



# DEVELOPING ETHYLENE-PROPYLENE-DIENE BLENDS FOR INDUSTRIAL APPLICATIONS

Ebtesam E. Ateia,<sup>[a]</sup> D. E. El-Nashar,<sup>[b]</sup> E.Takla<sup>[a]</sup> M. Abd Alla Mahmoud<sup>[a]</sup>

**Keywords:** Black filler; white filler; swelling measurements; mechanical properties; physico-chemical properties.

Different contents of high abrasion furnace black filler [HAF] and white filler [silica] are mixed with ethylene-propylene-diene monomer rubber [EPDM] cured by the conventional sulfur system. The thermogravimetric analysis (TGA) characteristics, physico-mechanical properties and swelling measurements of the prepared samples have been investigated. EDAX analyses were done to define the chemical composition of the investigated samples and to locate the dispersion of the fillers and their intensity. Comparison of the black and white fillers was performed and it was found that filler incorporation into the rubber matrix was one of the major parameters that enhanced the tensile strength and swelling resistance. The hardness of the investigated samples increased with increasing the filler concentration up to 40/60 phr (part per hundred parts of rubber). This increase can be attributed to greater and more uniform dispersion of filler into the rubber system. Carbon/silica are extensively used in the industry as cheapening filler with high reinforcing effect. Finally, the addition of precipitated silica at the expense of toxic carbon black (CB) is the main step in decreasing the health risk associated with the presence of CB-filled EPDM composites.

\* Corresponding Authors

Fax: No Fax

E-Mail: drebtesam2000@yahoo.com

[a] Physics Department, Faculty of Science, Cairo University, Giza, Egypt

[b] Department of Polymers and Pigments, National Research Centre, Dokki, Cairo, Egypt.

% and 200 % were determined using a Zwick tensile machine (model 1425).<sup>7</sup> Hardness was measured using the Shore A, durometer according to D2240-07; Equilibrium swelling of the investigated samples was carried out in toluene. The swelling percentage ( $Q$  %) of the samples was calculated by using the following equation.<sup>8</sup>

$$Q(\%) = 100 \frac{W - W'}{W'} \quad (1)$$

where  $W$  and  $W'$  represent the weights of the samples after swelling and free from dissolved matter respectively.

The swelling data were utilized to determine the molecular weight between cross-links  $M_C$  by applying Flory–Rehner relation.<sup>9,10</sup> The degree of cross-linking density ( $\nu$ ) is given as:<sup>9</sup>

$$\nu = \frac{1}{2M_C} \quad (2)$$

## Introduction

Ethylene-propylene-diene rubber (EPDM) is one of the most widely used synthetic elastomer, having both special and general-purpose applications. Fillers are incorporated into ethylene-propylene-diene polymer mainly to enhance service properties and in many cases to decrease the material cost. In most applications, carbon black (CB) and silica have been used as the main reinforcing fillers that increase the effectiveness of rubber. When carbon black (CB) is added into rubber, the tensile strength, tear strength, modulus and abrasion resistance are increased.<sup>1</sup> However, silica provides a unique combination of tear strength, abrasion resistance, aging resistance and adhesion properties.<sup>2,3</sup> Since silica and carbon black have unique advantages, the utilization of hybrid filler of silica and carbon black in rubber should give the benefits of both fillers. The addition of precipitated silica in CB-filled rubber can be applied to tire treads, wire and fabric coating, hoses, rubber-covered belts, engine mounts and cable jackets.<sup>4,5</sup> The effect of filler ratio on the physico-chemical and mechanical properties of EPDM has been studied to develop and characterize an applicable rubber with good mechanical properties and low cost.

## Experimental

All rubber ingredients were mixed with each other as that was mentioned in our previous work.<sup>6</sup> The tensile strength, elongation at break, Young's modulus and modulus at 100

## Results and Discussion

The TGA curves obtained for the investigated samples made with using carbon black and silica can be seen in Figure 1 and the calculated parameters are given in Table 1. The obtained TGA curves indicate three stages of degradation process. In the temperature range from room temperature to 250 °C there was no observed change in the weight of samples while above 250 °C a slow degradation could be observed up to  $\approx$ 350 °C. Above 350 °C, the decomposition rate is high, which shows the decomposition of organic polymeric materials.

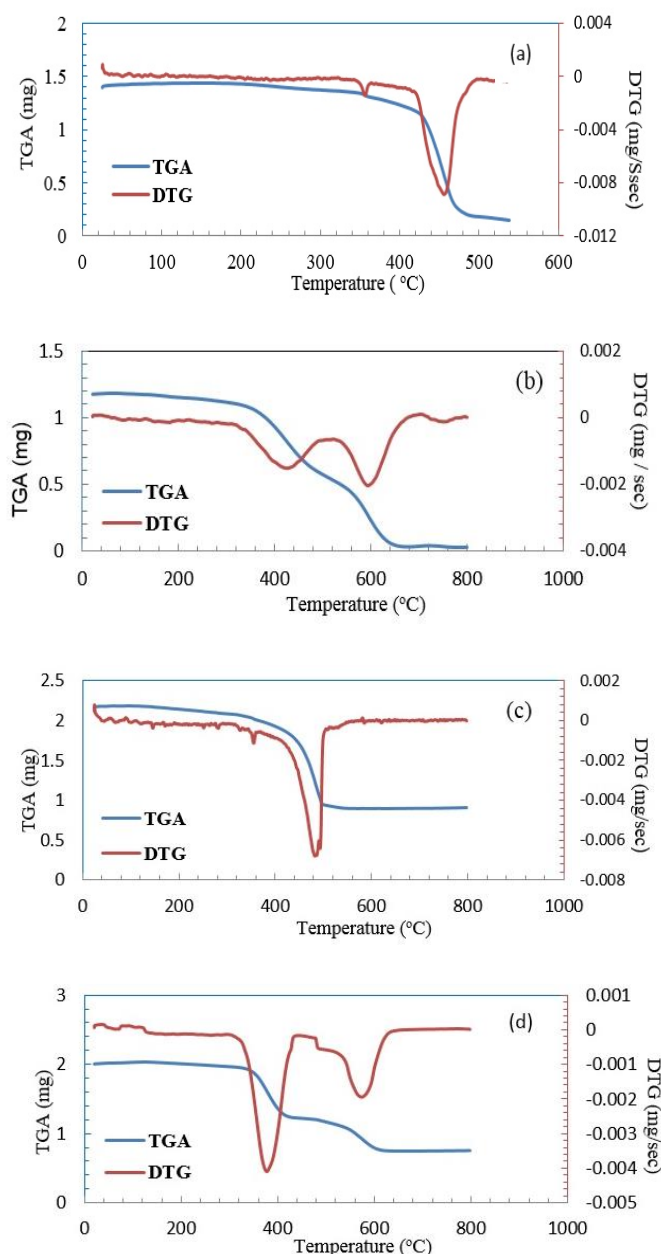


Figure 1. Thermogravimetric analysis curves for (a) EPDM without filler (b) 100 carbon / zero silica (c) zero Carbon/100 silica (d) 40 carbon / 60 silica

It is clear that the thermal stability of EPDM samples increased with increasing filler loading especially in the case of carbon black (CB). This can be due to the existence of C-C bonds with high binding energy. This approves the ability of CB in retarding the heat diffusion into EPDM matrix. However, the lowest thermal stability is obtained for EPDM loaded with 100 phr (phr: part per hundred parts of rubber), silica. This can be attributed to the lower binding energy of Si-C bonds compare to binding energy of C-C bond ( $346 \text{ kJ mol}^{-1}$ ).<sup>11</sup>

The DTG curves have only one degradation peak, corresponding to maximum weight losses of the investigated samples. The obtained data agrees well with the previous discussion.

DSC data (Table 1) provided information concerning the change of enthalpy associated with a physical or chemical change within a material.

The conventional Field Emission Scanning Electron Microscopy (FESEM) was used to provide information about the morphology of the investigated samples. This method provided detailed information about the size and distribution of fillers and then the filler-rubber interactions as well.<sup>12</sup> Figure 2. represents the FESEM for the EPDM without filler, 100CB/0 silica and the samples loaded with the optimum concentrations of carbon black and white silica of 40/60 phr respectively. It is clear that the cracks and vicinity were the main features of the EPDM without filler as shown in Fig.2a. Heavy agglomerations of carbon black were observed for EPDM loaded with 100CB/0 silica (Fig. 2b), which could be attributed to filler-filler interaction networking. The surface of 40 CB/60 silica containing samples was improved and became smoother due to the uniform dispersion of optimum filler concentration as shown in Fig.2c. A good dispersion of the silica filler in the rubber matrix<sup>13</sup> reduced the filler-filler interaction and increased the rubber-filler interaction.<sup>14</sup>

EDAX analyses were done to define the chemical composition of the investigated samples and to locate the dispersion of the filler and its intensity. EDAX analyses of the typical samples are given as inset in Fig. 2.

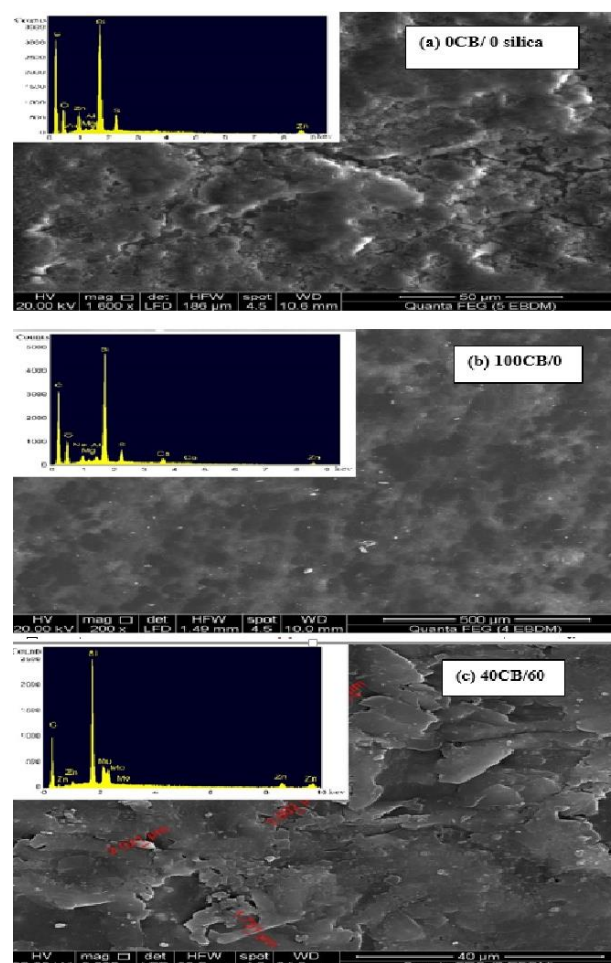


Figure 2. The FESEM images of (a) EPDM without filler (b) 100 carbon / zero silica (c) EPDM loaded with the optimum concentrations of carbon black and white silica respectively. Inset figures show EDAX analyses of the investigated samples.

**Table 1.** DSC and TGA parameters for the investigated samples.

Samples	Weight loss	DTG peak temp., °C	$\Delta H \text{ J g}^{-1}$	Thermal stability temp, °C	$T_g$ , °C
0 CB /0 silica	%	448	4.066	461	-19.8
100CB /zero silica	49.44 %	586	0.2557	766	-69.2
0 CB / 100silica	47.866 %	475	3.260	496	-57.29
40 CB /60 silica	37.815%	507	0.9721	604	-70.5

**Table 2.** Rheological parameters of EPDM filled with different concentrations of carbon black and silica.

CB/silica content	Properties						
	$M_L$ (1b.in)	$M_H$ (1b.in)	$t_{C90}$ (min)	$t_{S2}$ (min)	$CRI$ (min <sup>-1</sup> )	$\Delta t=(M_H-M_L)(1b.in)$	$\alpha_f$
0/0	5	41	7	3	25	36	0.0
100/0	8	59	9	6	33.33	51	0.44
80/20	11	71	11	8.5	40	60	0.73
60/40	13	85	14	12	50	72	1.07
40/60	16	90	16	14.5	66.67	74	1.20
20/80	11	86	13	10	33.33	73	1.09
0/100	10	83	10	6.5	28.58	73	1.02

**Table 3.** Swelling characteristics of EPDM filled with HAF black and Silica.

CB/silica content	Soluble fraction, $\Delta M\%$	The crosslink density, $\nu_{EANC} \times 10^{20}$	$1/Q$	$Q_f/Q_g$
0/0	203.7	1.454	0.441	0
100/0	101.2	6.087	0.901	0.489
80/20	86.8	11.836	1.318	0.334
60/40	96.6	17.471	1.686	0.261
40/60	95.8	38.323	3.003	0.147
20/80	103.8	23.573	2.070	0.213
0/100	135.8	18.640	1.761	0.250

The rheological features of the EPDM filled with HAF and silica are given in Table 2. The minimum torque  $M_L$ , which reflects minimum viscosity of the blends can be taken as a measuring tool of filler-filler interaggregate formation.<sup>15</sup>  $M_H$  is the maximum torque which reveals the cross-linking density of the loaded samples. The table shows that  $M_L$  values were gradually increased with increasing silica content (decreasing carbon black) up to a ratio of 40/60 phr of carbon black and silica respectively. On the other hand,  $M_H$  values were increased with larger rates than  $M_L$  values up to the same ratio of 40/60 phr then the values were decreased. This behavior was observed due to the presence of the fillers in the investigated samples which reduced the mobility of macromolecules and accordingly increased the torque of the vulcanizates up to optimum content.<sup>16</sup> This increase was the consequence of the creation of hydrogen bonds induced strong interactions between rubber and filler materials.<sup>17</sup> The difference between  $M_H$  and  $M_L$  was a rough estimation possibility of the crosslinking density of the prepared samples and it was identified as  $\Delta t$ . It nearly increased with increasing filler content. However, among the EPDM filled samples, the carbon/silica filler ratio 40/60 showed the highest  $\Delta t$ . This was an indication of the enhancement in the filler- filler interaction. The obtained data showed that the scorch time  $T_{S2}$  of the samples increased with increasing silica content up to the optimum ratio of 40/60 phr of filler content. This was because of the absorption of the accelerator by silanol groups on the silica

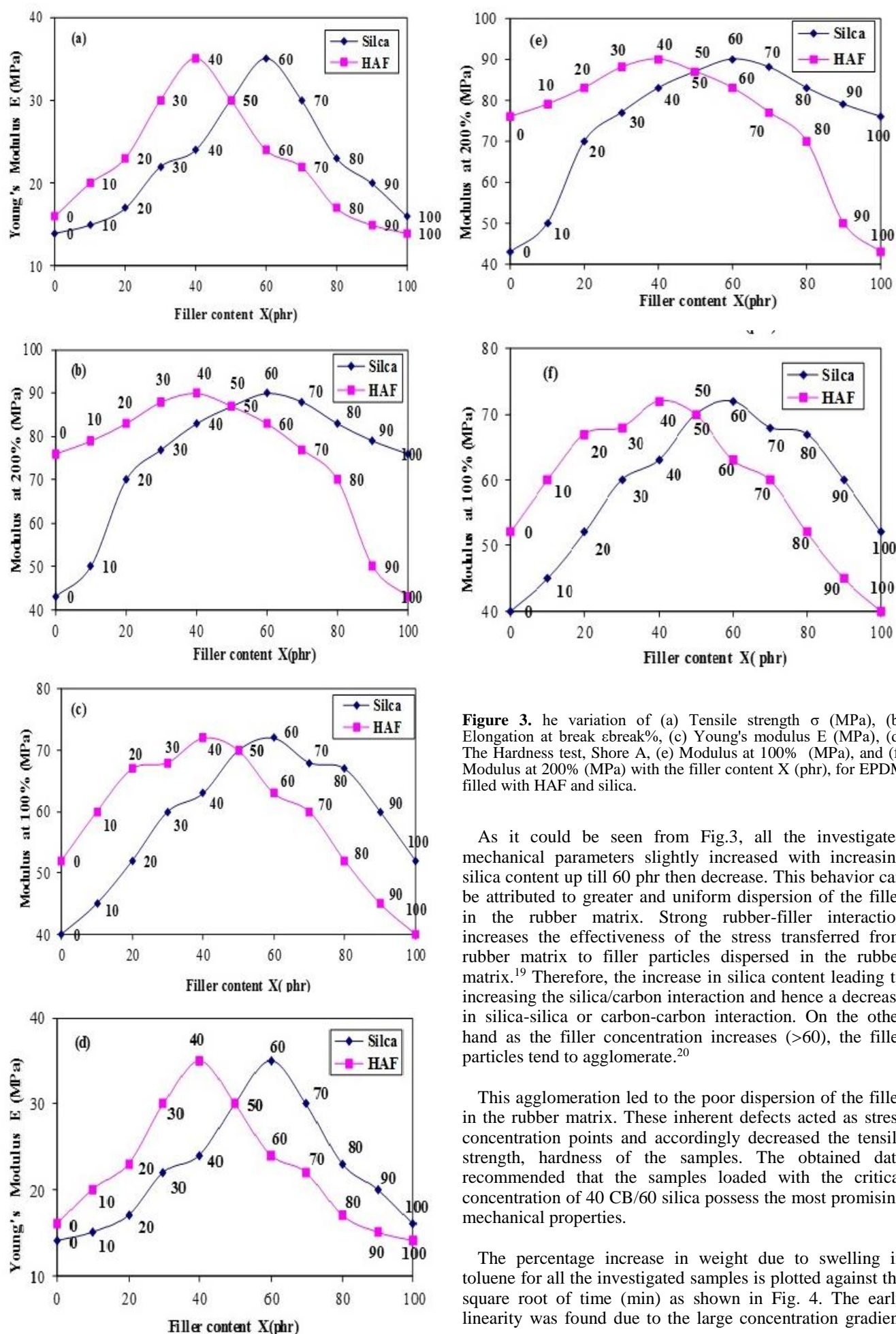
surface. The change in rheometric torque with filler content was used to distinguish the filler-matrix interaction or reinforcement. The reinforcement factor  $\alpha_f$  is determined from the following relation:<sup>18</sup>

$$\alpha_f = \frac{[\Delta L_{\max}(\text{filled}) - \Delta L_{\max}(\text{gum})]}{\Delta L_{\max}(\text{gum})} \quad (3)$$

where  $\Delta L_{\max}(\text{filled})$  and  $\Delta L_{\max}(\text{gum})$  are the variations in maximum torque through vulcanization for the filled and gum samples, respectively.

From the  $\alpha_f$  values listed in Table 2, it is clear that the values of  $\alpha_f$  for both HAF and silica are continuously increasing with the addition of both white and black fillers.

The effect of carbon black and white silica filler on mechanical parameters such as tensile strength  $\sigma$  (MPa), elongation at break  $\epsilon_{\text{break}}\%$ , Young's modulus  $E$  (MPa) and the hardness shore (A), modulus at 100% and 200 % of ethylene-propylene-diene (EPDM) polymers are shown in Figure 3.



**Figure 3.** The variation of (a) Tensile strength  $\sigma$  (MPa), (b) Elongation at break  $\epsilon_{\text{break}}$ %, (c) Young's modulus E (MPa), (d) The Hardness test, Shore A, (e) Modulus at 100% (MPa), and (f) Modulus at 200% (MPa) with the filler content X (phr), for EPDM filled with HAF and silica.

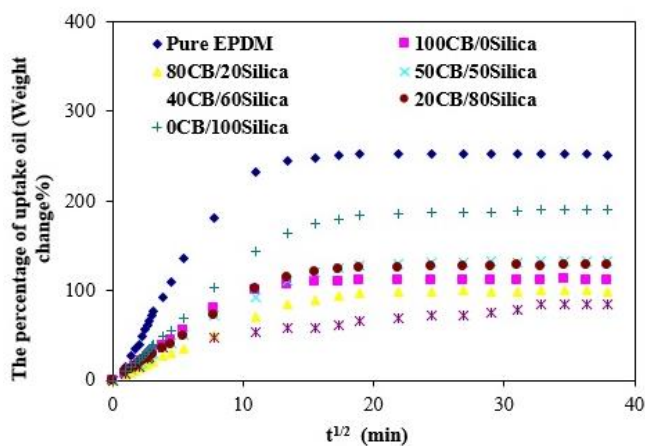
As it could be seen from Fig.3, all the investigated mechanical parameters slightly increased with increasing silica content up till 60 phr then decrease. This behavior can be attributed to greater and uniform dispersion of the filler in the rubber matrix. Strong rubber-filler interaction increases the effectiveness of the stress transferred from rubber matrix to filler particles dispersed in the rubber matrix.<sup>19</sup> Therefore, the increase in silica content leading to increasing the silica/carbon interaction and hence a decrease in silica-silica or carbon-carbon interaction. On the other hand as the filler concentration increases (>60), the filler particles tend to agglomerate.<sup>20</sup>

This agglomeration led to the poor dispersion of the filler in the rubber matrix. These inherent defects acted as stress concentration points and accordingly decreased the tensile strength, hardness of the samples. The obtained data recommended that the samples loaded with the critical concentration of 40 CB/60 silica possess the most promising mechanical properties.

The percentage increase in weight due to swelling in toluene for all the investigated samples is plotted against the square root of time (min) as shown in Fig. 4. The early linearity was found due to the large concentration gradient

of solvent in the samples. The stability of the curve meant that the rubber samples extraction or degradation of its soluble ingredients was extremely small. It was obvious that the swelling rate of CB filled EPDM samples were decreased higher than in case of the silica filled system.

The increase of the swelling rate in silica filled samples was the consequence of the filler aggregate formation in the rubber matrix. The precipitated silica possessing many hydroxyl groups on its surface and as a result, the intermolecular hydrogen bonds between hydroxyl groups were very strong. Hence it aggregated tightly as that was confirmed by FESEM results.



**Figure 4.** Solvent uptake percent versus square root of time for EPDM filled with HAF black and silica.

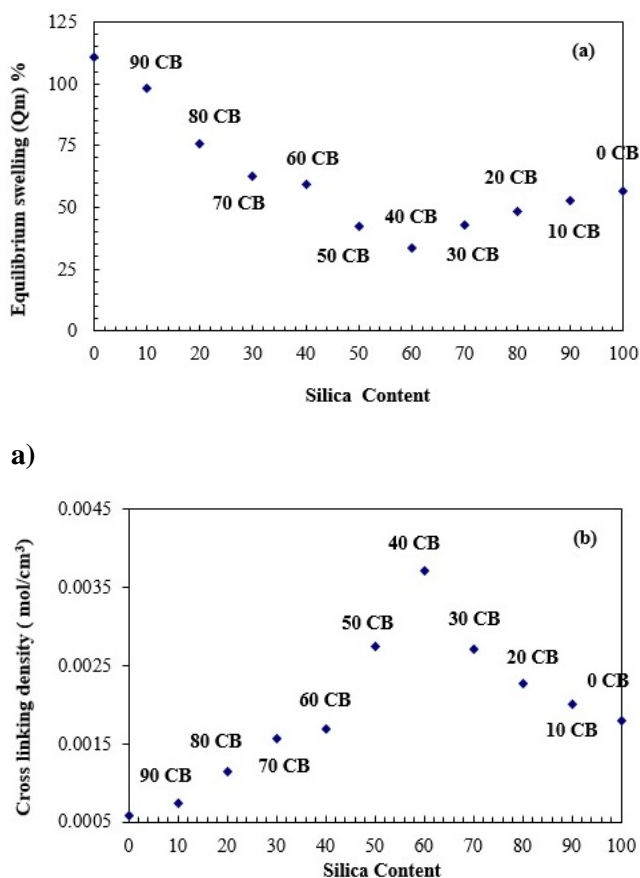
In general, the rubber swelling is influenced by numerous factors, such as density and crosslinking type, amount and type of elastomer and type of filler. The effect of interaction between rubber and the filler blend can be investigated and calculated using Lorenz and Parks equation<sup>21,22</sup>.

$$\frac{Q_f}{Q_g} = ae^{-z} + b \quad (4)$$

The subscripts  $f$  and  $g$  in Eq. 4 denote to the filled and unfilled rubber vulcanizates respectively,  $z$  is the ratio by weight of filler in the vulcanizate, while  $a$  and  $b$  are constants.

The obtained values of  $Q_f/Q_g$  and  $1/Q$  are presented in Table 3. The obtained data shows that the values of  $Q_f/Q_g$  decrease while the values of  $1/Q$  increase with the increasing carbon black content up to the optimum concentration 40/60 phr. Moreover, the lowest values of  $Q_f/Q_g$  and the highest ones for  $1/Q$  designate that, the higher the filler content, the stronger the rubber-filler interaction<sup>23</sup>. Finally, the obtained data indicates that 40 CB/ 60 silica was capable of producing greater rubber-filler interaction compared to each of CB and silica separately. This was due to the more homogeneous dispersion of 40 CB/60 silica within the rubber matrix as confirmed by the morphological study. The calculated cross-links density  $\nu$  (as shown in Table 3) confirmed the previous discussion.<sup>24</sup>

The dependence of maximum weight change and cross-linking density with filler concentration for the investigated samples can be seen in Fig.5. As it can be seen from the figure, the lowest swelling rate is obtained for samples loaded with the optimum filler concentration 40 CB/60 silica, which agreed well with the calculated data gave in Table 3.



**Figure 5.** The dependence of maximum weight change(a) and cross linking density (b) with filler concentration for the investigated samples.

## Conclusion

A significant enhancement of the property of the investigated EPDM samples by the addition of fillers could be achieved. Comparison of silica and carbon black additives demonstrated that carbon enhanced the thermal stability of EPDM. TGA studies revealed that the thermal stability of the investigated samples increased due to the incorporation of carbon black into the EDPM. The filler ratio 40 CB/60 silica appeared to be an excellent candidate for thread application to accomplish an overall good mechanical and physicochemical properties.

## References

- Mahapatra, S. P. Tripathy, D. K., *Cell. Polym.*, **2005**, *24*, 209-222.
- Laube, S. and Shell, J., *Meeting of the Rubber Division*, American Chemical Society, Savanna, **2002**.

- <sup>3</sup>Ismail, M. N. El-Sabbagh S. H. and Yehia, A. A., *J. Elastom. Plast.*, **1999**, *31*, 255-270.
- <sup>4</sup>Saad, A. G. El-Sabbagh, S. H., *J. Appl. Polym. Sci.*, **2001**, *79(1)*, 60-71.
- <sup>5</sup>Guy, L. Daudey, S. Cochet P. and Bomal, Y., *Raw Mater. Appl.*, **2009**, *62*, 383-391.
- <sup>6</sup>Hassan, H. H., Ateia, E., Darwish, N. A., Halim, S. F., Abd El-Aziz, A. K., *Mater. Des.*, **2012**, *34*, 533-540. <https://doi.org/10.1016/j.matdes.2011.05.005>
- <sup>7</sup>Leblanc, J. L., *Prog. Polym. Sci.*, **2002**, *27*, 627-687. [https://doi.org/10.1016/S0079-6700\(01\)00040-5](https://doi.org/10.1016/S0079-6700(01)00040-5)
- <sup>8</sup>Julve, D., Pérez, J., Ramos J. and Menéndez, M., *Rubber Chem. Technol.*, **2011**, *84(1)*, 74-87. <https://doi.org/10.5254/1.3544676>
- <sup>9</sup>De, S., Panda, P. K., Bhunia S, and Roy, M., *Polym. Plast. Technol. Eng.*, **2014**, *53(11)*, 1131-1141. <https://doi.org/10.1080/03602559.2014.886117>
- <sup>10</sup>Zhag, G. Q. Zhou, M. H., Ma, J. H. Liang, B. R., *J. Appl. Polym. Sci.*, **2003**, *90*, 2241-2245. <https://doi.org/10.1002/app.12888>
- <sup>11</sup>Clarson S. J. and Semlyen, J. A., "Siloxane Polymers," PTR Prentice Hall, New Jersey, **1993**, 567-615.
- <sup>12</sup>Yin, D., Zhang, Y., Peng, Z., Zhang, Y., *J. Appl. Polym. Sci.*, **2003**, *88*, 775-82. <https://doi.org/10.1002/app.11604>
- <sup>13</sup>Ichazo, M. N. Albano, C., Hernandez, M., Gonzalez J. and Carta, A., *Adv. Mat. Res.*, **2008**, *47-50*, 113-116. <https://doi.org/10.4028/www.scientific.net/AMR.47-50.113>
- <sup>14</sup>Wolff, S., Gori, U. Wang, M. J. and Wolff, W., *ERJ*, **1994**, *16*, 16-19.
- <sup>15</sup>Yan, H., Sun, K., Zhang Y. and Zhang, Y., *Polym. Test.*, **2005**, *24*, 32-38. <https://doi.org/10.1016/j.polymertesting.2004.07.011>
- <sup>16</sup>Li, Y., Wang, M. J., Zhang, T., Zhang F. and Fu, X., *Rubber Chem. Technol.*, **1994**, *67*, 693. <https://doi.org/10.5254/1.3538704>
- <sup>17</sup>Kaushik, P., Rajasekar, R., Dong Jin, K., Zhen Xiu, Z., Samir, K. P., Chapal, K. D., Jin, K. K., *Mater. Des.*, **2010**, *31*, 677. <https://doi.org/10.1016/j.matdes.2009.08.014>
- <sup>18</sup>Trakarnpruk, W., Porntangjitlikit, S., *Renew. Energy*, **2008**, *33*, 1558-1563. <https://doi.org/10.1016/j.renene.2007.08.003>
- <sup>19</sup>Leblanc, J. L., *Prog. Polym. Sci.*, **2002**, *27*, 627-687. [https://doi.org/10.1016/S0079-6700\(01\)00040-5](https://doi.org/10.1016/S0079-6700(01)00040-5)
- <sup>20</sup>Wolff, S., *Rubber Chem. Technol.*, **1996**, *69*, 325-346. <https://doi.org/10.5254/1.3538376>
- <sup>21</sup>Ismail, H., Ramly, A. F., Othman, N., *J. Appl. Polym. Sci.*, **2013**, *128*, 2433-2438. <https://doi.org/10.1002/app.38298>
- <sup>22</sup>Ward, A. A., Khalif, A. L., *J. Elastom. Plast.*, **2007**, *60*, 623-630.
- <sup>23</sup>Roy, K., Alam, Md. N., Mandal, S. K., Debnath, S. C., *J. Nanostruct. Chem.*, **2016**, *6*, 15-24. <https://doi.org/10.1007/s40097-015-0174-x>
- <sup>24</sup>Yatsuyanagi, F., Suzuki, N., Ito, M., Kaidou, H., *Polymer*, **2001**, *42*, 9523-9529. [https://doi.org/10.1016/S0032-3861\(01\)00472-4](https://doi.org/10.1016/S0032-3861(01)00472-4)

Received: 20.05.2017.

Accepted: 02.07.2017.