Mechanochemical Preparation of Devulcanized Ground Fluoroelastomers for the Enhancement of the Thermal Stability of Nitrile–Butadiene Rubber Vulcanizates

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ABSTRACT: Mechanochemically devulcanized ground fluoroelastomer (FKM) was used as a low-cost functional additive for the enhancement of the thermal stability of nitrile–butadiene rubber (NBR) vulcanizates. Without the use of any chemicals, the stress-induced mechanochemical devulcanization of ground FKM was achieved through solid-state mechanochemical milling at ambient temperature. The sol fraction of the ground FKM was increased from its original 1.4 to 19.8% after milling; this confirmed the realization of the mechanochemical devulcanization of FKM. Moreover, the oxygen-containing polar groups on the surface of the mechanochemically milled FKM benefitted its interfacial adhesion with the polar NBR matrix. The curing characteristics and mechanical properties of the devulcanized, FKM-filled NBR vulcanizates were investigated and compared with those of the untreated FKM-filled NBR vulcanizates. The results show that the mechanical properties of the devulcanized FKM-filled NBR vulcanizates were much better than those of the untreated FKM-filled NBR vulcanizates. The presence of the reclaimed FKM significantly increased the onset degradation temperature of the NBR vulcanizates as a result of the improved polymer–filler interaction, uniform dispersion, and high thermal stability of the reclaimed FKM. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: fluoropolymers; recycling; rubber; thermal properties; waste

INTRODUCTION

With the increasing public awareness of ecology and the state of the environment, there is substantial motivation to develop practical methods and apparatuses for devulcanizing ground rubbers, which have a three-dimensional crosslinked structure.[1,2] Another motivation for recycling rubber products is the economic benefit that could be gained by using devulcanized rubber in the replacement of virgin rubber.[3–8]

Fluoroelastomers (FKMs) are increasingly being used as high-performance seal materials in many industrial and space applications because of their excellent thermal, oil, and chemical resistances, which arise from their C—F bonds.[9,10] As a very expensive material, FKM's devulcanization has received more attention than that of many other rubbers because of the potential for greatly decreasing the cost of raw materials. However, the strong chemical bonds make it difficult to decrosslink and recycle.[11] The methods, such as chemical,[12] ultrasonical,[13] microwave,[14] and thermomechanical[15] devulcanization technologies, used for tire rubber and conventional rubber devulcanization cannot be simply transplanted onto FKM devulcanization.

In this study, we used an environmentally friendly method, solid-state mechanochemical milling, to devulcanize post-vulcanized FKM scraps without the use of any chemicals. The pan-mill equipment was designed in our laboratory for solid-state mechanochemical reactions of polymers and was based on a traditional Chinese stone mill. Because of its unique structure, the pan-mill equipment acted as pairs of three-dimensional scissors during milling, exerting very strong shear forces on the milled materials and showing multiple functions, including pulverizing, dispersion, mixing, and activation.[16–23] Our previous investigations[24–28] on the mechanochemical devulcanization of waste rubbers by pan milling suggested that the three-dimensional network in rubber vulcanizates can be effectively broken up to form decrosslinked structures in the presence of fairly strong shearing and squeezing forces. These mechanochemically devulcanized rubbers are softened and can be reprocessed, shaped, and revulcanized in a manner similar to that employed with

TABLE I
Curing Recipes for Reclaimed FKM-Filled NBR Compounds

Ingredient (phr)	Formulation code								
	1	2	3	4	5	6	7	8	9
NBR	100	100	100	100	100	100	100	100	100
Untreated FKM	—	40	80	120	160	—	—	—	—
Devulcanized FKM	—	—	—	—	—	40	80	120	160
Zinc oxide	4	4	4	4	4	4	4	4	4
Stearic acid	2	2	2	2	2	2	2	2	2
CBS	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
DM	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

virgin elastomers. Traditional rubber devulcanization approaches involve the use of chemicals to break down the crosslinked structure.[29,30] They always produce chemical sludges and residues that are harmful to both human life and the environment if not properly disposed of. The mechanochemical devulcanization approach based on stress-induced crosslink scission appears to be an ecologically benign technique compared with conventional solvent-based chemical devulcanizaiton. Another advantage of the solid-state mechanochemical milling process over other devulcanization technologies is that it is an energy-saving process because it is done at ambient temperature without heating.

The aim of this study was to prepare nitrile–butadiene rubber (NBR) vulcanizates with mechanochemically devulcanized FKM as a functional additive to enhance its thermal stability. The influence of mechanochemically devulcanized FKM on the composites' properties, including curing behavior, mechanical properties, and thermal stability, are discussed in detail.

EXPERIMENTAL

Materials

NBR, with a 33 wt% acrylonitrile content, was purchased from Nitriflex S. A. Industria e Comercio (Cotia, Brazil). It had a Mooney viscosity [$ML_{(1+4)}$ at 100°C] of 46. The waste FKM used in this study was scrap generated from the manufacturing processes of seal materials, which was post-vulcanized and kindly provided by Jiangsu Meiah Rubber & Plastics Technology Co., Ltd. (Danyang, China). Other compounding ingredients, such as zinc oxide, stearic acid, sulfur, the N-cyclohexyl benzthiazyl sulfenamide (CBS) accelerator, and 2,2-dibenzothiazole disulfide (DM), were obtained commercially.

Sample preparation

The mechanochemical devulcanization of ground FKM was achieved through high shearing and squeezing forces generated by the pan-mill mecha-

nochemical reactor. The details of the pan-mill equipment and operation procedure can be found in our previous publication.[16,17] The resulting material was blended with NBR on a two-roll mixing mill (diameter = 150 mm, working distance = 320 mm, speed of the slow roll = 15 rpm, friction ratio = 1 : 1.4) at a processing temperature of about 50°C. The compound recipes are listed in Table I. FKM powder was masticated with virgin NBR and then mixed with several compounding ingredients. The mixing time was 10 min. The vulcanization was carried out with a compression-molding press at 150°C and the application of a pressure of 10 MPa for the optimum cure time. Vulcanized sheets (2 mm thick) were obtained to evaluate the mechanical properties and thermal stability.

Characterization

The morphological development of reclaimed FKM during solid-state mechanochemical milling was observed with a JEOL JSM-5600 scanning electron microscope (JEOL, Ltd., Akishima, Japan). A thin layer of Pd–Au alloy was coated on the specimen to prevent charging on the surface. Scanning electron microscopy (SEM) was done at 20 kV.

The sol fractions of FKM before and after solid-state mechanochemical milling were measured by Soxhlet extraction methods with ethyl acetate as a solvent. The samples were refluxed in ethyl acetate for 24 h and then dried in a vacuum oven at 50°C for 6 h. The weights of the samples were recorded before and after the treatments.

X-ray photoelectron spectra (XPS) were recorded on an XPS spectrometer (XSAM800, Kratos, Manchester, U.K.) with a monochromatized Al Kα X-ray source (1486.6 eV photons). The X-ray spot sizes were 1000 and 300 μm for the acquisition of the survey and narrow scan regions, respectively. The binding energies were corrected to the carbon 1s peak located at 285.0 eV.

The curing characteristics of the NBR compounds were analyzed by a rubber curometer (R100E, Beijing Youshen Electronic Co., Ltd., Beijing, China) at
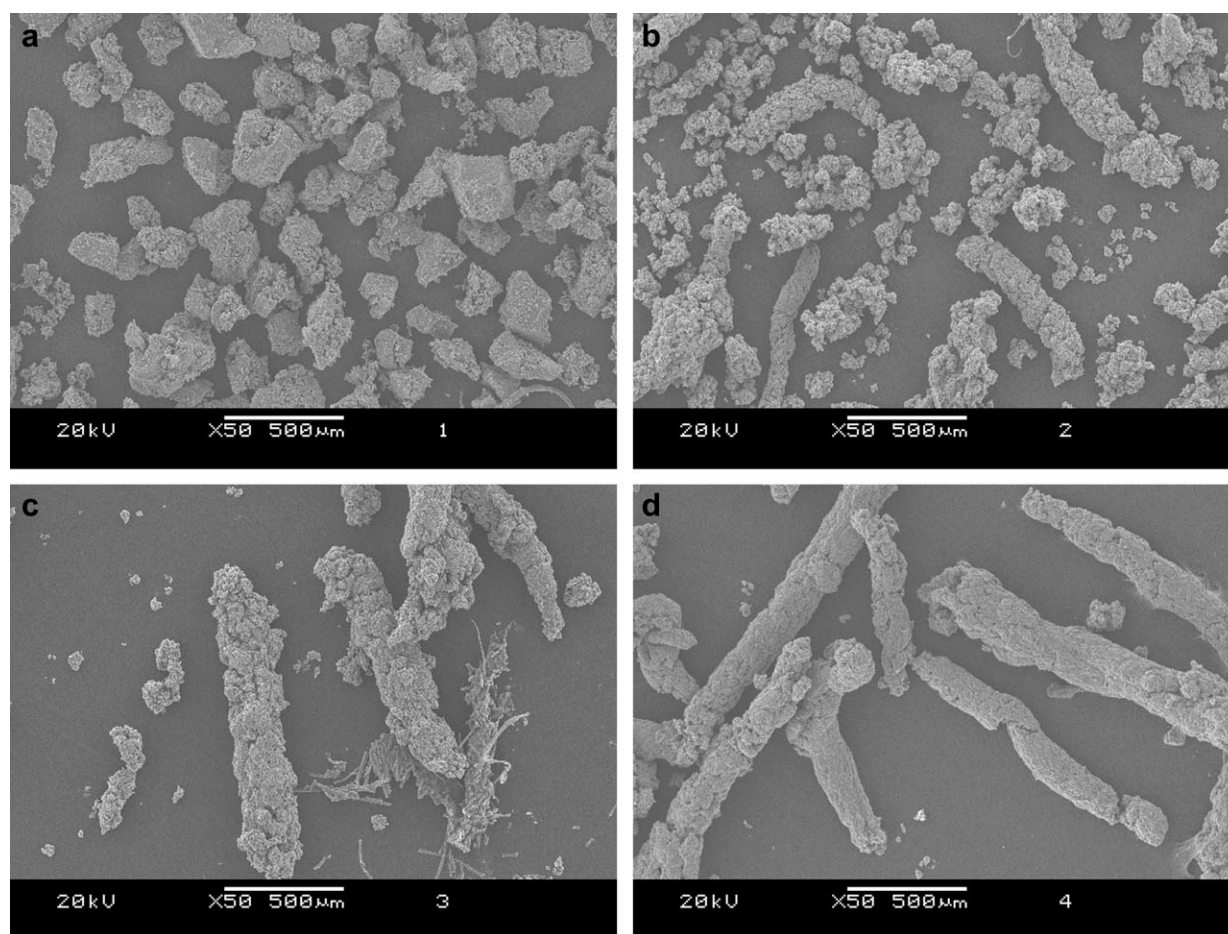
Figure 1 SEM photographs of ground FKM after various cycles of mechanochemical milling: (a) after 2 cycles of milling, (b) after 5 cycles of milling, (c) after 10 cycles of milling, and (d) after 20 cycles of milling.

150°C. On the basis of the curing curves, the minimum torque and optimum curing time were determined.

The stress–strain properties were measured according to ASTM D 412–80 specifications with dumbbell test pieces by an Instron 5567 universal testing machine (Instron corporation, Canton, MA, USA) at a crosshead speed of 500 mm/min. At least five measurements for each sample were made to eliminate experimental error. All of the tests were conducted at a room temperature of 23°C.

SEM (JEOL JSM-5600) was used to observe the morphology of the NBR/reclaimed FKM blends for further study. The samples were broken in liquid nitrogen, and the fractured ends of the specimens were sputter-coated with a thin layer of gold to avoid electrostatic charging during examination. To distinguish the FKM phase from the NBR matrix phase, fluorine dot mapping was done with an INCA OXFORD energy-dispersive X-ray spectrometer (Oxford Instruments, Oxfordshire, U.K.).

Thermogravimetric analysis (TGA) of the samples was performed with a thermogravimetric analyzer (TA Instruments, model no. 2050, New Castle, DE,

USA) attached to an automatic programmer from ambient temperature to 600°C at a programmed heating rate of 20°C/min in a nitrogen atmosphere. A sample weight of approximately 12 mg was used for the measurement. The temperature at which degradation was initiated ($T_{5\%}$) was evaluated.

RESULTS AND DISCUSSION

Morphological development of the ground FKM during solid-state mechanochemical milling

Figure 1 shows the SEM photographs of the reclaimed FKM after various cycles of mechanochemical milling. As shown clearly in the photographs, after two cycles of mechanochemical milling [Fig. 1(a)], the FKM chips changed into a fleecy powdery form. With increasing cycles of milling [Fig. 1(b–d)], the powdered FKM became sticky and reunited into thin strips. Further milling was likely to generate bigger and longer strips. After solid-state mechanochemical milling, the reclaimed FKM changed to a soft and sticky material at ambient temperature and exhibited a plastic-like characteristic. It could be easily milled to form a smooth and

TABLE II
Relative Element Contents of the Ground FKM before and after Mechanochemical Pretreatment as Determined by XPS

Element	Before milling	After 20 cycles of milling
C (%)	56.7	63.6
F (%)	32.6	21.8
O (%)	10.7	14.6

continuous sheet in a two-roll mill. As a result, the mechanochemically milled FKM could be processed in virtually the same manner as virgin rubbers. However, a sample without mechanochemical milling was difficult to masticate with the two-roll mill.

Sol fraction variation of the ground FKM during solid-state mechanochemical milling

It is well known that crosslinked rubber vulcanizates cannot be dissolved in any solvent. However, devulcanized rubber obtained by breakage of the crosslinked structure of rubber vulcanizates can be dissolved in suitable solvents. To investigate the breakage of the three-dimensional crosslinked structures of the ground FKM during solid-state mechanochemical milling, sol fraction measurement was used. The results indicate that the sol fraction of ground FKM significantly increased from its original amount of 1.4 to 19.8% after 20 cycles of pan milling. Because of the presence of nearly 30% of carbon black, which could not be dissolved in ethyl acetate, the 18.4% increase in the sol fraction suggested an efficient devulcanization of the ground FKM after mechanochemical milling. The stress-induced devulcanization of rubber vulcanizates, including FKM vulcanizates, through solid-state mechanochemical milling was well confirmed in our earlier studies.[24–28] The structural development of various rubber vulcanizates during pan milling was also reported in detail. The decrosslinked molecular chains of FKM may facilitate macromolecular entanglement between devulcanized FKM and the polymer matrix.

XPS analysis of the ground FKM before and after solid-state mechanochemical milling

When polymers are exposed to adequate stress in the solid state, the universal mechanochemical response is for the polymer molecules to break at the weakest points in the chain. As a result, free radicals can be generated. These free radicals can react with oxygen in air and form peroxide bonds on the reclaimed FKM surface. XPS analysis was performed to confirm whether any new functional groups were introduced onto the FKM surface. The surface compositions determined from the XPS analysis of

ground FKM before and after 20 cycles of milling are summarized in Table II. The results indicate that the oxygen content of the FKM surface significantly increased from its original amount of 10.7% to 14.6% after mechanochemical milling.

The C1s spectrum for the untreated FKM in Figure 2(a) could be fitted to three components, corresponding to $C-C/C-H$ (284.7 eV), $C-CF_2$ (286.0 eV), and CF_2 (291.0 eV), respectively.[31–33] These assignments agreed with those found in the Beamson and Briggs database. The C1s core spectrum of the mechanically milled FKM is shown in Figure 2(b). Compared with Figure 2(a), a new peak, with binding energies at 287.1 eV, appeared after milling and could be assigned to the $C=O$ species. The introduction of the oxygen-containing polar functional groups onto the FKM surface corresponded to the increase in surface energy. The devulcanized FKM with improved surface energy showed good compatibility with the polar NBR matrix.
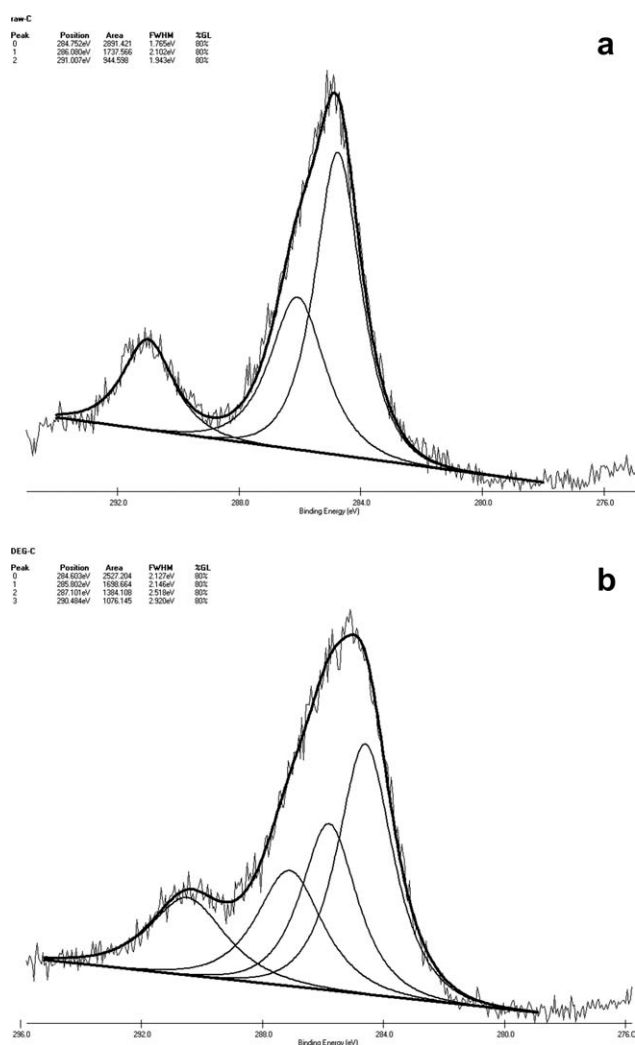

Figure 2 C1s core spectrum of ground FKM before (a) and after 20 cycles of milling (b), respectively.
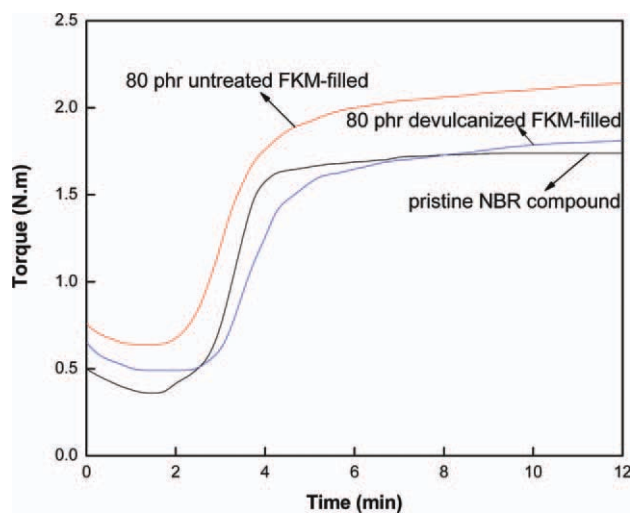
Figure 3 Typical curing rheographs of reclaimed FKM-filled NBR compounds. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Curing characteristics of the NBR/reclaimed FKM compounds

The inclusion of reclaimed rubbers in a virgin rubber formulation typically negatively affects the curing rheology of the compounds. For example, the minimum torque is usually increased remarkably with the addition of reclaimed rubbers. This is undesirable because the minimum torque value represents an index of rubber processing. The lower the minimum torque is, the better the processability of the rubber compounds will be.

To evaluate the effect of the mechanochemical pretreatment on the curing characteristics of the NBR/reclaimed FKM compounds, the curing behavior was tested by a rubber curometer. Figure 3 shows typical curing rheographs of those samples. As shown, the 80-phr devulcanized FKM-filled NBR compound exhibited a curing rheology similar to that of the virgin NBR compound. However, the ground FKM without mechanochemical pretreatment drastically affected the curing behavior of the NBR compounds by increasing the curing torque. The effect of the mechanochemical pretreatment on the minimum torque of the NBR/reclaimed FKM compounds is shown Figure 4. The results indicate that the devulcanized FKM-filled NBR compounds showed much lower minimum torques than the untreated FKM-filled NBR compounds regardless of filler loading. This indicated an enhanced processability after mechanochemical pretreatment.

Mechanical properties of the NBR/reclaimed FKM vulcanizates

The partial devulcanization and surface activation of reclaimed FKM due to the mechanochemical pretreatment should also influence its adhesion ability
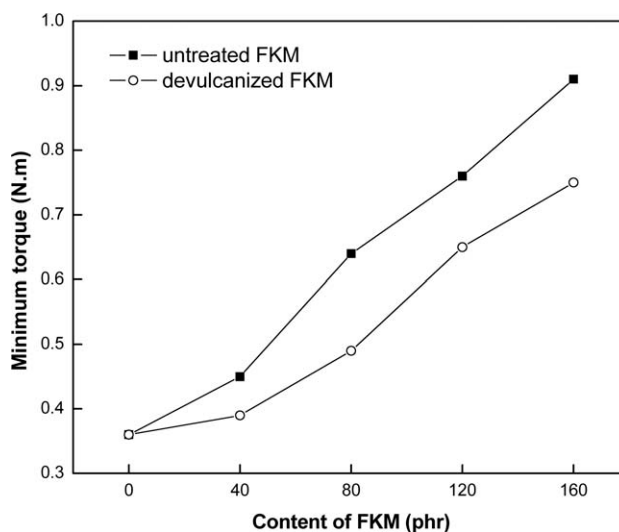
to the polar NBR matrix and thus alter the mechanical properties of the reclaimed FKM-filled NBR vulcanizates. The effects of the mechanochemical pretreatment on the tensile strength and elongation at break of the reclaimed FKM-filled NBR vulcanizates are shown in Figures 5 and 6, respectively.

It was obvious that the tensile strength and elongation at break of the devulcanized FKM-filled NBR vulcanizates were much better than those of the untreated FKM-filled NBR vulcanizates, and this effect was more evident with increasing FKM content. For the 160-phr FKM-filled NBR blends, the tensile strength was increased by 19.4%, and the elongation at break increased by 39.0% through the mechanochemical pretreatment of FKM. The increases in tensile strength and elongation at break were ascribed to the improved interfacial bonding between the devulcanized FKM and the NBR matrix.
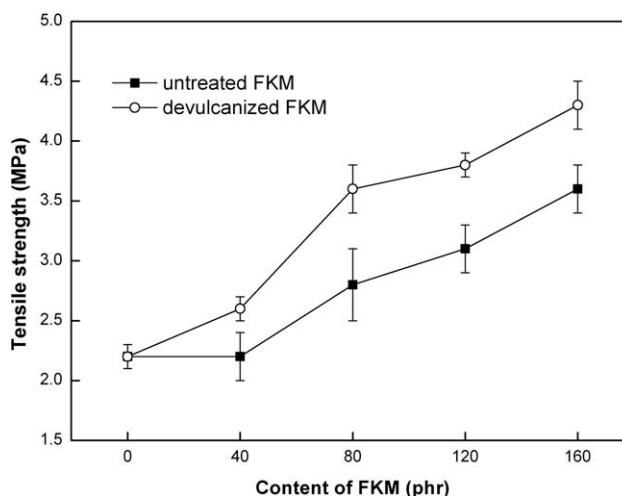

Figure 4 Effect of mechanochemical pretreatment on the minimum torque of reclaimed FKM-filled NBR compounds.

Figure 5 Effect of mechanochemical pretreatment on the tensile strength of reclaimed FKM-filled NBR vulcanizates.
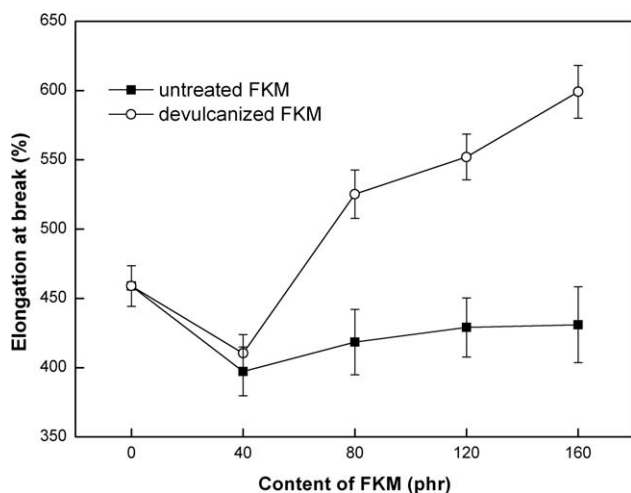
Figure 6 Effect of mechanochemical pretreatment on the elongation at break of reclaimed FKM-filled NBR vulcanizates.

The hydrophobic surface of the untreated FKM restricted the wetting of FKM by hydrophilic NBR matrices. However, oxygen-containing polar functional groups were introduced onto the surface of the mechanochemically milled FKM after solid-state mechanochemical milling. Thus, interfacial bonding between the devulcanized FKM and polar NBR matrix was improved. Furthermore, solid-state mechanochemical milling resulted in the partial devulcanization of FKM, as confirmed by the sol fraction measurements. The decrosslinked molecular chains of FKM facilitated macromolecular entanglement between the devulcanized FKM and the NBR matrix. As a result, the mechanical properties of the NBR/reclaimed FKM blends were remarkably enhanced.

The enhanced interfacial adhesion between the reclaimed FKM and NBR matrix were also be verified by SEM–energy-dispersive spectroscopy (EDS) studies. Figure 7(a,c) shows the SEM images of the
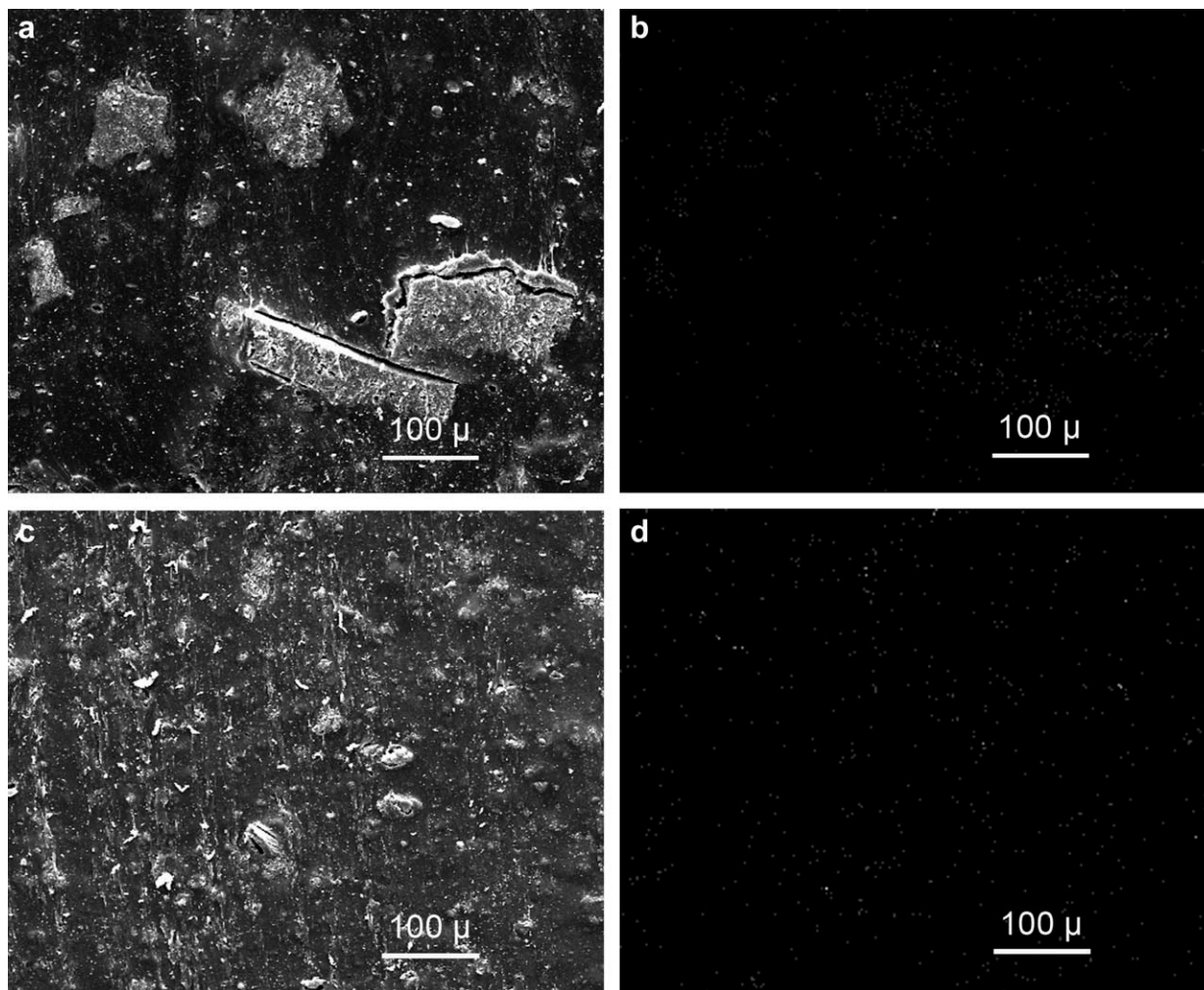

Figure 7 SEM photographs and F distribution of fractured surface of NBR/reclaimed FKM blends with and without mechanochemical pretreatment: a, c-fractured surface micrographs, without mechanochemical pretreatment (a) and with mechanochemical pretreatment (c); b, d-F distribution corresponding to a and c, by EDS analysis.
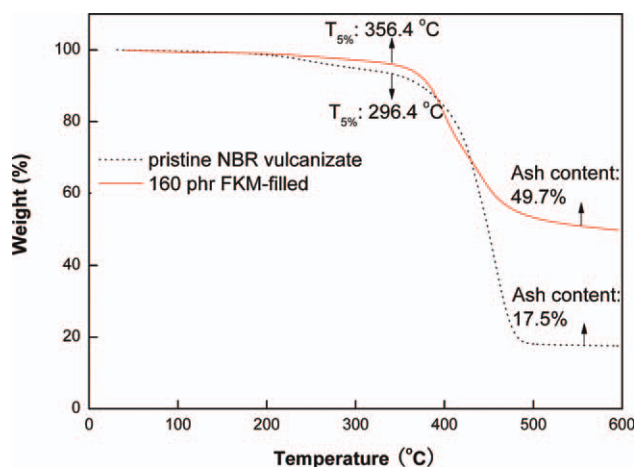
Figure 8 TGA curves of NBR vulcanizates with and without the incorporation of devulcanized FKM. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

liquid-nitrogen-fractured surface of the NBR/reclaimed FKM blends before and after the mechanochemical pretreatment of ground FKM, respectively. A clear interface could be seen in the untreated FKM-filled NBR blend; this indicated poor adhesion between the two phases. In contrast, the devulcanized FKM particles were well coated and firmly embedded in the NBR matrix; this meant that a much stronger interfacial adhesion was obtained compared to that in the untreated FKM-filled NBR vulcanizates. To distinguish the FKM phase from the NBR matrix phase, fluorine dot mapping was done with an EDS instrument. As shown in Figure 7(b,d), the dispersion of FKM particles in the NBR matrix was significantly improved after mechanochemical pretreatment. The results provide morphological evidence for the improved mechanical properties.

Thermal stability of the NBR/reclaimed FKM vulcanizates

One of the most valuable properties of FKMs is their heat-resistant characteristics. They have been widely used to blend with various rubbers (e.g., ethylene–propylene–diene monomer rubber, acrylic rubber, NBR) for the enhancement of thermal stability in the rubber industry.[34,35] With the high cost of virgin FKM in mind, the replacement of virgin FKM by reclaimed FKM has received much attention from rubber product manufacturers.

To investigate whether the addition of devulcanized FKM would enhance the thermal stability of NBR vulcanizates or not, TGA measurements were performed. Figure 8 shows the TGA curves of the pristine NBR vulcanizate and the devulcanized FKM-filled NBR vulcanizate. As indicated in the figure, $T_{5\%}$ of the pristine NBR vulcanizate was found

to be around 296.4°C. The incorporation of 160-phr devulcanized FKM into the NBR vulcanizate notably increased $T_{5\%}$ to 356.4°C. The observed increase in the thermal stability of the devulcanized FKM-filled NBR vulcanizate may have been due to the high thermal stability of FKM and the interaction between the mechanochemically treated FKM and the NBR matrix.

CONCLUSIONS

Partially devulcanized FKM was successfully prepared through a mechanochemical route and was used as functional filler to enhance the thermal stability of NBR vulcanizates. On the basis of the experimental results, the following conclusions were drawn:

1. The fairly strong shearing and squeezing forces exerted by the pan mill decrosslinked the three-dimensional networks of FKM and introduced oxygen-containing polar functional groups onto the FKM surfaces.
2. The devulcanized FKM-filled NBR compounds had better processability compared to the untreated FKM-filled NBR compounds.
3. The tensile strength and elongation at break values of the NBR/reclaimed FKM vulcanizates were significantly increased through the mechanochemical pretreatment of FKM. SEM–EDS studies indicated that better interfacial adhesion between the reclaimed FKM and NBR matrix was achieved after the mechanochemical pretreatment.
4. The addition of devulcanized FKM to the NBR vulcanizates notably enhanced the thermal stability of the vulcanizates. The high thermal stability of FKM and the interaction between the mechanochemically treated FKM and NBR matrix were the main reasons for the increase in the $T_{5\%}$ values of the vulcanizates.

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