EFFECT OF RECLAIMED RUBBER CONTENT IN NR/CARBON BLACK VULCANIZATES USING MICROWAVE IRRADIATION SYSTEM

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Abstract

This work examined the effect of tire-tread reclaimed rubber content on physical and mechanical properties of natural rubber, vulcanized by microwave (MW) irradiation and thermal cure (CT) systems. The results suggested that the properties of the vulcanizates from CT method was higher than those from MW method except for the swelling level in toluene. The differences in the results between these two curing systems could be explained in terms of the density and the type of crosslinks present in the NR compounds. The microwave cure was more effective as the reclaimed content was increased.

Introduction

The polymer reclaiming process involves the fracture of higher molecular weight polymer molecules to lower ones [1]. Recent technology to use the reclaimed rubbers in the virgin polymer materials has attracted many rubber industries. Most work in the field have investigated the cure characteristics and the products properties obtained by the incorporation of the reclaimed rubber, in various forms, into different virgin materials (mainly natural rubber). Sombatsompop and Kumnuantip [2-3] introduced tire-tread reclaimed rubber into two natural rubber grades and investigated various properties of the blends. They found that the Mooney number, shear viscosity and cure rate increased with reclaimed content, while the cure time was independent of the reclaimed content. The property changes of the reclaimed/NR blends were mainly associated with the crosslink precursor or untreated curatives, and the amount of carbon black present in the reclaimed rubber. Sreeja & Kutty [4] studied the cure characteristics and mechanical properties of NR/reclaimed rubber blends using EV system. They observed that the scorch time and tensile properties of the blends reduced with the reclaimed loading.

It has been widely known that the properties of the vulcanizates are very much dependent on the conditions where the green rubbers are cured, these including cure time and temperature used, design of vulcanizing recipes, as well as the type of curing systems. The last factor is referred to as the methods used for curing the rubber compounds. The most simple curing system used in the rubber industry is direct heating (conventional thermal curing). Many published works have suggested that the duration and mould temperature are the main parameters that control the degree and type of crosslinks to be formed, and these directly affect the properties of the vulcanizates. Microwave curing has increasingly become one of the interesting curing systems in many applications, such as food industries, dried wood systems, concrete curing, and shape-setting of thermosets and rubbers[5]. The main advantages of the microwave cure include faster curing times, improved efficiency of curing, and enhanced mechanical properties of the products [6]. Subjects on the effects of microwave curing on the changes in cured material properties in comparison with those by conventional thermal method are still unclear and open for discussion, since its information are still rare in literature, especially when some secondary materials like reclaimed and carbon black are incorporated.

In this work, tire-trade reclaimed rubber were loaded into natural rubber compounds having 60phr of carbon black which were then cured by two different methods, these including conventional thermal and microwave methods. The physical and mechanical properties of the cured rubbers were then examined and compared.

Experimental

Raw materials

The rubbers used in this work were NR (STR20CV) supplied by Tech Bee Hung Co., Ltd. (Bangkok, Thailand) and tire-trade reclaimed rubber (UCD-103 grade) supplied by Union Commercial Development Co., Ltd. (Samutsakorn Thailand). The reclaimed rubber comprised of 24% carbon black, 15% acetone extract and 6% ash. The ratio of NR:reclaimed rubber used 100:0, 70:30 and 40:60 (%wt). All rubber blends were loaded with 60 phr carbon black (N330), supplied by Thai Carbon Black Co., Ltd. (BKK, Thailand).

Rubber sample preparation

The formulation of the rubber compounds was as follows: 100 phr rubber blended (NR : reclaimed rubber ; 100:0, 70:30 and 40:60 by weight), 60 phr carbon black, 5.0 phr zinc oxide (ZnO), 2.0 phr stearic acid, 0.5 phr mercaptobenzthiazole (MBT), 0.2 phr diphenylguanidine (DPG), and 3.0 phr sulfur. In the mastication step, the natural rubber was masticated on a laboratory two-roll mill (Yong Fong Machinery Co., Ltd., Samutsakon, Thailand) for 5 min and was then blended with the tire-trade reclaimed rubber for another 5 minutes. In the compounding step, the rubber and filler were compounded with prepared vulcanization chemicals on the two-roll mill for another 10 min, and the compounds were then kept at 25^{o}C at 50% humidity before further use.

Design and construction of microwave apparatus

The microwave vulcanization oven consisted of three magnetrons, each magnetron giving microwave power 1,000 watt. Three waveguides in rectangular shape used were 90mm wide, 80mm deep and 40mm high. The microwave oven body was made from stainless steel whose cavity size had 30 cm high, 40 cm wide and 50 mm long. The mould used was made of Teflon and it can produce vulcanized rubber sheet of 2mm thick.

Vulcanization methods of rubber blends

For conventional thermal (CT) curing: The resultant rubber compound was compression-molded using a hydraulic press (LAB TECH Co., Ltd., Bangkok, Thailand) at 170 kg/cm^2. For comparison purposes,the cure time was fixed at 3 minutes for all rubber compounds. The cure temperatures used were 145^{o}C for NR compounds, and 150^{o}C for NR with reclaimed rubber.

For microwave (MW) curing: The resultant rubber compound was placed in the microwave apparatus. The temperature of the vulcanizates was determined by immediately measuring it after stopping the microwave irradiation using a IR probe. The cure temperatures used for this method was the same as used in the CT method for any given reclaimed contents (145^{o}C for the compounds with no reclaimed rubber and 150^{o}C for those with reclaimed rubber). By trial and error experiment, the cure time used for MW method was 3 minutes, above this value causing an over-curing of the rubber compounds.

Characterization

Physical properties: The physical properties of the vulcanizates were carried out through sorption-desorption behavior and crosslink density determination. The sorption method is referred to as the amount of toluene uptake (or release), whose experimental procedure can be found elsewhere [3]. The crosslink density determination was achieved by use of the Flory-Rehner equation, whose experimental details can be obtained elsewhere [2].

Mechanical properties: Various mechanical property evaluations were performed. The tensile properties (modulus at 100% elongation, ultimate tensile stress, and %elongation at break) of the vulcanizates were tested according to ASTM D 412-92 (1998); the tests being carried out with a universal testing machine (Autograph AG-I, Shimadzu, Tokyo, Japan). Tear strength was determined specified by ASTM D 624-00(2000) using angle-shaped samples and a Shimadzu tear strength testing machine. The testing speeds for tensile and tear properties were 500 mm/min. Vulcanizate hardness was carried out using Shore A Instrument & M.F.G., model PN71500 by ASTM D 2240-97 (1997).

Results and discussion

Figure 1 shows the effect of reclaimed rubber content on crosslink density of the NR/CB vulcanizates cured by conventional thermal (CT) and microwave (MW) methods. It can be observed that the addition of reclaimed rubber had a significant effect on the crosslink density for both curing systems. The crosslink density greatly increased with reclaimed rubber content. This was because loading the reclaimed rubber into the NR/CB compounds would automatically increase the carbon black contents into the rubbers [2]. It is widely evidenced that carbon black can perform as a physical crosslinker in the rubber matrix as a result of the rubber molecules being absorbed into the black surface during compounding [7-8]. The detail of the rubber-carbon black interaction can be found elsewhere [9]. Considering the effect of curing type, it was found that the MW method gave a slightly lower crosslink density than the CT method. The effect of reclaimed rubber content on the change in crosslink density in the MW method was similar to that in the CT method, this indicating that the crosslinking reaction as a result of reclaimed rubber loading, which had occurred in these two curing methods were the same.

Although the chemically crosslinking reactions of the rubbers from these two curing methods were the same as stated in the explanation given for Figure 1, their mechanisms of the heat generation and its transfer to the rubber were probably different. In CT method, the heat was generated by external heating system and was transferred as a result of the thermal conduction from the mould to the rubber compound where the cross-linking process took place. It was predictable that, during compression moulding, temperatures across the thickness of the vulcanized sheet were not uniform, and this would lead to differences in cure times across the sheet thickness. For MW method, the temperatures across the sheet thickness were thought to be the same since the heat was generated simultaneously throughout the rubber sheet during the curing. The mechanism of the rubber curing by microwave involves changes in polarization of the

materials caused by microwave absorption. When the microwave passed into the rubber compounds (now regarded as absorber material), the electric field would occur inside the compounds as a result of microwave absorption. This electric field activated the changes in motions (rotations and vibrations) and polarizations of the rubber molecules, which then caused molecular frictions and the heat in the rubber compound, the curing being then initiated [10-11]. It should also be noted that the presence of carbon black was necessary when curing by microwave since the natural rubber itself is a low dielectric loss material that does not react with microwave [10]. In order to achieve the curing, carbon black needs to be added because carbon black has a relatively high dielectric loss, and this will increase the dielectric loss property of the blend and thus be induced by microwave irradiation [10].

Figure 2 illustrates the sorption-desorption behavior of the NR/CB vulcanizates in toluene as a function of reclaimed rubber content for CT and MW curing methods. It was found that the higher reclaimed rubber content the lower the toluene uptake. This was expected because the decrease in toluene uptake was caused by the increase in crosslink density as a result of the carbon black in the reclaim. The increased crosslinks resulted in a restriction in mobility of rubber molecules which prevented the penetration of the solvent molecules into the rubber [3,12]. Comparing the sorption behaviour of the vulcanizates from two different curing systems, it was found that the rate and the mole% uptake (or release) of toluene in vulcanizates for CT method were greater up to 600 minutes, and after than, the mole% uptake of toluene in the vulcanizates for CT method was lower.

In this preliminary study, since the heating mechanisms between the CT and MW methods were different the types of crosslinks formed in the rubber compounds would probably be different. It was postulated that the crosslink types in the vulcanizates cured by CT method tended to be more polysulfides while those by MW method were mainly mono- and di-sulfides. This was because the MW curing was likely to be more instantaneous and rapidly than the CT curing for a given crosslink density, this being analogized with a crosslinking process having a greater ratio of accelerator/sulfur in a rubber compound. Work by Sombatsompop [13] stated that faster curing in rubber vulcanization system tended to produce more mono- and di-sulfidic crosslinks than polysulfidic ones. If this postulation was validated one could now be able to explain all the differences in toluene uptake/release as mentioned in Figure 2. Previous investigations [12,14] suggested that the monosulfidic and disulfidic linkages had less free volume and flexibility of crosslinked rubber chain as compared to the polysulfidic linkages. Therefore, the ability of toluene to penetrate the vulcanizates cured by the MW method, which containing more mono- and di-sulfidic crosslinks, would be less.

Figures 3, 4 and 5 show the effect of reclaimed content on tensile modulus, ultimate tensile stress (UTS) and elongation at break of the NR/CB compounds cured by CT and MV methods, respectively. It can be seen that the tensile modulus progressively increased with reclaimed content, and, for a given reclaimed content, the tensile modulus of the vulcanizates by MW method was lower. These could be explained in terms of the differences in crosslink densities and types as discussed. The values of UTS and elongation at break were also found to deceased reclaimed rubber content, this involving the heterogeneity and defects present the NR phase caused by the addition of reclaimed rubber, the detailed explanation being found in previous work [2].

Figure 6 shows a plot of tear strength of NR/CB containing different contents of reclaimed rubber. It was found that the tear strength of microwave cured vulcanizate was lower than that of the conventional cured vulcanizate. This was again associated with the differences in crosslink densities and types formed in the vulcanizates. The changes in hardness results for the vulcanizates cured by CT and MW methods are shown in Figure 7. It was found that the changing trend was similar to the tensile modulus results.

Overall, it could be concluded under the experimental conditions used in this work, that the mechanical properties of the NR/CB vulcanizates cured by CT method were higher than those by MW method, except for the resistance to toluene penetration, the differences in the properties between these two methods being minimized as the reclaimed content was increased.

Conclusion

The effect of reclaimed rubber content on the crosslink density, swelling behaviors and mechanical properties of the NR added with 60phr carbon black was studied. The microwave cure gave vulcanizates with lower mechanical performance, but increased the resistance to toluene uptake. The differences in the vulcanizate properties due to curing methods were associated with the crosslink density and type present in the vulcanizates.

Acknowledgements

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Key words

Natural rubber, reclamation, microwave, mechanical properties, rubber reinforcement.

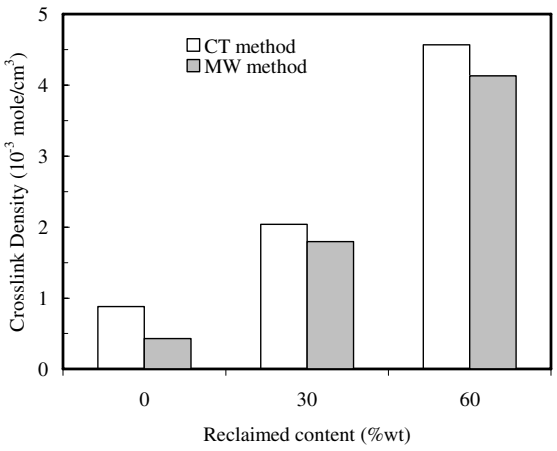

Figure 1. Crosslink density versus reclaimed content in NR/CB vulcanizates by CT and MW methods

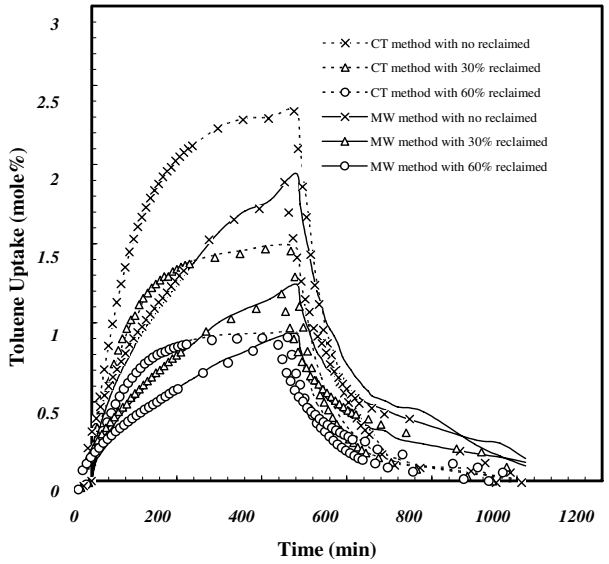

Figure 2. Toluene uptake in NR/CB compounds with various reclaimed contents by CT and MW methods

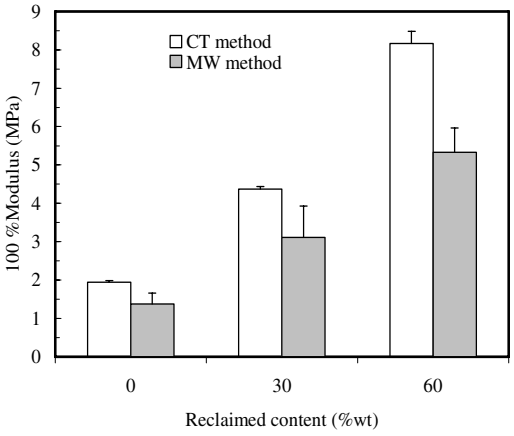

Figure 3. Tensile modulus for NR/CB vulcanisates at different reclaimed contents by CT and MW methods

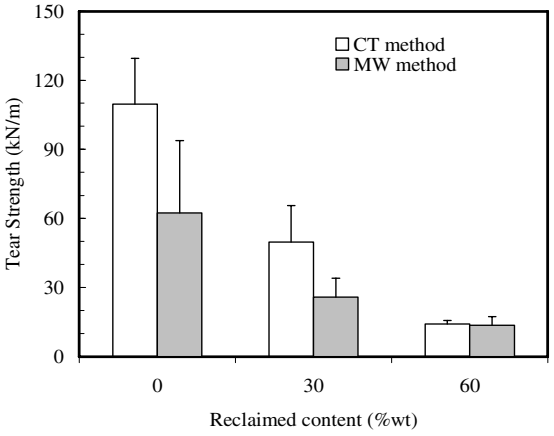

Figure 6. Tear strength of NR/CB vulcanisates at different reclaimed contents by CT and MW methods

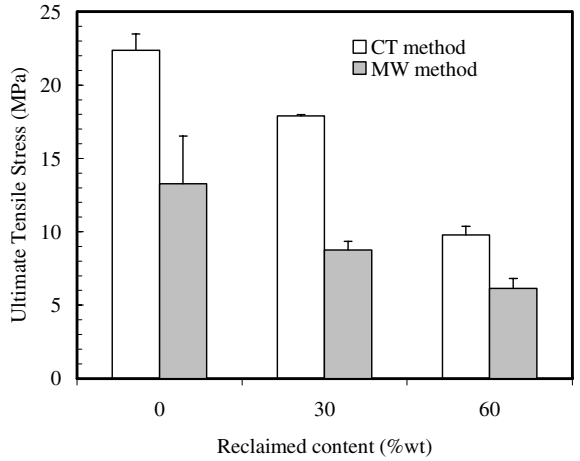

Figure 4. UTS of NR/CB vulcanisates at different reclaimed contents by CT and MW methods

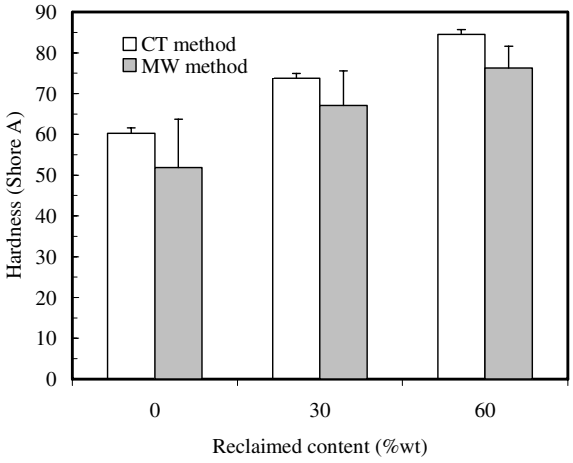

Figure 7. Hardness versus reclaimed content for NR/CB vulcanisates by CT and MW methods

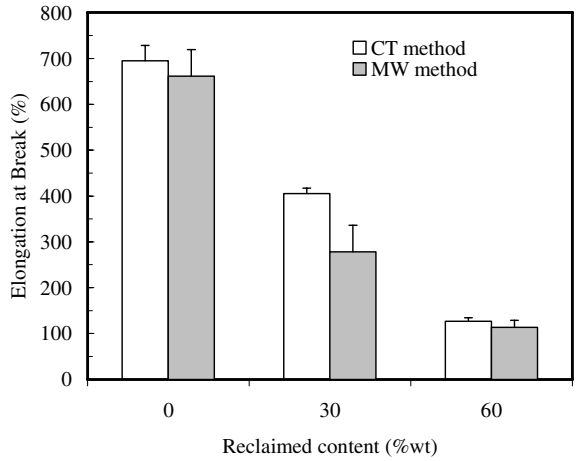

Figure 5. Elongation at break of NR/CB vulcanisates at different reclaimed contents by CT and MW methods