Songklanakarin J. Sci. Technol.
41 (1), 159-164, Jan. – Feb. 2019

http://www.sjst.psu.ac.th

Original Article

Performance of treated distillate aromatic extract oil-coated petroleum-based sulfur on properties of natural rubber/acrylonitrile butadiene rubber blends

Pathompong Pangamol[1] and Chomsri Siriwong[2*]

[1] *Rubber Technology Research Center (RTEC), Faculty of Science, Mahidol University, Salaya Campus, Phutthamonthon, Nakhon Pathom, 73170 Thailand*

[2] *Materials Chemistry Research Center, Department of Chemistry, Faculty of Science, Khon Kaen University, Mueang, Khon Kaen, 40002 Thailand*

Received: 22 September 2016; Revised: 19 August 2017; Accepted: 11 October 2017

Abstract

Petroleum-based sulfur is one of the sulfur types used in rubber vulcanization. The use of such sulfur still faces poor dispersion in the rubber matrix especially in acrylonitrile butadiene rubber (NBR) and its blends. The use of oil as a dispersing agent acts as a key factor to improve the dispersibility of the sulfur. The effects of treated distillate aromatic extract (TDAE) oil-coated petroleum-based sulfur on the properties of natural rubber/acrylonitrile butadiene rubber (NR/NBR) blends were studied. In this work, sulfur was coated with 20 wt% TDAE-oil and then the effects on the properties of NR/ NBR blends were investigated. The results revealed that the TDAE oil-coated sulfur offered a significant improvement in sulfur dispersion without significant changes in cure behaviors which led to an enhancement of mechanical properties.

Keywords: petroleum based sulfur, TDAE oil, NR/NBR blends, mechanical property, rubber vulcanization

1. Introduction

Rubber blends are being used increasingly in the rubber industry. When properly adjusted, the blends combine the best features of the individual blend components and the desired properties are obtained. Natural rubber (NR) is widely recognized to have good mechanical properties, i. e. high tensile and tear strengths, because it is able to crystallize upon stretching which is also known as strain-induced crystallization. Moreover, NR has excellent elasticity and dynamic properties. However, due to the existence of numerous reactive double bonds on its molecular backbone, NR is highly vulnerable to degradation by thermal aging and ozone attack. In addition, oil resistance of NR is relatively poor due to its non-polarity resulting in limited use in some applications. In order to tackle this problem, blending NR with polar synthetic rubbers such as acrylonitrile butadiene or nitrile rubber (NBR) is preferred.

NBR is a copolymer of acrylonitrile and butadiene. The polar group from the acrylonitrile makes NBR oil-resistant. A higher proportion of acrylonitrile imparts a greater resistance to oil. The blending of NR and NBR is intended to produce a vulcanizate with the best properties from each component, i.e. high oil resistance of NBR and good strength of NR. In practice, however, the result is often disappointing in terms of properties and service life due to the large difference in their polarity. In addition to rubber incompatibility, the poor properties of the final products might also arise from the maldistribution of crosslinks, i.e. one phase is over-crosslinked, whereas another is poorly crosslinked. For blends of two rubbers differing in polarity such as NR and NBR, maldistribution of crosslinks can arise through the

*Corresponding author
Email address: schoms@kku.ac.th

preferential solubility of the curatives and vulcanization intermediates.

The curing system of the NR/NBR blend generally includes sulfur and thiourea derivatives with the addition of other conventional accelerators (Hoffmann, 1989). Apart from the curing system, the discrepancy in the polarity of the blend partners could also bring about high interfacial tension which is detrimental to the mechanical properties of the blend (Tinker, 1998). The addition of a suitable compatibilizer is therefore essential. Typically, there are 2 main systems of vulcanization used in the rubber industry: sulfur and peroxide (Hoffmann, 1989). Thanks to its low investment cost, adjustable cure behaviors, and superior mechanical properties, sulfur vulcanization is preferably used in the rubber industry. Generally, the sulfur used in the rubber industry includes sulfur and oil-coated sulfur (Akiba & Hashim, 1977; Nehb & Vydra, 2000; Struktol Company of America, 2004). The former has been used since the vulcanization process was discovered, whereas the latter was developed recently and introduced as a vulcanizing agent to alleviate some problems.

Sulfur coated with oil offers a dust-free alternative and it has a low electrostatic force, which can provide safety during the mixing process (Ash & Ash, 2008; Dick, 2009; Struktol Company of America, 2004). According to the literature (Pangamol *et al.,* 2013, 2014), the sources of sulfur have no profound effect on the properties of the rubber vulcanizates. Both natural-based and petroleum-based sulfurs offer the rubber with similar properties when they were used as vulcanizing agents (Pangamol *et al.,* 2013, 2014). Nevertheless, poor sulfur dispersion still occurs especially in NBR. In order to solve such a pending problem, oil-coated sulfur has been introduced. As reported in previous work (Pangamol *et al.*, 2015), treated distillate aromatic extract (TDAE) oil can be used to improve dispersion of the petroleum-based sulfur in the NR matrix leading to an improvement in the crosslink distribution and thus an improvement in the mechanical properties of the rubber vulcanizates. Moreover, it was reported that petroleum-based sulfur coated with 20 wt% of TDAE oil gave good dispersion of sulfur in NBR (Pangamol *et al.,* 2015). It is therefore interesting to use the sulfur coated with 20 wt % of TDAE oil as a vulcanizing agent for the NR/NBR blend. In the present work, the effect of oil-coated petroleum-based sulfur on the properties of the NR/NBR blends at various blend ratios was investigated. The improvements in mechanical properties of the blends were explored.

2. Materials and Methods

NR (grade STR-5L) and NBR containing 35 wt% of acrylonitrile content were purchased from Union Rubber Product Co., Ltd., Bangkok, Thailand, and JSR Co., Ltd., Japan, respectively. Zinc oxide and stearic acid were supplied by Chemmin Co., Ltd., Bangkok, Thailand. Petroleum-based sulfur was provided by IRPC (Public) Co., Ltd., Rayong, Thailand. N-cyclohexyl-2-benzothiazolesulfenamide (CBS) was purchased from Flexsys, Antwerp Belgium. The TDAE oil supplied by P. S. P. Specialties Co., Ltd., Bangkok, Thailand was used as a dispersing agent to prepare the oil-coated petroleum-based sulfur.

2.1 Preparation of oil-coated petroleum based sulfur

The TDAE oil-coated sulfur was prepared by the dry blending technique using a high speed mixer (Labtech Engineering Co., Ltd., Samutprakarn, Thailand). The physical characteristics of the TDAE oil used (Chartreenuwat, 2013) in this work are tabulated in Table 1. The TDAE oil content and blending time were kept constant at 20 wt% and 3 min, respectively.

Table 1. Physical characteristics of the treated distillate aromatic extract oil used in this work.

Properties	Test method	Value
Density/g.cm^{-3} at 15 °C	ASTM D4052	0.96
Viscosity/ mm^{2}s^{-1}	ASTM D445	
40 °C		759.5
100 °C		26.6
Total acid number	ASTM D664	0.03
Carbon type/%wt	ASTM D2140	
C_A*		30
C_N**		41
C_P***		29
Viscosity-Gravity-Constant (VGC)	ASTM D2501	0.882
Aniline point/°C	ASTM D611	73.7
Sulfur/%wt	ASTM D2662	3.6

C_A*=Aromatic carbon; C_N**=Naphthenic carbon; C_P***=Paraffinic carbon

2.2 Preparation of the NR/NBR blends

The NR/ NBR blends were prepared using a lab-scale internal mixer (Haake Rheocord 90, Essen, Germany) with a fill factor, rotor speed, mixing time, and mixing temperature of 0.8, 40 rpm, 8 min, and 50 °C, respectively. Table 2 shows the compound formulations used in this work. The amount of sulfur used in this work excluded the oil content and thus the actual weight of oil-coated sulfur used during mixing was calculated in order to keep the content of active sulfur constant.

Table 2. Compound formulations used for preparing the blends.

Chemicals	Amount, phr*	Function
NR	100, 75, 50, 25, 0	Raw rubber
NBR	0, 25, 50, 75, 100	Raw rubber
Zinc oxide	3	Activators
Stearic acid	1	Activators
CBS	1	Cure accelerator
Sulfur (all types)	2	Curing agent

*phr=parts per hundred of rubber
NR=natural rubber; NBR=acrylonitrile butadiene rubber; CBS=N-cyclohexyl-2-benzothiazolesulfenamide.

2.3 Property investigation of the rubber vulcanizates

The cure behaviors of the blends, e.g., scorch time (t_s2) and optimum cure time (t_c90) including minimum torque (ML) and maximum torque (MH) were determined using a moving die rheometer (MDR TechPro MD+, Mesa, AZ, USA) at 150 °C according to ISO 6502. Afterwards, the blends were compression molded using a hydraulic hot press at 150 °C based on the cure time as pre-determined from the MDR.

Mechanical properties of the rubber vulcanizates were measured by the Instron 5566 universal testing machine (Norwood, MA, USA) in accordance with ISO 37 (die type 2) at a load cell and a crosshead speed of 1 kN and 500 mm.min^{-1}, respectively. Hardness of the vulcanizates was determined by Shore A hardness tester (Cogenix Wallace, Burlington, UK) as per ISO 48. Moreover, photographs of the blends were also recorded.

The Mooney-Rivlin equation was conducted to determine the degree of crosslinking (crosslink density) of the rubber vulcanizates. Equations 1 and 2 are based on the phenomenological theory of rubber elasticity (Campbell *et al.*, 1992; Meissner, 2000).

$$F = 2A_0(\lambda - \lambda^{-2})(C_1 + C_2\lambda^{-1}) \quad (1)$$

$$\frac{\sigma}{(\lambda - \lambda^{-2})} = 2C_1 + \frac{2C_2}{\lambda} \quad (2)$$

where F is the force required to stretch the rubber specimen, A_0 is the cross-sectional area of the un-stretched specimen, σ is equal to F/A_0, λ is the extension ratio, and C_1 and C_2 are material constants.

By plotting $\sigma/(\lambda-\lambda^{-2})$ against $1/\lambda$ obtained from equation 2, both C_1 and C_2 can be determined. Then, the physically manifested crosslink density (n_{phy}) or the overall crosslink density can be finally assessed according to equation 3.

$$n_{phy} = \frac{C_1}{RT} \quad (3)$$

where R is the gas constant (8.314 J.mol^{-1}.K^{-1}) and T is the absolute temperature.

3. Results and Discussion

Cure characteristics of the NR/NBR blends with uncoated and TDAE oil-coated sulfurs are listed in Table 3 . The results revealed no profound discrepancy in cure behaviors with an increasing NR/NBR blend ratio. At a given blend ratio, there were slight differences in cure behaviors. The TDAE oil-coated sulfur system offered slightly shorter scorch time and cure time than the uncoated sulfur system. This was possibly due to two reasons: (1) the enhanced degree of sulfur dispersion brought about by the TDAE oil having good compatibility and solubility with NBR matrix (Dasgupta *et al.*, 2007; Dick, 2009; Guo *et al.*, 2008) and (2) the increase in sulfur content from the existing sulfur in the TDAE oil (Table 1). The torque difference of the blends is shown in Figure 1. Our results showed that neat NBR had the highest magnitude of torque difference due to the presence of the acrylonitrile group in its chemical structure leading to high polarity which, in turn, tends to hold the structure together. Moreover, the polar acrylonitrile group makes NBR become stiffer than NR (Hoffmann, 1989; Dick, 2009). In addition, the magnitude of the torque difference decreased with increasing NR ratio in the blend. This might be due to the dilution effect. The oil-coated sulfur system provided a higher magnitude of torque difference than the uncoated sulfur system. This is attributed to the enhanced degree of sulfur dispersion brought about by the good compatibility and solubility of the TDAE oil with rubber matrix. In other words, the TDAE oil is capable of acting as an effective dispersing agent for sulfur. Better dispersion of sulfur leads to more homogeneous crosslinking and, hence, possibly an increase in effective crosslinks.

Table 3. Cure characteristics of the NR/NBR blends.

NR/NBR ratio	T-0[a]		T-20[b]	
	t_s2, min	t_c90, min	t_s2, min	t_c90, min
0/100	4.52	10.06	4.50	9.13
25/75	5.34	9.39	4.06	8.05
50/50	5.08	8.04	4.10	6.47
75/25	4.41	6.52	4.30	6.36
100/0	7.36	10.09	8.08	10.33

[a]the uncoated blend
[b]the blend with 20 wt% treated distillate aromatic extract oil coated sulfur
NR=natural rubber; NBR=acrylonitrile butadiene rubber.

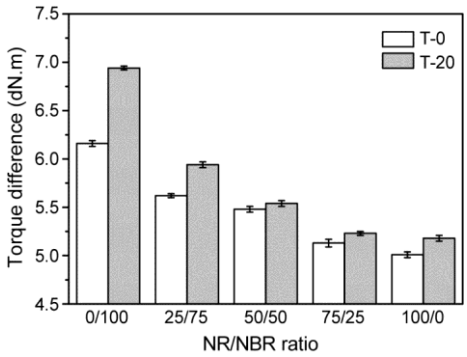

Figure 1. Torque difference of the uncoated NR/NBR blends (T-0) and 20 wt% treated distillate aromatic extract oil-coated sulfur (T-20).

Figures 2 and 3 illustrate hardness and tensile modulus (M100) results of the blends. Both systems showed similarity in hardness and M100 trends. The lower hardness and M100 values were observed at the higher NR ratio. When the NR ratio changed, the trend of hardness and M100 results was similar to that of the torque difference. As discussed earlier, the polarity of the petroleum-based sulfur leads to better solubility and compatibility with NBR than NR. With higher NR in the blend, the solubility and compatibility are thus reduced which, in turn, decreases the hardness and M100 of the blend. It could be seen that the oil-coated sulfur system provided higher magnitudes of hardness and M100 than the uncoated sulfur system due to the improved dispersibility of sulfur in the NBR phase.

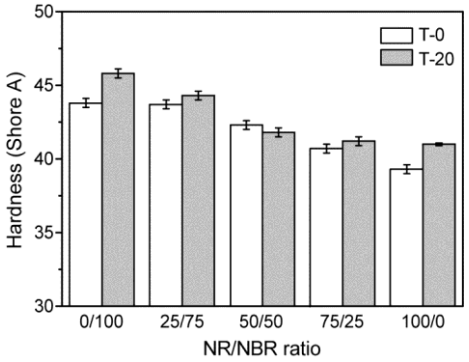

Figure 2. Hardness of the uncoated NR/ NBR blends (T-0) and 20 wt% treated distillate aromatic extract oil-coated sulfur (T-20).

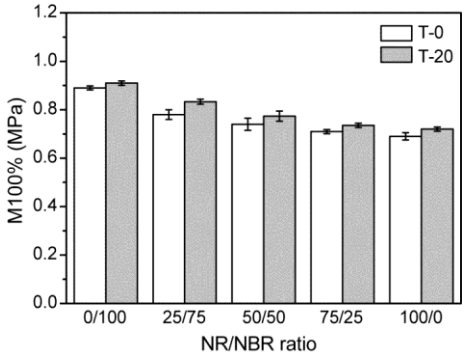

Figure 3. Tensile modulus (M_{100}) of the uncoated NR/ NBR blends (T-0) and 20 wt% treated distillate aromatic extract oil-coated sulfur (T-20).

Tensile strength and elongation at break of the vulcanizates cured with uncoated and oil-coated sulfurs are exhibited in Figures 4 and 5, respectively. The magnitude of tensile strength increased with an increasing NR ratio in the blends resulting from the strain-induced crystallization of NR (Campbell *et al.*, 1992; Dick, 2009; Hoffmann, 1989; Toki, 2006). At a given blend ratio, the vulcanizates cured with oil-coated sulfur provided higher tensile strength than those cured with uncoated sulfur. This is attributed to the improvement of sulfur dispersion in the rubber matrix along with the increment of crosslink density.

The result of elongation at break also agreed well with the tensile strength results. Similarly, the magnitude of elongation at break increased with the increasing NR ratio. In addition, the higher elongation at break was observed in the blends cured by oil-coated sulfur. This was attributed to the good sulfur distribution in the blends as evident in Figure 6. In this study, the tensile strength and elongation at break of neat NR in the uncoated sulfur system were unexpectedly low, possibly due to the poor sulfur dispersion and, thus, uneven crosslink distribution leading to the ineffective stress transfer capability (Sae-Oui *et al.*, 2007; Zaimova *et al.*, 2012). Therefore, poor tensile strength and elongation at break were observed.

Figure 6 shows photographs of the NR/NBR blends cured by uncoated and oil-coated sulfurs. A number of dark spots observed in the blends cured by uncoated sulfur resulted

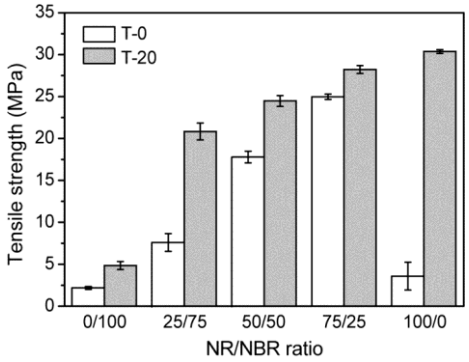

Figure 4. Tensile strength of the uncoated NR/NBR blends (T-0) and 20 wt% treated distillate aromatic extract oil-coated sulfur (T-20).

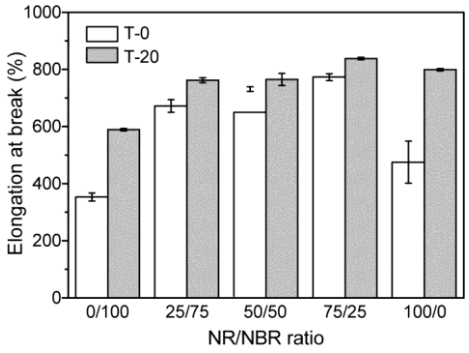

Figure 5. Elongation at break of the uncoated NR/NBR blends (T-0) and 20 wt% treated distillate aromatic extract oil-coated sulfur (T-20).

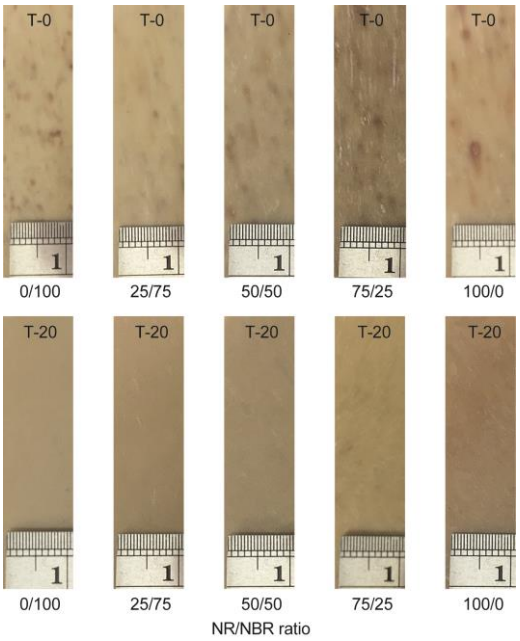

Figure 6. Photographs of the uncoated NR/NBR blends (T-0) and 20 wt% treated distillate aromatic extract oil-coated sulfur (T-20). Scale = centimeter.

from poor sulfur dispersion. As can be well seen, in the case of oil-coated sulfur, no dark spots were observed. This result clearly confirmed that the oil coating plays an important role in the improvement of sulfur dispersion in the blend, leading to the enhancement in mechanical properties.

The crosslink density was calculated from the Mooney-Rilvin equation and the results are exhibited in Figure 7. The results revealed that the crosslink density tended to increase as the NR content increased. The increasing crosslink density observed with the increasing ratio of NR was not in accordance with the results of our other experiments which showed than NBR had better solubility with petroleum-based sulfur. This unexpected result might have something to do with the limitations of this method which was not suitable for measurement of a blend of more than one type of polymer. The oil-coated sulfur system showed higher crosslink density than the uncoated sulfur system. This result agreed well with previous results in which the oil-coated sulfur caused better sulfur dispersion than the uncoated sulfur (Figure 6).

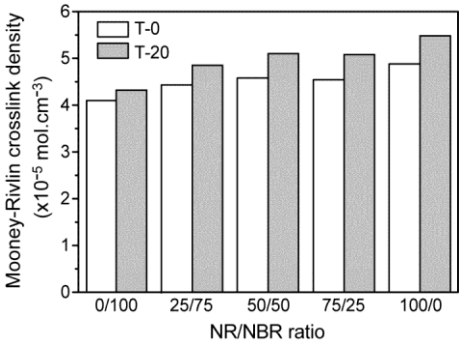

Figure 7. Mooney-Rivlin crosslink density of the uncoated NR/NBR blends (T-0) and 20 wt% treated distillate aromatic extract oil-coated sulfur (T-20).

4. Conclusions

Compared with the uncoated petroleum-based sulfur, the TDAE oil-coated sulfur offered greater dispersibility in the NR/NBR blends which led to an improvement of cure behaviors and enhancement of the mechanical properties. As a consequence, the coating of sulfur with TDAE oil can be considered as an efficient method to improve sulfur dispersion in rubber.

Acknowledgements

The authors thank the Rubber Technology Research Center (RTEC), Faculty of Science, Mahidol University and Academic Affairs Promotion Fund, Faculty of Science, Khon Kaen University, Fiscal year 2016 (RAAPF) for financial and instrumental support throughout this work.

References

Akiba, M., & Hashim, A. S. (1997). Vulcanization and cross-linking in elastomers. *Progress in Polymer Science, 22*(3), 475-521.

Ash, M., & Ash, I. (2008). *Handbook of fillers, extenders, and diluents* (2nd ed.). New York, NY: Synapse Information Resources.

Campbell, D. S., Chapman, A. V., Goodchild, I. P., & Fulton, W. S. (1992). Experimental determination of the mooney-rivlin constant for natural rubber vulcanisates. *Journal of Natural Rubber Research, 7*(3) , 168-180.

Chartreenuwat, T. (2013). *Physical characteristics of the treated distillate aromatic extract oil used in this work* (Master's thesis, Mahidol University, Bangkok, Thailand).

Dasgupta, S., Agrawal, S. L., Bandyopadhyay, S., Chakra borty, S., Mukhopadhyay, R., Malkani, R. K., & Ameta, S. C. (2007). Charaterization of eco-friendly processing aids for rubber compound. *Polymer Testing. 26*, 489-500.

Dasgupta, S., Agrawal, S. L., Bandyopadhyay, S., Chakra borty, S., Mukhopadhyay, R., Malkani, R. K. and Ameta, S. C. (2008). Charaterization of eco-friendly processing aids for rubber compound: Part II. *Polymer Testing, 27*, 277-283.

Dick, J. S**. (**2009). *Rubber technology: Compounding and testing for performance* (2nd ed.). Munich, Germany: Hanser.

Guo, R., Talma, A. G., Datta, R. N., Dierkes, W. K., & Noordermeer, J. W. M. (2008). Solubility study of curatives in various rubbers. *European Polymer Journal, 44*, 3890-3893.

Hoffmann, W. (1989). *Rubber technology handbook*. Munich, Germany: Hanser.

Meissner, B. (2000). Tensile stress-strain behavior of rubber-like networks up to break: Theory and experimental comparison. *Polymer, 21*(41), 7827-7841.

Nehb, W., & Vydra, K. (2000). *Sulfur. Ullmann's encyclopedia of industrial chemistry*. Weinheim, Germany: Wiley-VCH Verlag.

Pangamol, P., Sirisinha, C., Hu, Y., & Urquhart, S. G. (2013). Potential use of petroleum based sulfur in rubber industry. *Industrial and Engineering Chemistry Research, 52*, 17179-17183.

Pangamol, P., Sae-Oui, P., & Sirisinha, C. (2014). In potential use of petroleum-based sulfur in rubber industry. *Energy Procedia. 56*, 474-480.

Pangamol, P., Sirisinha, C., & Sae-oui, P. (2015). Dispersion enhancement of petroleum-based sulfur in natural rubber by the use of TDAE oil coating technique. *Kautschuk gummi kunststoffe, 3*, 48-53.

Sae-Oui, P., Sirisinha, C., & Hatthapanit, K. (2007). Effect of blend ratio on aging, oil and ozone resistance of silica-filled chloroprene rubber/ natural rubber (CR/NR) blends. *Express Polymer Letters, 1*(1), 8-14.

Struktol Company of America. (2004). *Struktol rubber handbook*: *Application of processing agents-Examples*. Stow, OH: Author.

Tinker, A. J., & Jones, K. P. (1998). *Blend of natural rubber: Novel techniques for blending with speciality polymers*. London, England: Chapman and Hall.

Toki, S., Hsiao, B. S., Kohjiya, S., Tosaka, M., Tsou, A. H., & Datta, S. (2006). Synchrotron X-Ray studies of vulcanized rubbers and thermoplastic elastomers. *Rubber Chemistry and Technology, 79*(3), 460-488.

Zaimova, D., Bayraktar, E., Katundi, D., & Dishovsky, N. (2012). Elastomeric matrix composites: effect of processing conditions on the physical mechanical and viscoelastic properties. *Journal of Achievements in Materials and Manufacturing Engineering, 50*(2), 81-91.