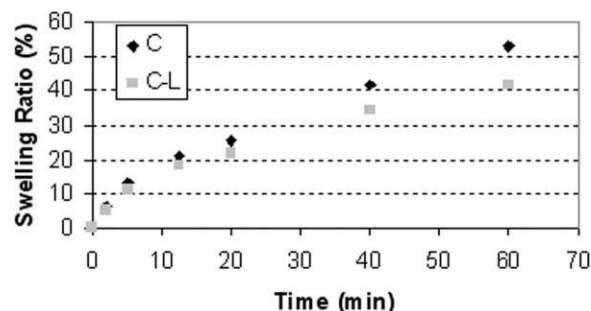


Figure 5 Swelling behavior of CR-based compounds in toluene.

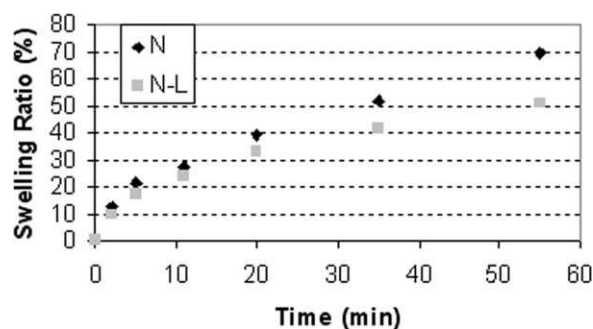


Figure 6 Swelling behavior of NBR-based compounds in toluene.

Cross-link density of the samples calculated through employing above equations is shown in Table V. These results show that adding of leather fibers to NBR and CR compounds conclude to considerable increase in cross-link density of compounds which affects the maximum torque (MH) in rheometric characteristic of these compounds (Fig. 1). It can be explained that the presence of functional groups and chromium ions on the surface of leather fibers affect the activity of the accelerators and activators used in curing system conclude to increase in cross-link density and maximum torque of rheometry.

CONCLUSIONS

According to results obtained in this work employing of 5 phr of leather fibers in elastomeric compounds does not affect the compound processability, but considerably increases hardness of the vulcanized compounds due to increasing of cross-link density and rigid fibrous structure of leather fibers

which was confirmed by measuring of cross-link density and evaluating torque of rheometry.

Tensile strength of NBR-based compound was improved because of increase in cross-link density and due to compatibility between NBR and leather fibers. Strength properties of CR-, CIIR-, and EPDM-based compounds decreased a little by using leather fibers, which exhibited a lower compatibility between these elastomers and leather fibers.

Rebound resilience and also thermal degradation properties of the compounds did not change considerably by using leather fibers but its liquid resistance was improved.

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