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Rheological Properties of a Reclaimed Waste Tire Rubber through High-Pressure High-Temperature Sintering

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Abstract. High-Pressure High-Temperature (HPHT) sintering method has successfully revulcanized waste tire rubber (WTR) without any additional virgin rubber. The crumb rubber cleaned from its fabric and metals was reclaimed by applying high pressure (25 MPa) and high temperature (200 °C) for an hour along with common vulcanization agents such as sulfur, zinc oxide, and stearic acid. Dynamic properties of reclaimed WTR were assessed through shear rheology test on MCR302 Rheometer, Anton Paar, Austria. The results indicated that under steady test, the yield stress occurred at 31 kPa at 5% linear viscoelastic limit. The storage modulus ranged from 0.6 to 0.7 MPa under excitation frequency of 0.1 to 100 Hz and 1% strain amplitude. Under ramp strain amplitude, the storage modulus showed Payne Effect phenomenon at 0.8 to 1 % strain amplitude and 1 Hz excitation frequency. In general, the resulted dynamic properties was comparable with non-reclaimed rubber based on a literature survey. The results confirmed that HPHT sintering method was capable of reclaiming 100% WTR without an additional virgin rubber and achieving acceptable dynamic properties.

INTRODUCTION

Tire rubbers are originated from a high-quality rubber. Therefore, their wastes represent a large potential source of raw material for the rubber recycling industries [1,2]. Nowadays, the recycling of WTR is relatively in low scale applications because of the stringent requirements for quality of rubber products [3]. Therefore, the use of waste rubber is usually for secondary raw materials such as for conventional composite where the quality is not the main requirement of the resulted products. In other ways, the waste rubber is utilized for repeat use (re-use and re-treading), physical recycling (reclaiming, grinding and surface activation), recovery of base chemicals (pyrolysis, gasification, and hydrogenation) and energy recycling (incineration) [4,5]. Nevertheless, the use of waste rubber for those mentioned strategies is still considered as a non-environmental friendly solution due to the harmful effluence [6].

Nowadays, ecofriendly rubber product is encouraged to minimize the waste rubber problem as well as economically reduce the production cost [7,8]. Reclaiming waste tires were usually performed by blending WTR with virgin rubber or by revulcanizing the dead rubber by treating it in physical and/or chemical ways. Morin et al. [9] and Tripathy et al. [10] proposed HPHT sintering to reclaim tire rubber based on supporting research by Tobolsky and coworkers [11–14]. Departing from fundamental theory of rubber scission and reformation, Morin et al. [9] discovered that HPHT successfully reclaims WTR without the incorporation of virgin rubber. In this process, the reclaimed rubber yields about 35-40% recovery of the original tire. The mechanical properties of that process were improved by Tripathy et al. [10] by incorporating phthalimide, which raised the recovery yield to about 75% of the original rubber. Those results encouraged future efforts to achieve waste rubber revulcanization with a minimal use of virgin rubber. Thus far, the utilization of waste rubber, particularly for reclamation, has resulted in recycled rubber-based products with mechanical properties that equal those of the predecessor products.

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Waste rubber reclamation has been undertaken by various revulcanization strategies involving chemical, biological, physical, and mechanical processes [8]. Chemical devulcanization requires a reaction that involves organic compounds, oils, and solvents. This process is undertaken by mixing the rubber powder with a peptizer and recurring agent [15]. Biological devulcanization is usually carried out by involving a microbial desulfurization which can metabolize the sulfur present in the rubber matrix [1]. Some microorganisms were introduced for devulcanization such as *Sulfolobus acid ocaldarius, Nacardia*, *Thiobacillus*, and *Gordonia desulfuricans 213E* (NCIMB 40816) [4]. Besides chemical and biological devulcanization, physical treatment for disentangling the rubber crosslink is more favorable. It is usually conducted through irradiation techniques such as microwave [8]. In the microwave methods, microwave energy in certain controlled dose at specific frequency and level of energy is utilized to cleave carbon-carbon bonds. Meanwhile, in mechanical devulcanization, plasticizing process of the waste rubber as a result of breaking down the chemical bonds is dominantly caused by shearing of rubber particulates in high temperature. The crumb rubber is located in an open two-roll mixing mill and/or twin screw at high temperatures.

Among various techniques mentioned, mechanical revulcanication is one of preferred method due to its economic value and fast process. High Pressure High Temperature (HPHT) sintering proposed by Morrin et al. [9] was successfully reclaiming waste rubber without incorporation of virgin rubber. The working principle of HPHTS method is simultaneous compaction under high pressure (about 14-25 MPa) and high temperature (180 – 200 °C). This method, of course, provided some advantages such as simple execution and less production cost compared to other methods that are still need virgin rubber. The mechanical properties of the reclaimed waste rubber achieved 35-40% recovery of the original rubber (before reclaiming) [10]. Improvement of the work was conducted by Tripathy et al. [10] by modifying the additives. In general, the previous studies on mechanical properties of reclaimed waste tire were carried out under static tests. Consequently, the dynamic properties of reclaimed waste rubber were less paid attention. Dynamic properties of rubbery material is an important thing since the application of rubber lies in dynamic condition. Therefore, this study intends to reveal the dynamic properties of reclaimed waste rubber through HPHTS coined technique introduced by Morrin et al. [9].The dynamic properties of reclaimed rubber are obtained through the rheological test as the focus of this article.

SAMPLE PREPARATION

The waste rubber from vehicle tires (WTR) was provided by PT. Bengawan Sumber Baru, Indonesia, in powder form. The WTR was separated from metals and yarns, and had size about 60 mesh or an average particle size of 250 microns. The crumb rubber may consist of mixing between synthetic (SBR, EPDM) and natural rubber (Isoprene). The samples are prepared by coined method HPHTS [9,10] using custom made hydraulic hot press with temperature controlled heating. Sintered specimens of the recycled rubber powders are obtained by placing approximately 2 g of powder into a 30 mm diameter mold for an hour, applied pressure of 25 MPa and heating temperature of 200 °C. During sample preparation, the starting temperature is about 27 °C transiently increasing until 200 °C for 17-20 minutes. After reaching the desired temperature, the heater controller maintains supplying electric current to the heater elements based on the temperature set point. This step is kept for an hour. The hot mold is then cooled to room temperature (about 45-60 minutes). The mechanism of compaction can be seen in Fig. 1.

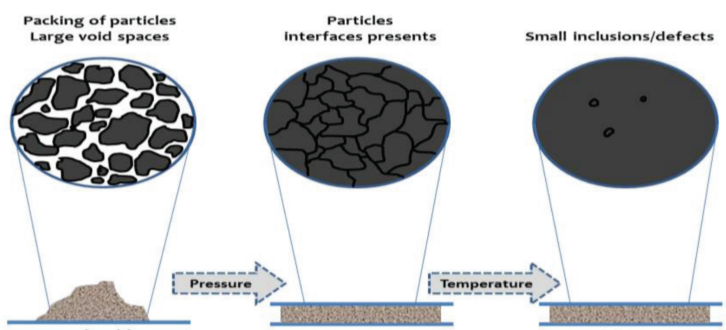


FIGURE 1. Schematic diagram of HPHT process [9].

RHEOLOGICAL MEASUREMENT

Rheological behavior of many materials especially hyperelastic materials is often characterized through viscoelastic examination. Reclaimed waste rubber belongs to materials that behave like a solid when they are experiencing rapid deformation. Meanwhile, the materials undergo flowing as liquid materials when they are subjected to the very slow deformation. According to this phenomenon, the stress and strain are independent on time. When the MREs are subjected to a particular force, the deformed body can experience relaxation resulting in the decrement of stress value in time until the acting force completely disappears. The viscoelastic relationship between stress and strain in the normal direction is stated in linear form as described in Kevin-Voight model (See Eq.1). Therefore, this relationship is also well-known with linear viscoelasticity:

$$\tau = G\gamma + \eta \frac{d\gamma}{dt} \tag{1}$$

Where, G is complex shear modulus, ε is a strain, η is dynamic viscosity, and t is time. The delayed deformation when force is removed can be given through relaxation time as (Eq.2)

$$\boldsymbol{\lambda = G/\eta} \tag{2}$$

The linear viscoelastic properties of the smart materials are usually revealed by subjecting the materials into dynamic or harmonic or cyclic loadings. It can be in constant stress or constant strain. The constant strain is commonly used for its simplicity implementation in the oscillating machine. When the MRE sample is subjected to oscillating strain in time domain as $\gamma = \gamma_a \sin(\omega t)$, a stress also develops an indirect response in time domain as $\tau = \tau_a \sin(\omega t + \delta)$. The phase shift indicates the specific characteristic of viscoelastic materials; while, the associated quantity to figure out the property is $\tan \delta$ or loss tangent/loss factor. The key property of the MREs can be calculated by simple relationship as stated in Eq.3,

$$|G^*(\omega)| = \frac{\tau_a}{\gamma_a} \tag{3}$$

Where, G^* is complex shear modulus. These values, G^* and $\tan \delta$, are key viscoelastic characteristics of the MREs [16]. The complex modulus consists of real and imaginary parts as expressed as follows,

$$G^* = G' + iG'' \tag{4}$$

Where, G' is called the storage modulus, while G'' is the loss modulus. These two values are subtle explanation of viscoelastic properties of the MREs. The values are related to the phase shift and storage modulus. The term storage modulus indicates that the energy is stored during deformation (strain) and it can be recovered later. Meanwhile, the loss modulus can be understood as the loss energy when deformation is happen and is converted into another form of energy (heat). The quantity of storage modulus and loss modulus can be determined from the relationship below (Eq.5 and 6, respectively),

$$G' = G^* \cos \delta \tag{5}$$

$$G'' = G^* \sin \delta \tag{6}$$

The completely elastic solid materials will exhibit that the storage modulus is equal to the complex shear modulus ($G' = G^*$). In solid elastic materials, the stored energy experienced during deformation will be released simultaneously when the deformation is fully reversed. If the loss modulus is equal to the complex modulus ($G'' = G^*$), the material is classified into completely viscous. The ratio between loss modulus and storage modulus is named by loss tangent or loss factor. The mathematical formulation is stated as follows (Eq.7)

$$\tan \delta = \frac{G''}{G'} \tag{7}$$

In the physical illustration, the loss tangent represents the ratio between lost energy and storage energy during deformation. It can determine the ability of material in dissipating energy.

The viscoelastic properties of the reclaimed waste rubber were observed in rotational shear mode by means of a parallel-plate rheometer (model Physica MCR 302, Anton Paar, Austria) equipped with an MR device MRD 70/1T without employing electromagnet feature. The schematic of the rheological test using rheometer is shown in Fig. 2. The diameter of the parallel plate disk was 20 mm (PP20/MRD/T1/P2). A temperature controlled Viscotherm VT2, Anton Paar, was also utilized to maintain the desired testing temperature of 25 °C. The testing conditions were divided into steady state and oscillatory motions. The rheological measurement system using a parallel-plate is described by the standards ISO 6721-10 and DIN 53019-1 [17].

The steady state measurement was applied by twisting the sample in a continuous strain sweep with a very low strain rate. The treatment was nearly similar to a static shear test. Therefore, the results of the steady-state tests were used to determine the relationship between shear stress versus shear strain. Meanwhile, the oscillatory testing was performed by applying dynamic oscillatory shear in current, frequency, and strain ramps. The dynamic shear can be used for measuring the rheological properties such as the shear storage modulus, G', the loss modulus, G'', and the loss (damping) factor, $\tan\delta = G''/G'$, as a function of the frequency and strain amplitudes.

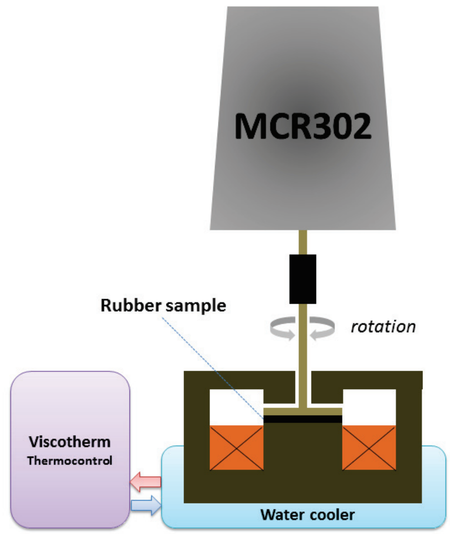


FIGURE 2. Schematic measurement of the rheological test.

RESULTS AND DISCUSSION

The stress-strain relationship of reclaimed WTR was evaluated under steady state rotary shear. This kind of testing is relatively obscure since only minor information such as shear stress-strain and Linear Viscoelastic (LVE) region can be revealed under a low degree of strain. The results of previous research on the shear steady state properties of MREs can be found elsewhere [18]. Figure 3 shows the stress-strain relationship. During testing, the shear rate was set at 5 rad/s at a 0 to 10% ramp linear strain. Under off-state conditions, the stress increased slowly until it had almost reached a steady value at greater than 10% strain. From the figure, it can be seen that the yield stress occurred at 31 kPa, 5% strain viscoelastic limit. Under a larger strain, the reclaimed WTR exhibits a highly non-linear plastic flow in which the carbon black particles as a filler experience slippages between the particles and the reclaimed rubber matrix. At this stage, the stress overshoot appears to be significantly influenced by the shear orientation of the filler-rubber interactions. Another point of view about overshoot at the yield point was that the static friction caused by the surface roughness of reclaimed WTR samples and the moving plate, which was a normal force, might contribute to the ultimate yield stress.

The frequency swept tests of the reclaimed WTR were conducted at room temperature. The sample was subjected to oscillating frequencies that ranged from 0.1 to 100 Hz. The frequency was elevated under linear ramp conditions at constant strain amplitude of 1%. A normal force was maintained at about 15 N. The rheological properties of the sample under a frequency ramp are plotted in Figure 4 (a) and (b) for the storage modulus, loss modulus, and loss tangent. The x-axes were in logarithmic scale due to interest in the rheological responses at low frequencies. Meanwhile, the y-axes were set on a linear scale (for loss factor) to more easily identify the increment parameters in the axis. The storage modulus reached 0.6 MPa which exhibited reasonable value of reclaimed rubber modulus. It maintains in a nearly constant trend as the excitation frequency increased to 95 Hz, then dropped slowly at higher frequencies. The drop may have been caused by slippage between the oscillating plate and the surfaces of the MREs. Meanwhile, the loss modulus steadily increases from low until high frequency. It can be inferred that under higher excitation frequency, the dissipative part plays dominantly compared to the storing part. This phenomenon is marked by the increment of loss factor in Fig. 4(b). Loss tangent or loss factor is always characterized by the intrinsic damping of viscoelastic materials, the degree of which depends on the phase-lag between the stress and strain relationships that result from harmonic loadings. A higher phase-lag causes a higher loss modulus value, which is reversed for the storage modulus. Therefore, an evaluation of the loss tangent characteristics of materials, particularly elastomeric materials, is meaningful when it is conducted in ramped frequencies.

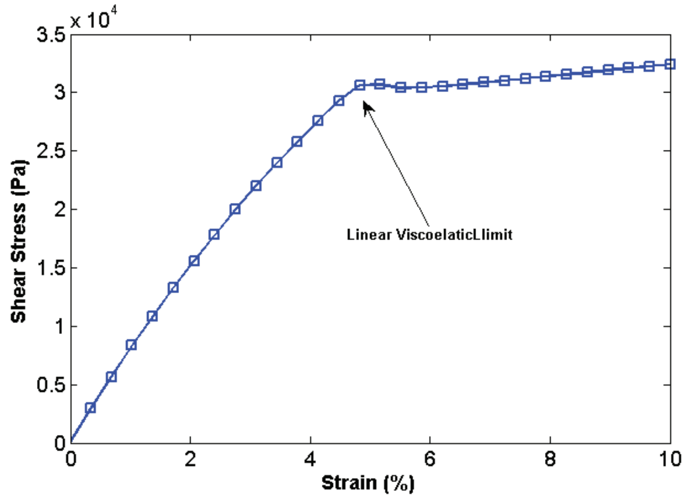
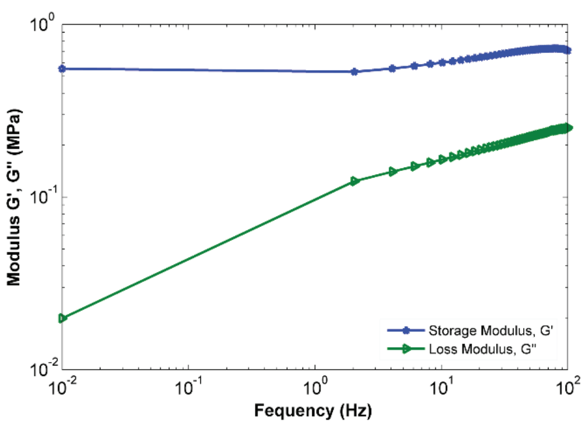
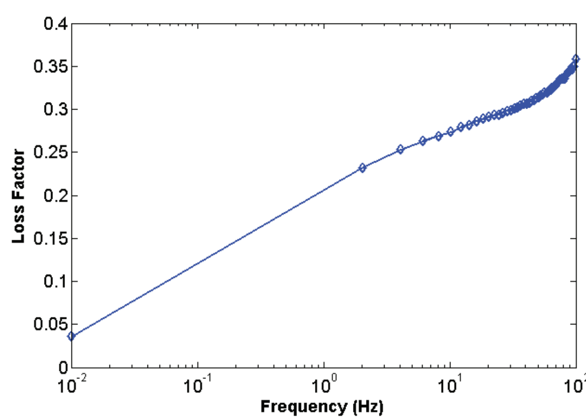


FIGURE 3. Stress-strain relationship under steady state shear



(a)



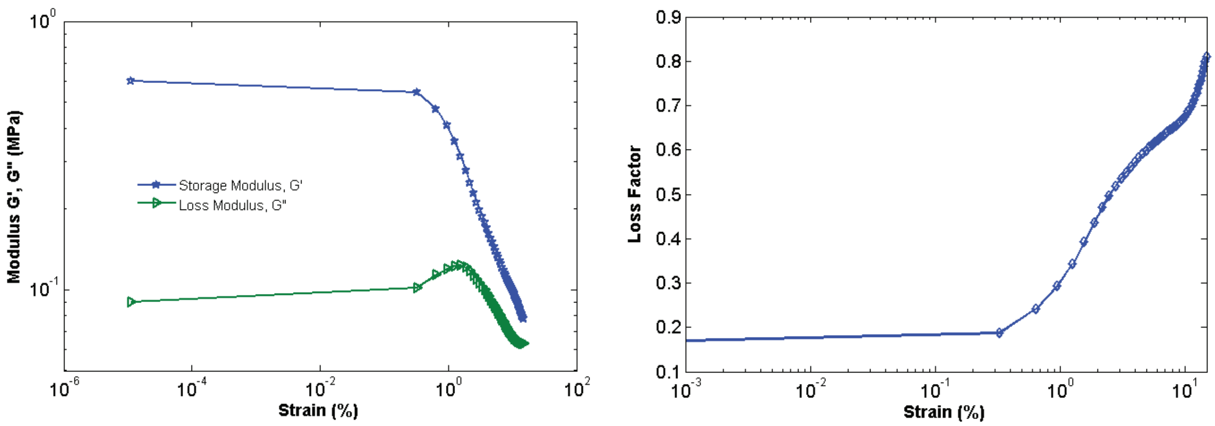
(b)

FIGURE 4. Moduli and loss factor under ramp frequency

The rheological properties of reclaimed WTR were also evaluated under strain amplitude enhancement. The reclaimed WTR was subjected to sinusoidal or harmonic loadings with various excitation amplitudes. In this present study, the strain amplitude was set from 0.01 to 10% ramped logarithmically. This range is commonly applied to the strain dependence testing of particles used to fill rubber such as carbon black, silica and so on. The frequency was fixed at 1 Hz.

Studies on particle-filled rubber under dynamic loading have been becoming an open topic for many years. The issue has been addressed on the Payne effect that occurs when the filled rubber is subjected to an altered strain. The existence of filler within elastomers, in general, makes the properties highly nonlinear [19]. Payne [20,21] observed that when the carbon black was loaded into the rubber, the particle chains have retained to a certain extent. The filled rubber exhibited a sharp decrement as the strain increased from 0.01 to 5% in a phenomenon known as strain softening. The mechanism of the Payne effect is rather complex, and has more to do with the breakdown and reformation of the filler network in rubber. The Payne effect has drawn attention from researchers, and it has been of great importance in some industries since the range of strains most frequently encounters a degree of nonlinearity, particularly in tire applications, but many controversies remain on the question of the mechanism that is responsible for the Payne effect.

Figure 5(a) and (b) portrayed moduli and loss factor characteristics, respectively. The reclaimed WTR showed clearly Payne effect as illustrated in Fig. 5(a) when the storage modulus drops at about 0.8 to 1 % strain amplitudes. This region can be referred to linear viscoelastic limit based on dynamic properties. Viscoelastic region based on dynamic loadings can be identified when the storage modulus drops 10% of the initial value, and at the same time, the loss factor increases immediately. The high value of loss factor indicates that the carbon black plays significantly as a dissipative element within the rubber.



(a) (b)

FIGURE 5. Moduli and loss factor under ramp strain amplitude

CONCLUSION

A reclaimed WTR specimen has been successfully fabricated reclaimed using High-Pressure High Temperature (HPHT) coining technique at Pressure of 25 MPa and Temperature of 200 °C. The rheological performances of the samples regarding stress-strain relationship, moduli, and loss factor were undertaken to utilize a rheometer. Based on the steady-state shear loading, the shear yield stress achieved 31 kPa with the LVE limit at 5%. Under dynamic loading, the properties of reclaimed WTR were also determined. The storage modulus reached 0.5 to 0.7 MPa under excitation frequency of 0-100 Hz. The loss modulus increased from 0.02 to 0.25 MPa at the altered excitation frequency of 0-100 Hz. The toss factor enhanced from 0.035 to 0.35 at the same ramp excitation frequency. Completion of the rheological test was subjecting the sample with ramp strain amplitudes. Based on the test, when the strain amplitude increased from 0.01 to 10%, the storage modulus dropped from 0.6 to 0.07 MPa at LVE limit 0.8 to 1 %. Meanwhile, the loss factor ranged at 0.15 to 0.81. The current study was successfully revealed the rheological properties of reclaimed WTR in which this characterization would be useful for consideration of reclaimed WTR application in static and dynamic conditions.

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