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INFLUENCE OF CONTINUOUS FLOW BEAD-MILLING PROCESS PARAMETERS ON SULFUR CURATIVE AND ITS PERFORMANCE FOR ELASTOMERIC RUBBER COMPOSITES

MOHAMAD FIRDAUS OMAR[1,2], FATHILAH ALI[1*], MOHAMMED SAEDI JAMI[1], AZLIN SUHAIDA AZMI[1], FARAH AHMAD[1], MOHD ZAHID MARZUKI[3]

[1]Department of Chemical Engineering and Sustainability, Kulliyyah of Engineering, International Islamic University Malaysia, P.O. Box 10, 50728 Kuala Lumpur, Malaysia.
[2]SC Johnson Asia Pacific Sdn. Bhd., UOA Corporate Tower, The Vertical, 8, Jalan Kerinchi, Bangsar South, 59200 Kuala Lumpur, Malaysia.
[3]Faculty of Chemical Engineering, Universiti Teknologi MARA (UiTM) 40450 Shah Alam, Selangor, Malaysia.

**Corresponding author: fathilah@iium.edu.my*

ABSTRACT: Bead-milling is an eco-friendly and feasible method for physical modification of materials that has been extensively used in many industrial applications impacting on particle size and overall products' performance. While previous studies explored various bead-milling parameters in different applications, limited research conducted on sulfur curative dispersion, necessitating a thorough investigation of its performance after bead-milling is applied. The primary objectives of the present study were to explore the influence of bead-milling process parameters, particularly rotational speed and flow rate on the sulfur curative dispersion characteristics and to analyze its behavior within the rubber elastomer matrix. Taguchi's L9 orthogonal array experimental design was employed to identify the optimal rotational speed and flow rate of a 60-L bead-milling machine on the sulfur curative dispersion. It was found that higher rotational speed (800 rpm) and lower flow rate (350 L/h) of the bead-milling process resulted in smaller sulfur particle sizes, leading to slight improvement on tensile strength of the rubber elastomer and hindered the formation of severe sulfur crystals on the casted rubber elastomer – and vice versa. This research provides valuable insights to determine the ideal bead-milling process for sulfur curative, enhancing the mechanical properties and overall performance of elastomeric rubber composites.

KEYWORDS: *bead-milling, sulfur, rubber.*

1. INTRODUCTION

Bead-milling is an eco-friendly method known for modifying materials via friction, collision, impact, and shear from milling beads and the chamber wall – altering particle size, surface properties, morphology, and functional characteristics including solubility, water absorption, swelling, pasting, and gelation of materials [1–3].

Numerous researchers have employed the bead-milling process to alter their products or materials and achieve desired attributes – such as investigations on multi-wall carbon nanotubes (MWCNTs) and bead-milling process parameters for aluminium-magnesium (Al–Mg) alloy powder which reported increasing milling time and speed yields smaller crystallite sizes by 83%, enhancing MWCNT distribution and diffusion into the Al–Mg matrix [4]. A study on wheat gluten protein using bead-mill process proved significant improvements such as breakage of disulfide bonds, increased sulfhydryl groups, heightened hydrophobicity, improved foaming capacity, reduced particle size, and enhanced whiteness that diversifies the applications of wheat gluten [5]. In the context of drug nanocrystal suspensions, utilizing finer milling beads (0.1 mm yttrium stabilized zirconia) was found optimal to stabilize ultrafine drug suspensions that remain homogeneous even after refrigeration [6]. Furthermore, bead-milling enhances the stability and performance of 1.5% cesium lead bromide ($CsPbBr_3$) perovskite quantum dots/polymethyl methacrylate composite with significant performance in terms of luminous efficiency in a white light-emitting diode [7]. These studies reflected bead-milling's wide application scope across industries like chemicals, nanomaterials, food processing, and pharmaceuticals, impacting particle size, surface morphology, stability, and overall product performance.

A curing agent or "curative" is a chemical used to initiate reactions, particularly for cross-linking elastomer molecules such as rubber. Colloidal or dispersed sulfur yields fine particles that suspend well and "insoluble sulfur" is preferred over soluble to prevent "sulfur blooms" which can hinder rubber adhesion and product performance [8,9]. Extensive research explored various methods on sulfur characteristics enhancement – involving ball-milling for dispersion [10], modified sulfur for compatibility [11], and nano-additives for mechanical properties [12]. that aim to enhance sulfur's properties and dispersion within rubber which may lead to the development of high-performance elastomeric materials.

While various milling parameters' effects on products are studied, there is a relative lack of studies or exploration on sulfur dispersion, particularly on its dispersion performance after bead-milling. This research investigates how flow rate and rotational speed affect its performance in the rubber matrix – optimizing bead-milling for sulfur to yield elastomeric items with superior properties via characterizations on visual and tensile properties by using Light Emitting Diode (LED) magnifier lens and universal testing machine respectively.

2. MATERIALS AND METHODS

2.1. Sulfur Curative Preparation and Rubber Elastomer Casting

Dispersion of sulfur curative raw materials inclusive of sulfur powder, sodium salt of naphthalene-sulfonic acid (surfactant), and deionized water at weight percentage of 60%, 6% and 34% respectively was done in a 4-tonne mixing tank at 800 rpm for 30 minutes before the dispersion was pumped to the 60-Litre bead-milling machine with various rotational speed and flow rate using Taguchi's L9 orthogonal array from control factors and levels in Table 1. Yttrium-stabilized zirconia beads of 140 kg and 0.9 mm diameter were used in the milling chamber. Four sulfur samples after the bead-milling based on their particle size, D_{90} (90% of the particles in the sulfur curative having a size smaller than or equal to the reflected value) were then chosen for latex compounding where the compounding materials were obtained commercially. The compounded latices were left to mature for 48 hours and the rubber films were then casted with a pre-determined parameters setting for rubber vulcanization.

Table 1: Control factors with their respective levels for sulfur curative bead-milling

Factors		Unit	Levels		
			1	2	3
A	Rotational Speed	rpm	800	700	
B	Flow Rate	L/h	750	550	

2.2. Characterizations

The D_{90} value of sulfur curative dispersion's particle size was determined using a Particle Size Analyzer of LA-960V2 model. Total Solids Content (TSC) was calculated with the aid of oven at 100 ºC to observe water input/output to the dispersion. The dispersion's pH was measured by using pH meter while the dispersion viscosity was measured with a Brookfield viscometer. The casted elastomeric rubber samples' properties were analyzed mechanically using a universal testing machine supplied by GT Instruments Sdn. Bhd. (Model: Al-3000) to measure tensile strength with verified thickness (0.06 ± 0.005 mm), and LED magnifier lens for visual characterization.

3. RESULTS AND DISCUSSION

3.1. Sulfur Curative Properties

Table 2 shows the specifications of sulfur curatives achieved through varying bead-milling process parameters. Triplicate samples of sulfur curatives were taken and recorded their properties for each run and averaged out.

Table 2: Sulfur curative specifications results

Run No.	Rotational Speed (rpm)	Flow Rate (L/h)	pH	TSC (%)	Viscosity (cP)	Particle Size, D_{90} (µm)
1	800	750	9.5	61.31	472	7.750
2	800	550	9.5	62.99	610	6.718
3	800	350	9.6	61.63	598	6.154
4	700	750	9.7	62.05	470	8.650
5	700	550	9.9	61.84	646	7.760
6	700	350	9.5	62.31	616	6.820
7	600	750	9.7	62.43	370	9.998
8	600	550	9.7	62.69	432	8.444
9	600	350	9.5	61.89	518	7.214

It can be roughly observed that particle size and viscosity demonstrated variations across the different runs, while pH and TSC were observed to constant to less variations. This variation in particle sizes may be able to influence the resulting dispersion's stability and performance within rubber matrix.

3.2. Influence on the Resulting Rubber Elastomer

From the observations of rubber elastomer film surfaces through an LED magnifier lens, a significant presence of sulfur crystals/blooms on the rubber film surface at a lower rotational speed of 600 rpm and a higher flow rate of 750 L/h. Comparatively, sulfur produced with a higher rotational speed and lower flow rate in bead-milling, showed considerably fewer sulfur blooms on the surface.

Figure 1 illustrates the tensile strength mechanical properties of the casted rubber elastomer films across the four different sulfur curative sets, comparing their respective particle sizes. The mechanical properties underwent testing to assess the mechanical behavior of the rubber elastomer samples according to ASTM D3578 standard and remarkably passed the minimum requirement of the standard (≥ 18 MPa) [13], and the values for each set remained closely aligned, with slight improvements in tensile strength evident for Set A which featured the smallest particle size, showing the highest tensile strength value, which apparently contributed to this positive impact.

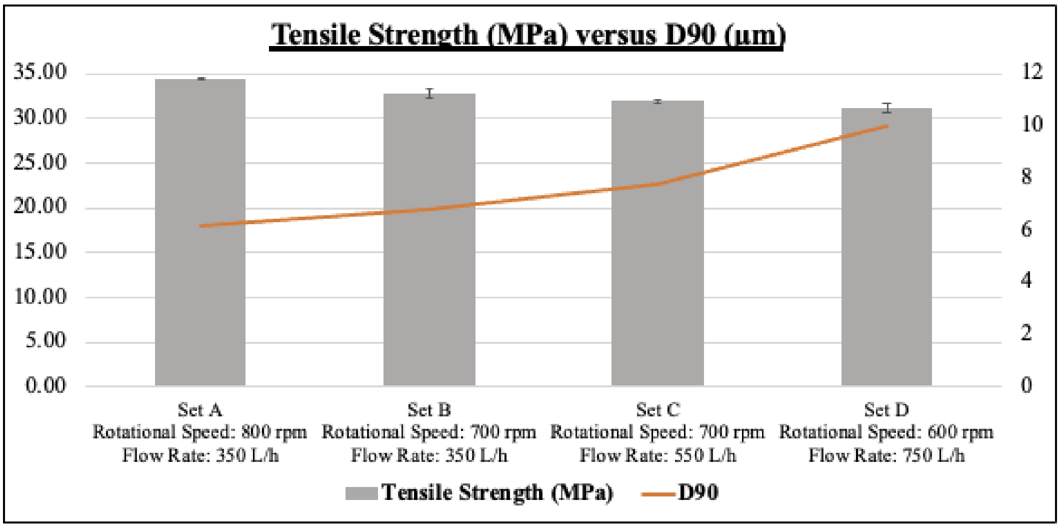

Fig. 1. Tensile strength of casted rubber elastomer films with different bead-milled sulfur curative.

4. CONCLUSION

In this study, it is proved that at the highest rotational speed (800 rpm) and lowest flow rate chosen (350 L/h) resulted in sulfur with the smallest or reduced particle size. Observations of sulfur crystals surfaced on rubber films highlighted various effects of bead-milling settings – particularly Set A with fewer blooms due to higher rotational speed and lower flow rate resulting in smaller particle size. All rubber films met the ASTM D3578 standard for strength, and the smallest sulfur particles showed the highest tensile strength and vice versa.

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