

Influence of Additives on Thermal Properties and Morphological of Magnetorheological Elastomer

Ku Zarina Ku Ahmad^{1*}, MHA Khairi², SA Mazlan²

¹ *Fakulti Kejuruteraan, Universiti Pertahanan Nasional Malaysia, Kem Sg Besi, 57000 Kuala Lumpur, Malaysia.*

² *Malaysia Japan International Institute of Technology, Universiti Teknologi Malaysia, Jalan Sultan Yahya Petra, 54100 Kuala Lumpur, Malaysia*

**Corresponding author E-mail: kuzarina@upnm.edu.my*

Abstract

Magnetorheological elastomers (MREs) are categorized as part of the smart materials class whose rheological properties can be altered under the influence of a magnetic field. MREs are fabricated by embedding soft magnetic particles such as carbonyl iron particles (CIPs) in a rubber matrix such as silicone and natural rubber. In this project, epoxidized natural rubber (ENR-50) is used as a base material with carbonyl iron particles. Sucrose Acetate Isobutyrate (SAIB) ester is added to the formulation to improve the viscosity and enhance the MRE properties. The isotropic MRE is fabricated using two roll mill and a compression mould. Various tests comprise mechanical, morphology, thermal and magnetic tests were conducted for MRE characterization purpose. The results showed that the addition of SAIB on the MRE had reduced 53% of viscosity in the rubber matrix compared to non-ester based MRE. Dispersion of magnetic particles is improved by the addition of ester as observed through Field Emission Scanning Electron Microscope (FESEM). Additionally, the thermal stability was also improved. Tensile strength of MRE consisting SAIB ester achieved maximum strength of 12.3 MPa and an elongation of 620% compared to non-ester based MRE.

Keywords: *ester; epoxidized natural rubbers; magnetorheological elastomers; magnetic; morphological.*

1. Introduction

The potential of MRE using epoxidized natural rubber (ENR-50) as a base matrix has not really been explored by researchers [1]. ENR-50 possesses some unique properties beyond the normal characteristic of natural rubber, for instance oil resistant, low rolling resistance, gas tight and high wet skid resistance [2]. These properties are suitable for use in load bearing, automotive application and mechanical field [2]. In this study, the non-phthalates ester plasticizer i.e. sucrose acetate isobutyrate (SAIB) ester was incorporated into ENR-50 to reduce the viscosity of the matrix and increase the mobility of magnetic particles in a matrix thus enhancing the relative MR effect. SAIB ester was chosen because of its strong polar ester [3] and compatibility with ENR-50 which is another strong polar rubber [4]. Both components are environmentally friendly materials generated from natural resources [2,5]. Furthermore, SAIB ester has an excellent solubility and is compatible with the polymer and remains low in volatility over a wide temperature range. Consequently, the main technical contribution of this work is to solidly investigate the enhancement of MR effects based on the plasticizer SAIB ester incorporated with ENR-50. The influence of SAIB ester on the microstructure and other properties of ENR-50 based MREs are experimentally observed and analysed in details.

2. Experimental

2.1. Materials

Major constituents of a typical MRE are elastomers matrix, magnetic particles and additives. The fabrication process of these isotropic MREs consists of two steps; mixing and curing. Epoxidized natural rubber (ENR-50) was used as the matrix and being manufactured by Malaysian Rubber Board. The magnetic particles are carbonyl iron particles (CIPs) having 5.931 μ m average diameter. Sucrose acetate isobutyrate (SAIB) ester was used as plasticizer additive and was obtained from Sigma Aldrich (M) Sdn Bhd. Additionally, the stearic acid and zinc oxide (ZnO) are used as activators. Meanwhile, the sulfur and N-Cyclohexylbenzothiazole-2-sulphenamide (CBS) are used as a vulcanizing agent and an accelerator, respectively. The carbon black was used as reinforcing agents. Mixing and compounding methods for MREs were carried out using conventional rubber-mixing/compounding equipment (two roll mill). The first stage of compounding involves softening of the rubber on its own in the two roll mill (mastication). After mastication, rubber additives (other than accelerators and sulphur) and magnetic particles were then added and homogeneously dispersed in the rubber. Afterwards, the rubber compound was divided into four samples with different SAIB ester contents but at a constant content of CIPs at 60 wt. % as shown in Table 1.

Table 1: Composition of the samples (weight percentage).

Sample	SAIB Ester	CIPs	ENR-50 Compound
1	0	60	40
2	5	60	35
3	7.5	60	32.5
4	10	60	30

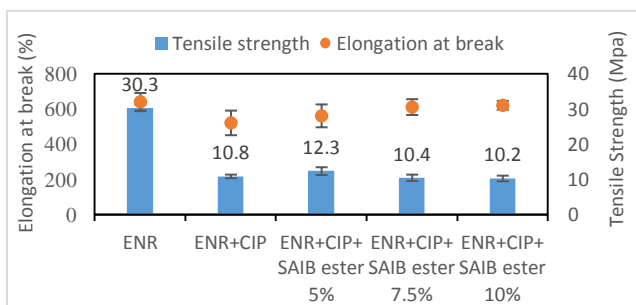
After compounding and measurement of curing time, a predetermined amount of MRE compound is weighted and inserted into a sheet mould producing 2 mm and 1mm thickness MREs for shaping and curing. For isotropic MREs, the compound is typically cured in a compression moulder at the respective cure time (t_0) determined with the Monsanto moving die rheometer (MDR 2000) under an approximate pressure of 10-12 MPa. The curing temperature and pressure are important to ensure that the compound flows following the shapes according to the mould

2.2. Characterization

The thermal decomposition behaviour of MREs with different content of SAIB ester were determined using a Perkin Elmer Simultaneous Thermal Analyser (STA) Model 8000. The thermal analyses of the specimen were determined by heating the sample from 32°C to 600°C approximately, at a rising heating rate of 10.00°C min⁻¹ using Nitrogen gas (N₂) at inert atmosphere and a flow rate of 10°C min⁻¹ as the sweeper gas. The analyses were done using computerised Pyris Software Orientation. Morphology inspection was conducted to study the distribution of magnetic particles. The MREs was observed at an accelerating voltage of 10 kV, with 500, 1000 and 2000 times magnification. The samples were fractured at room temperature to investigate the microstructure of the nanocomposite. All specimens were examined with a Gemini 500, Carl Zeiss FESEM. The activation voltage varied from 2 to 5 kV with magnification of 1000x and 5000x. The EDX analysis was then performed, using Oxford Instruments EDX model 7353, to study the dispersion of elements on the fractured samples.

3. Results and Discussion

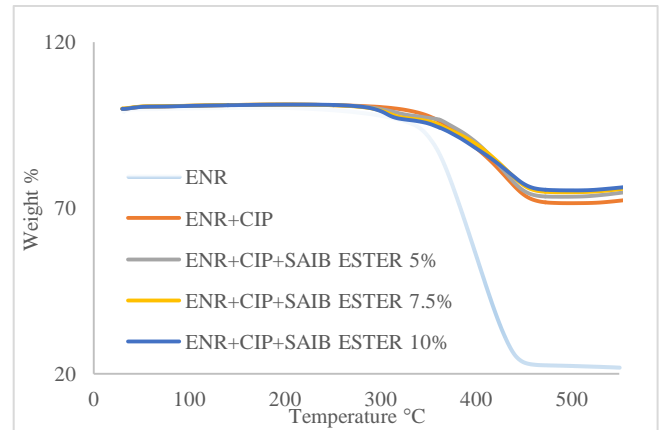
Fig. 1 shows the tensile strength and elongation at break of MRE as a function of the SIB ester plasticizers content. The addition of CIPs to the rubber matrix causes the decrement (~64.4%) of the tensile strength due to the worsening reinforcing effect by the CIPs [6]. Generally, SAIB ester decreases the strength and enhances the flexibility by reducing the rubber viscosity, which is consistent with the general expectation for a plasticized polymer [7]. Incorporation of SAIB ester into polymer reduces the viscosity or cross-link density which eases rubber chains mobility.

**Fig. 1:** Tensile strength and elongation at break as a function of SAIB ester

Hence, tensile strength was decreased due to the reduction of cross link density. On the other hand, elongation at break is increased with the addition of SAIB ester content. The percentage of elongation at break is improved by 19 % with the 10 wt. % SAIB ester content caused by the interaction of rubber molecular chains and SAIB ester. Wang et al. 2015 [6] and Ren et. al 2015 [8] have

reported that SAIB ester curled around the CIPs which provided a strong interaction on the surface of the MRE. Therefore, the MRE can stretch more due to the increment in MRE flexibility by reducing its viscosity.

MRE is a novel polymer composite material and the thermal stability of its matrix is critical to increase its durability and age resistance. The thermal stability of a polymer can usually be evaluated using TGA. The effect of ester content on thermal stability of MRE is determined using thermogravimetric analysis in nitrogen is shown in Fig. 2

**Fig. 2:** TGA thermograms of MRE with different content of SAIB ester

Obviously, ENR without CIP and SAIB ester has the least mass residue (22 %) among other samples, while ENR with CIP and 10 % SAIB ester showed the highest mass residue (76 %) due to the highest presence of ester. Sample without ester shows a one stage weight loss during thermal decomposition while all the samples with ester present shows additional stage weight loss during thermal decomposition. Khan et al. [9] reported similar results. However, the depicted onset and degradation values are higher than the reported value due to the addition of 60 % carbonyl iron particles. The thermal decomposition of MRE without ester begins at 335°C – 370°C and completes at 442°C – 444°C, representing ~78 % mass loss. However, MRE with additional ester represent undergo first stage thermal decomposition at temperatures between 31°C – 303°C while the second stage occurred at 270°C – 350°C and followed by the third stage which occurred at 330°C - 450°C, representing mass loss of ~20%. The first mass loss in ENR/CIP/SAIB is supposed to be from the addition of ester which starts at 250°C and ends at 370°C. The curve and value are similar as Reda et. al [10] reported in his research. The final stage represents the remaining residue in the sample. Degradation temperatures obtained from these thermograms are summarized in Table 2. The thermal stability of the neat ENR and ENR/CIP/SAIB ester blends were characterized based on the temperature at which 20 % (designated as T₂₀) weight losses were recorded and presented in Table 2. The thermal stability corresponding to 20 % decomposition is found to be 371°C in the case of neat ENR while the blends exhibit higher values.

Table 2: Parameters evaluated from the TGA curves of the blends.

Sample	Initial decomposition, T ₂₀ (°C)	Final decomposition, T _f (°C)	Ash at 550 °C (%)
ENR	371	442	22
ENR+CIP	429	444	72
ENR+CIP SAIB ester 5%	433	445	75
ENR+CIP SAIB ester 7.5%	437	450	76
ENR+CIP SAIB ester 10%	438	451	76

A derivative curve weight loss of MRE confirms the point at which weight loss is most apparent (Fig. 3). The various degradation steps with maximum decomposition temperatures are as listed in Table 3. Based on Table 3, it can be concluded that the incorporation of SAIB ester enhanced the thermal stability of the ENR. This result could be attributed to the fact that ENR/CIP/SAIB ester blend performs more intense molecular interactions and greater crosslinking than ENR/CIP blend, leading to higher thermal stability [11].

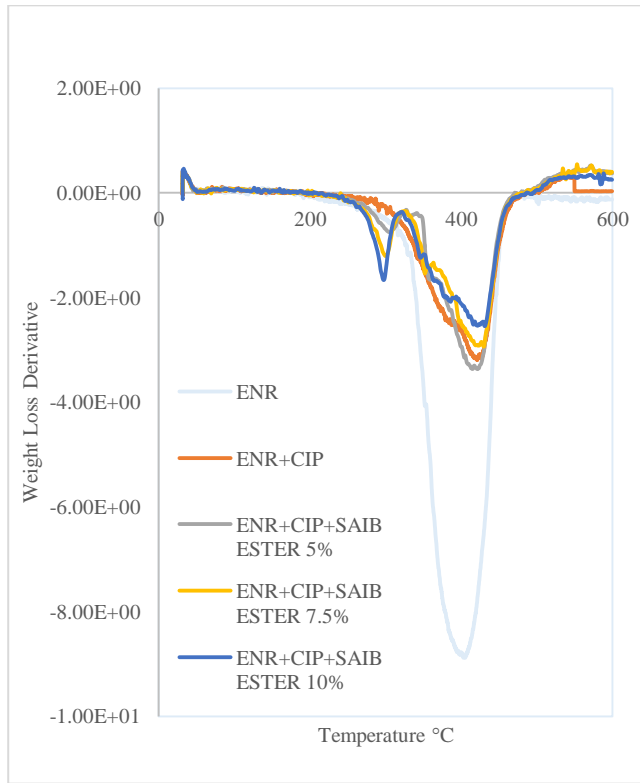


Fig. 3: DTG thermograms of MRE with different content of SAIB ester

Table 3: Degradation temperatures from DTG curves

Sample	Number of degradation steps	First decomposition temperature,	Second decomposition temperature,
		T_{max1} (°C)	T_{max2} (°C)
ENR	1	405	-
ENR+CIP	1	420	-
ENR+CIP+SAIB ester 5%	2	282	421
ENR+CIP+SAIB ester 7.5%	2	279	429
ENR+CIP+SAIB ester 10%	2	279	431

Fig. 4 shows the FESEM images of the plain ENR while Fig. 5 shows the blends of ENR/CIP and ENR/CIP/SAIB ester. Compared to blends, ENR displays smoother fracture surface and fewer drapes present showing typical characteristic of ductile fracture under tensile loads. This is consistent with the results showing the tensile strength of blends is higher than that of ENR. It seems that the rougher the surface is; the better tensile strength of the blend will be. All fabricated MREs exhibit an isotropic condition. Fracture surfaces of blends show spherical shape dimples from pull out CIP. Apparently, there are significant differences in the texture of the matrix when SAIB was added to the rubber matrix. When SAIB ester is added to ENR matrix the surface roughness increases with the increase in SAIB ester loading. The bonding between ENR and CIP is improved as there is no obvious phase separation observed (refer to Figure 5(b), (c) and (d)). From the high magnification FESEM image, it can be seen that the CI particles bond well with the matrix (Figure 6b). However, in the absence of the

SAIB ester, some cracks are clearly observed between the CI particle and the neat ENR (Figure 6a). Ge et al. [12] in his research also observed the similar findings. From fractography observation, the SAIB ester can enhance the compatibility between the CI particles and the ENR matrix as there are no such gaps and cavities seen, indicating that CIPs have been well embedded in the matrix.

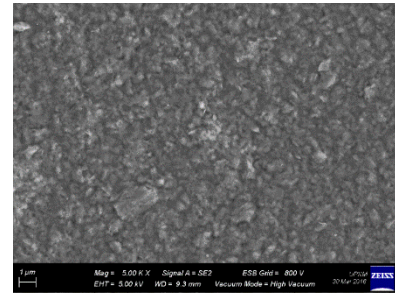


Fig. 4: Representative of SEM micrographs (5000x magnification) module of the fracture surfaces of ENR

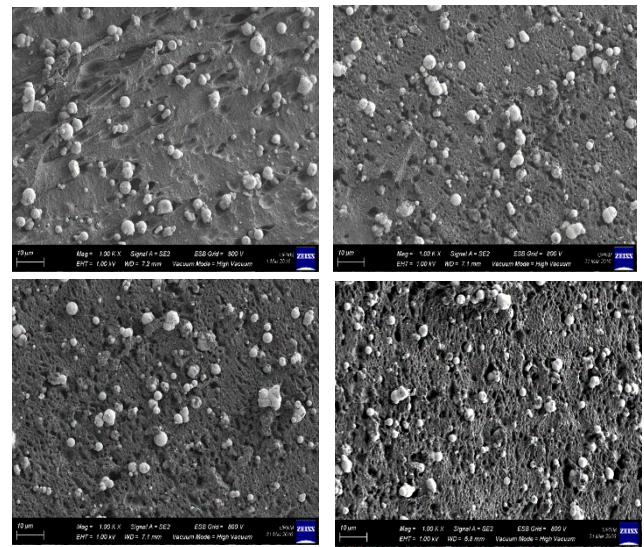


Fig. 5: Results of FESEM at magnification of 1000x, morphology of ENR/CIP with varying weight percentage of SAIB ester a) 0% b) 5% c) 7.5% d) 10%.

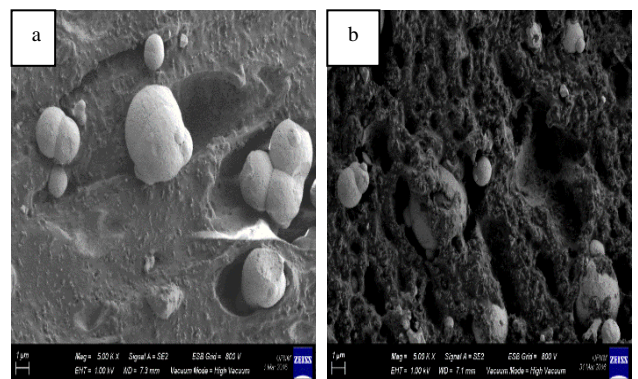


Fig. 6: FESEM image of (a) ENR/CIP and (b) ENR/CIP/SAIB ester at 5000x

EDAX analysis is executed to trace the element contained in ENR/CIP and SAIB ester and also provides the confirmation of CIP distribution in ENR matrix. The presence and distribution of chemical elements on the fractured samples could be determined by using EDX, in which the software maps the elements found on the SEM image through X-ray analysis. It also permits estimation of the quantity of the elements in terms of atomic and weight percentages. EDX mapping images (SEM images and the corresponding EDX mapping image of the elements: C, O, S, Fe and Zn) on the surface of ENR/CIP/SAIB ester are presented in Fig.

7 while Fig. 8 displays the element spectrum present in the analysis. With regards to carbon, the C-map in combination with the point spectrum suggests the presence of a carbon coating as contamination of the entire particle surface. From these figures, elemental maps demonstrate that the CIP particles are regularly dispersed across the ENR matrix surface proving that the distributions of CIP for this MRE are isotropic.

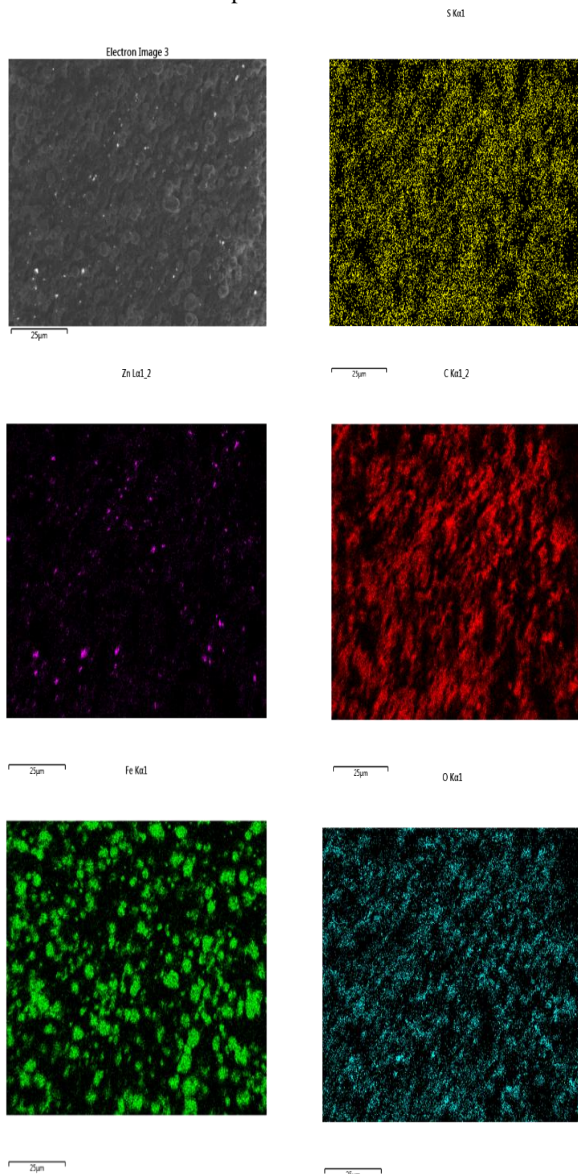


Fig. 7: Elemental mapping on the ENR/CIP/SAIB ester fracture surface: S (yellow), Zn (purple), C (red), Fe (green), and O (blue), magnification 500X.

4. Conclusion

In this study, tensile strength was reduced by 17% as the SAIB ester was increased from 5 to 10 wt.%. Meanwhile, the elongation at break was increased by 19% at 10 wt.% content of the SAIB ester. Thermal stability was increased as the degradation temperature increased and high ash content is recorded at 600 °C due to more intense molecular interactions activities and greater cross-linking than ENR/CIP blend properties. FESEM images verified that the CIPs were dispersed uniformly and embedded in the ENR matrix within isotropic condition. Though the 10 wt.% SAIB ester was added, the agglomerations of CIPs were not observed in the matrix. Moreover, the interface between the ENR matrix and CIPs was not significant enough, indicating that the CIPs were well embedded in the ENR 50 matrix

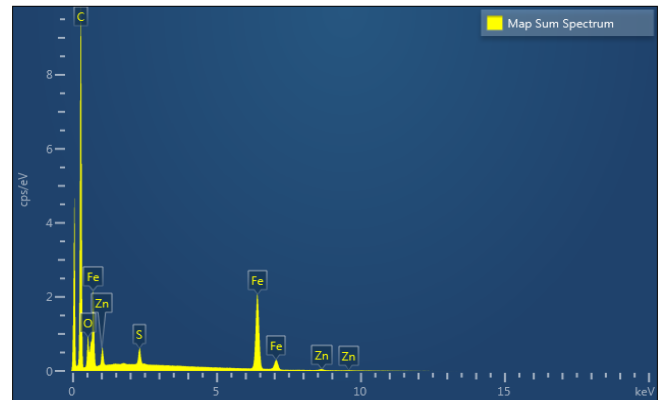


Fig. 8: EDX spectra of ENR/CIP/SAIB

Acknowledgement

The authors gratefully acknowledge Universiti Pertahanan Nasional Malaysia for their financial support under UPNM/2015/GPIP/2/TK/02. Heartfelt appreciation is extended to Malaysia Japan International Institute of Technology for generously providing the facilities used in this project.

References

- [1] Ubaidillah, Joko, S., Agus, P. and Mazlan, S.A." Recent Progress on Magnetorheological Solids: Materials, Fabrication, Testing and Applications", *Advanced Engineering Materials*, Vol. 17, No.5, (2015), pp. 563-597.
- [2] Gong, X.L., Zhang, X.Z. and Zhang, P.Q. "Fabrication and Characterization of Isotropic Magnetorheological Elastomers": *Polymer Testing*; Vol 24, No. 5, (2005) pp 669-676
- [3] Gong, X.L, Fan, Y., Xuan, S., Xu, Y. and Peng, C. "Control of the Damping Properties of Magnetorheological Elastomers by Using Polycaprolactone as a Temperature-Controlling Component": *Industrial & Engineering Chemistry Research*: Vol 51, No. 18, (2012), pp 6395-6403.
- [4] Fan, Y., Gong, X.L, Xuan, S., Qin, L and Li, X. "Effect of Cross-Link Density of the Matrix on the Damping Properties of Magnetorheological Elastomers": *Industrial & Engineering Chemistry Research*, Vol 52, No.2, (2013), pp771-778.
- [5] Hu, Y., Wang, Y.L., Gong, X.L., Gong, X.Q., Zhang, X.Z. and Jiang, W.Q. "New Magnetorheological Elastomers based on Polyurethane/Si-rubber hybrid": *Polymer Testing*; Vol 24, No. 3, (2005), pp 324-329
- [6] Wang,Y.,Zhang, X.,Oh, J and Chung, K. "Fabrication and properties of magnetorheological; elastomers based on CR/ENR self crosslinking blends": *Smart Materials and Structures*, Vol 24, No. 9, (2015), pp 95006
- [7] Lim, H and Hoag, S.W. "Plasticizer Effects on Physical-Mechanical Properties of Solvent Cast": *AAPS PharmSciTech*, Vol14, No. 3, (2013), pp 903-910.
- [8] Ren, Y., Zhao, S., Yao, Q., Li, Q., Zhang, X and Zhang, L. "Effects of plasticizers on the strain-induced crystallization and mechanical properties of natural rubber and synthetic polyisoprene": *RSC Adv*, Vo 5, No. 15, (2015), pp 11317-11324.
- [9] Khan, I., Poh, B. T., & Lee, K. E. "Material Properties and Statistical Analysis of Natural Rubber-Based Adhesives": *Journal of Polymers and the Environment*, Vol 21, No. 3, (2013), pp 833-849.
- [10] Reda S. Y., "Evaluation of antioxidants stability by thermal analysis and its protective effect in heated edible vegetable oil": *Ciência. Tecnol. Aliment.*, Campinas, Vol 31, No. 2, (2011), pp 475-480.
- [11] Zhang, C., Wang, W.,Yun Huang , Yonghao Pan , Long Jiang , Yi Dan , Yongyue Luo , Zheng Peng. "Thermal, mechanical and rheological properties of polylactide toughened by expoxidized natural rubber": *Materials and Design*, Vol 45, (2013), pp 198-205.
- [12] Ge, L., Gong, X., Fan, Y., and Xuan, S. "Preparation and mechanical properties of the magnetorheological elastomer based on natural rubber/rosin glycerin hybrid matrix": *Smart Material. Structure*, Vol 22, No. 11, (2013).