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EFFECT OF ZINC OXIDE ON DISPERSION AND HOMOGENEITY OF PTFE IN NR/NBR RUBBER MATRICES

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ABSTRACT

The effect of zinc oxide (ZnO) on the dispersion and homogeneity of polytetrafluoroethylene (PTFE) in the blend of natural and nitrile rubber matrices (NR/NBR) has been investigated. The rubbers and additives were mixed on a two-roll mill and vulcanized by a steam-heated press. The findings from the chemical resistance test showed that the rubber blend with 8 parts per hundred of rubber (phr) of ZnO has better resistance towards organic solvents (acetone, heptane and toluene) and the degree of swelling reduced compared to rubber blend with lower amount of ZnO. Futher investigations on the scanning electron microscopy (SEM) of the rubber compound blend with ZnO showed that the PTFE agglomerations were reduced with particle sizes ranging in the order of 2-8 µm. The decrease in the particles sizes allows an increase in the PTFE surface area with better dispersion and homogeneity in the rubber matrices to be achieved, with reduced solvent uptake by the rubber.

Keywords: Zinc Oxide; Polytetrafluoroethylene (PTFE); Natural Rubber (NR); Nitrile Rubber (NBR); dispersion; homogeneity; rubber matrices.

1. INTRODUCTION

Polytetrafluoroethylene or PTFE is well known for its high resistance to chemicals and solvents with an upper service temperature of around 260 °C (Stachowiak & Batchelor, 1993). Due to these unique properties, PTFE has been used in a wide variety of applications (Gangal, 1989). This includes the automotive applications such as seals, O-rings gaskets, etc (Drobny, 2007) and also blended with polymers or reinforced as composite materials for special applications (Morgan, Stewart, Thomas, & Stahl, 1991; Crandell, 1955; Kaufman & Gonzales, 1968). Nevertheless, its low adhesion and inert behavior restricts its dispersion and compatibility with other materials especially rubbers. Recently, newly developed PTFE micropowders have been incorporated successfully in elastomers. The modified PTFE micropowders are fine coagulated powder which are produced by emulsion polymerization and has low molecular weight commonly used as an additive in a variety of applications (Lee, Patel, Cox, & Andries, 2005; Lahijani, 2003). One of the succesful studies is the blending of modified PTFE micropowders with chloroprene (CR) and ethylene-propylene-diene (EPDM)

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ESTEEM Academic Journal
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rubbers (Khan, Lehmann, & Heinrich, 2009b; Khan, Franke, Lehmann, & Heinrich, 2009a). Khan et al. (2009a) had succeeded in producing modified PTFE micropowder which enabled this polymer to chemically couple with elastomer. Their experimental results showed that the incorporation of this modified PTFE micropowders in the rubber could improve the physical and tribological properties of the compounds, apart from enhancing the dispersion and compatibility of the PTFE micropowders in rubber matrices. A prior study in Harvik Rubber Industry on the blending of PTFE micropowder with natural rubber/nitrile (NR/NBR) rubber has showed that the PTFE micropowder was not dispersed uniformly in the rubber and the addition of homogenizing agent did not help in enhancing the homogeneity of PTFE in the rubber compound. Furthermore, PTFE micropowder tends to form clumps of particles during mixing and blending operations. The aim of the present work is to investigate the effect of the incorporation of ZnO as the activator in enhancing the dispersion and homogeneity of PTFE in rubber matrices. These PTFE-filled NR/NBR rubber blend is formulated and improvised to be used as rubber component for protection against exposure to chemicals and solvents.

2. METHODOLOGY

2.1 Materials

The grade of natural rubber used in this study was SVR 3L obtained from Hokson Rubber Trading Sdn. Bhd. This type of natural rubber is manufactured in Vietnam. Meanwhile, the type of acrylonitrile butadiene rubber or nitrile rubber used was Krynac 3330 with medium acrylonitrile (ACN) content of 33 %, viscosity ML1+4(100 ℃) of 40, and specific gravity (0.98). The PTFE micropowders is Zonyl MP1100 (average particle size distribution of < 8 µm) emulsion grade which is an electron beam modified (500 kGy) PTFE micropowder produced by Dupont, Wilmington, Delaware, USA. DPG (N,N-diphenylguanidine) with specific gravity (1.19@25 ℃), density (0.4 g/cm^3) was used as vulcanization accelerator in rubber milling and was obtained from Hifull Chemical Industry Co Ltd, China. Sulphur (specific gravity of 2.06) and Sipernat® 820A were used as vulcanizing agent and fillers, respectively. Zinc oxide (ZnO) obtained from Metoxide Malaysia Sdn. Bhd was used as an activator to accelerate the vulcanization in compounded rubber.

2.2 Blending and Mixing

Table 1 shows the rubber compositions of each mixing. The samples were subjected to chemical degradation test to determine their resistance to selected solvents based on different polarities which were heptane, acetone and toluene. NR/NBR/PTFE blends with and without ZnO were first mixed on a two-roll mill according to the rubber blend compositions. This was followed by the addition of constant amount of additives such as fillers, accelerators, activators and vulcanizing agent into the rubber. Approximately 2 mm sheets were drawn out from the mills and the optimum cure time (t_{90}) was determined using a rotorless rheometer. The rubbers were vulcanized using a steam-heated press that was carried out at a temperature of 152 ℃ for 10 minutes.

2.3 Resistance to Swelling

To evaluate the chemical resistance of the samples, about 5 g of dried rubber samples were weighed and then immersed in a beaker that contained about 20 ml tested solvent for 23 hours at room temperature. The 23 hours of swelling test is in compliance with the requirement by

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European Standard EN 13 832-3 ‘Requirement for boots highly resistant to chemicals under laboratory conditions’. The percentage changes in mass of the samples Q% can be calculated according to the following equation (Khalaf, Yehia, Ismail & El-Sabbagh, 2012):

$$Q\% = \frac{Ws - Wd}{Wd} \times 100 \tag{1}$$

where Ws and Wd is the weight of the swelled and the dried sample, respectively.

Table 1: Rubber blends compositions.

	Rubber and additives compositions (phr)			
	1	2	3	4
NR	40	40	40	40
NBR	60	60	60	60
PTFE Micropowder	30	30	30	30
ZnO	-	3	5	8

2.4 Microstructural Analysis by SEM/EDX

The microstructural analysis was carried out using Scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX) to compare the effect of ZnO on the rubber matrices in NR/NBR/PTFE compound. The dispersion of PTFE and the agglomerate particle sizes were also estimated using SEM.

3. RESULTS AND DISCUSSION

3.1 Swelling Analysis of NR/NBR/PTFE Blend With and Without ZnO

Figures 1 to 3 show the graphs of the effect of solvents (acetone, heptane and toluene respectively) on the mass of rubber compound, blended with and without ZnO. The amounts of ZnO used varied from 0, 3, 5 to 8 phr based on the requirement for rubber formulations. It can be seen that after 23 hours of immersion, the mass of rubber samples increased as the immersion hours increased. The 3 phr ZnO added in the rubber blends did not show any significant change in the rubber swelling, as the change in the mass of the rubber samples showed a similar trend to the rubber blend without ZnO. However, an increase from 5 to 8 phr of ZnO added to the rubber blend significantly reduced the rubber swelling. It is presumed that the addition of ZnO contributes to the enhancement of PTFE dispersion and homogeneity in the rubber matrices. The PTFE agglomerates reduced in sizes during the shear mixing with ZnO thus allowing a high surface area of agglomerates to be dispersed throughout the rubber matrices. The better dispersion of PTFE in the rubber matrices with fine particle sizes allow a homogenized blend in the rubber, hence better resistance of the rubber to solvents could be achieved.

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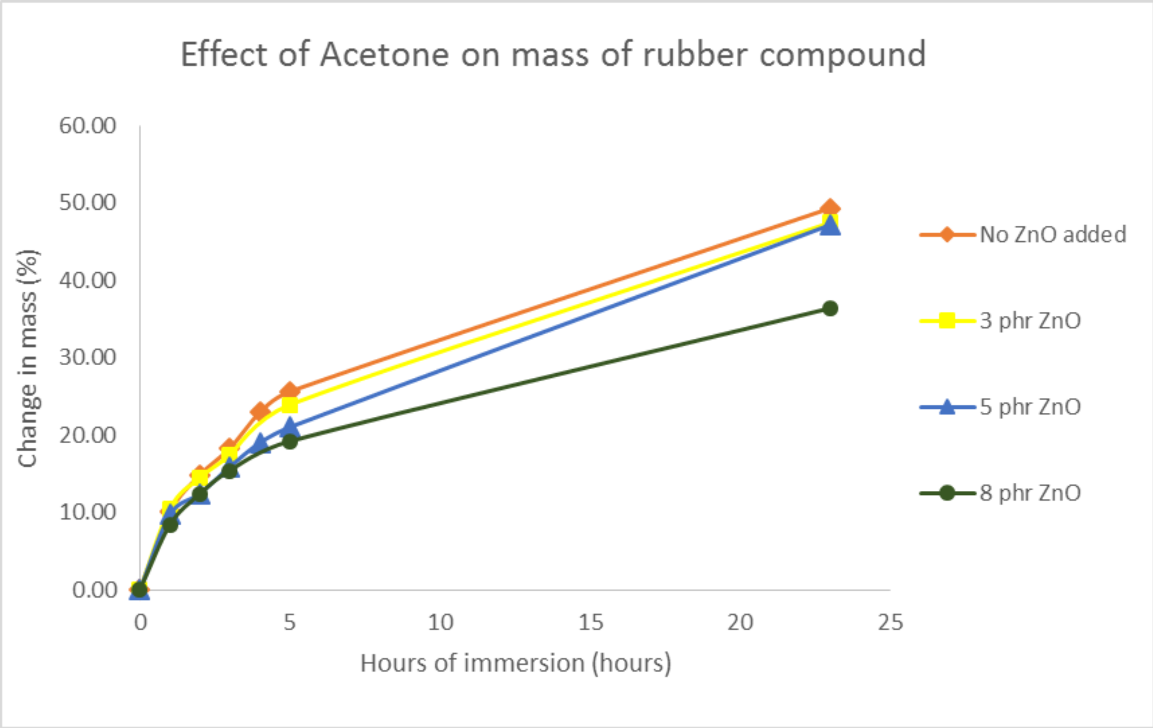

Figure 1: Effect of Acetone on the mass of rubber compound.

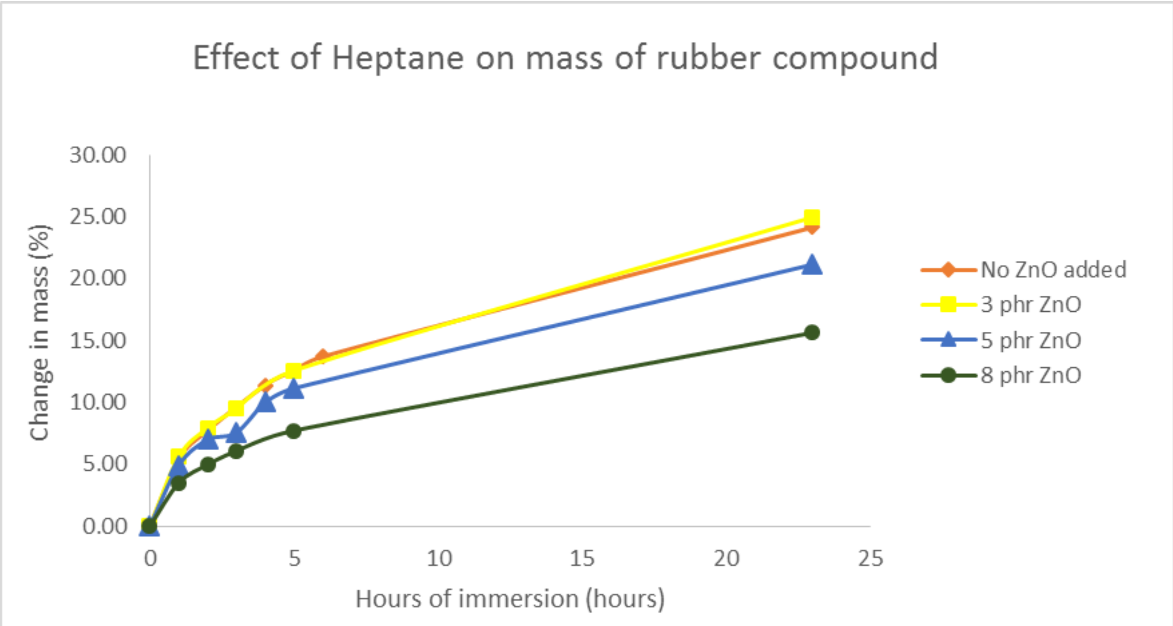

Figure 2: Effect of Heptane on the mass of rubber compound.

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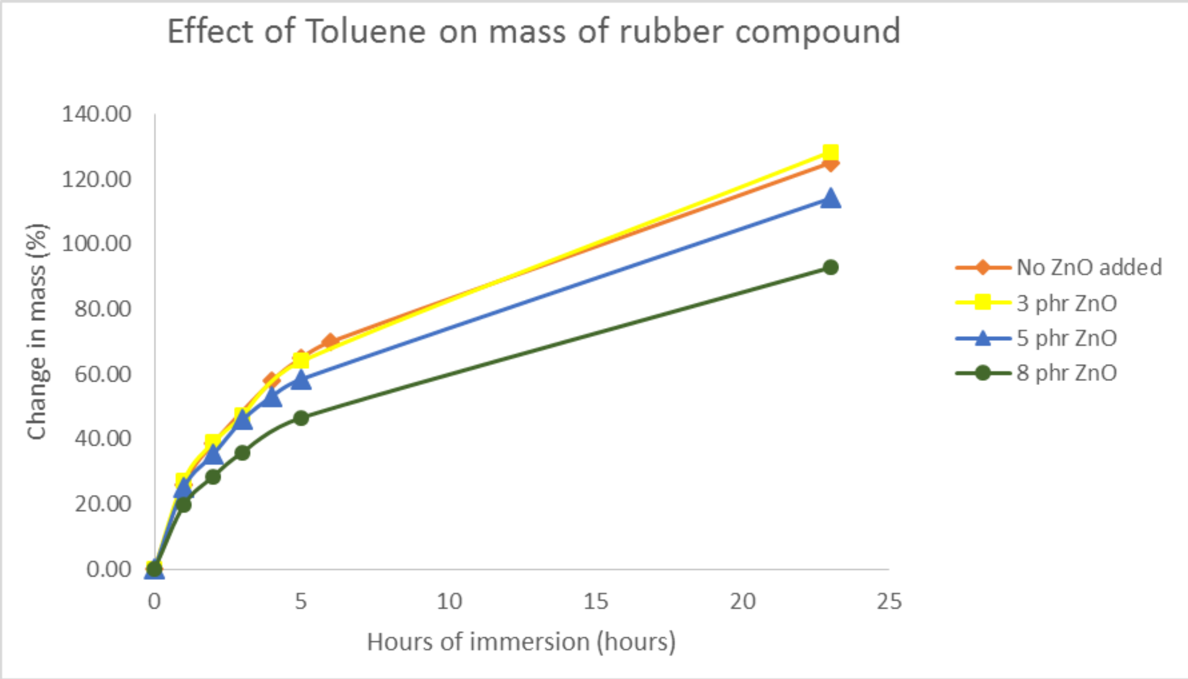

Figure 3: Effect of Toluene on the mass of rubber compound.

3.2 Microstructural Analysis by SEM/EDX

To further support the findings, the SEM analysis of the PTFE-filled rubber was performed to determine the homogeneity of PTFE in rubber matrix blended with and without ZnO. Figure 4 shows the SEM micrographs of overall rubber surfaces of the NR/NBR/ PTFE rubber blend without ZnO (sample 1). The diagram shows few agglomerations of PTFE along with rubber lumps found on the rubber surface with particles sizes varying considerably. A further enhanced image was made at a magnification of 2kX to estimate the average of large PTFE particle sizes. It was found that the average of large PTFE agglomerates was in the order of 6-22 µm as shown in Figure 5.

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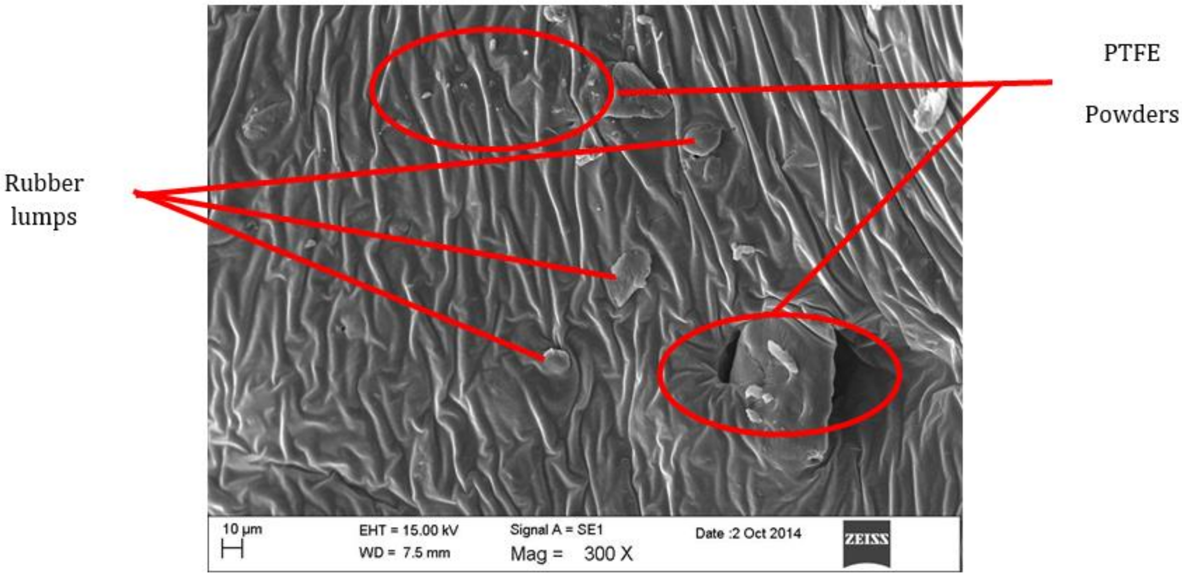

Figure 4: The PTFE powders in the rubber blend without ZnO.

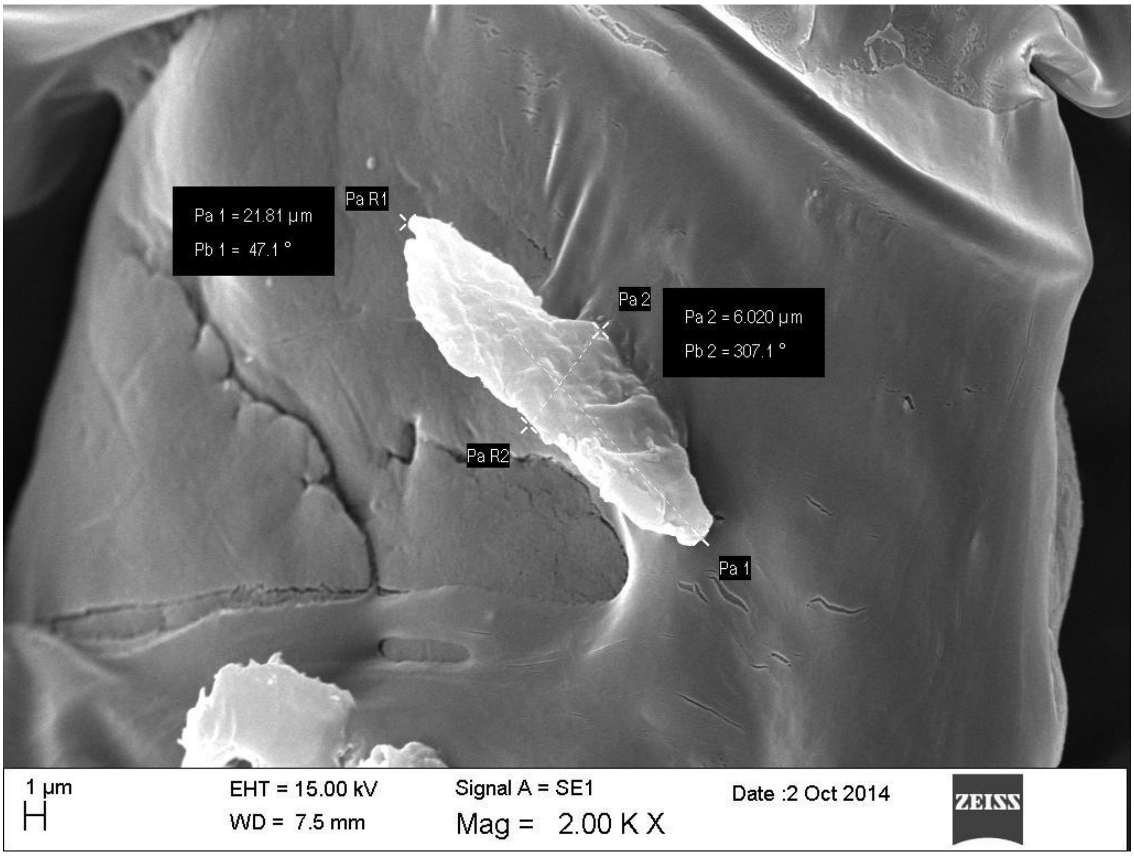

Figure 5: The average particle sizes of large PTFE particle.

Meanwhile, for the PTFE-filled rubber blend with 8 phr ZnO, the overall view of the rubber surfaces by SEM at the same magnification as in Figure 4 shows that there was less agglomerations of PTFE found on the rubber surface and the sizes of the agglomerate particles had reduced. The largest agglomerates of PTFE could only be found at a higher

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magnification of 2kX and the average of this particle size of PTFE was in the order of 2-8 μm (Figure 6 – Right).

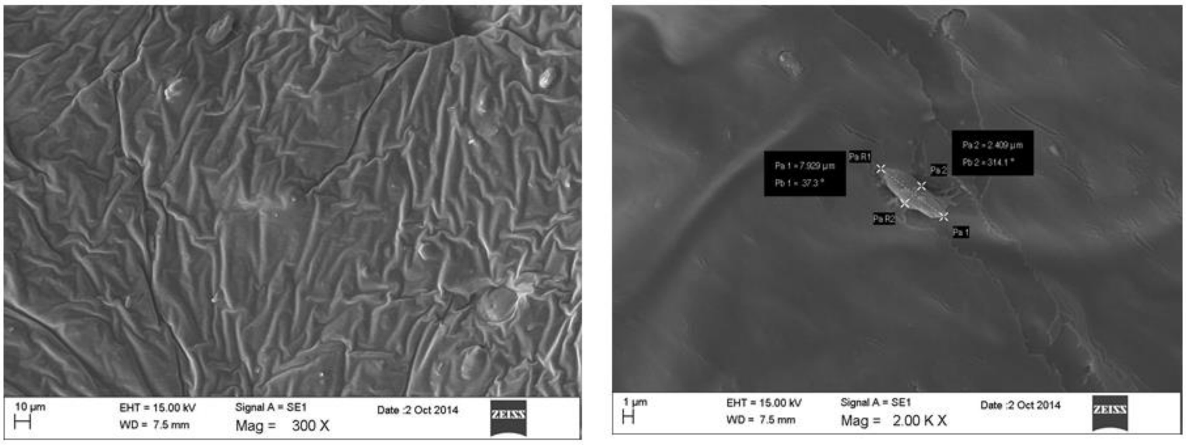

Figure 6: (Left) The PTFE powders in rubber blended with ZnO, (Right) The average particle size of large PTFE powder.

The reduced solvent uptake by the blend of the rubber is due to the presence of ZnO during rubber mixing with PTFE which helped to increase the dispersion of PTFE in rubber matrices. ZnO is an activator in rubber compounding normally used in small proportion to increase the effectiveness of accelerators (Nagdi, 1993). The presence of ZnO during PTFE blending could activate the carboxylic acid group in the PTFE to combine with rubber matrices (Khan et al., 2009a), hence enhanced dispersion can be achieved. The SEM-EDX image in Figure 7 shows that the ZnO element disperses uniformly in the rubber matrices as well as the fluorine element (represents the PTFE micropowder) which also uniformly disperses in the rubber. Consequently, the addition of ZnO during rubber blending reduces the PTFE agglomerates and increases the surface area of PTFE, hence reduced solvent uptake by the rubber could be achieved.

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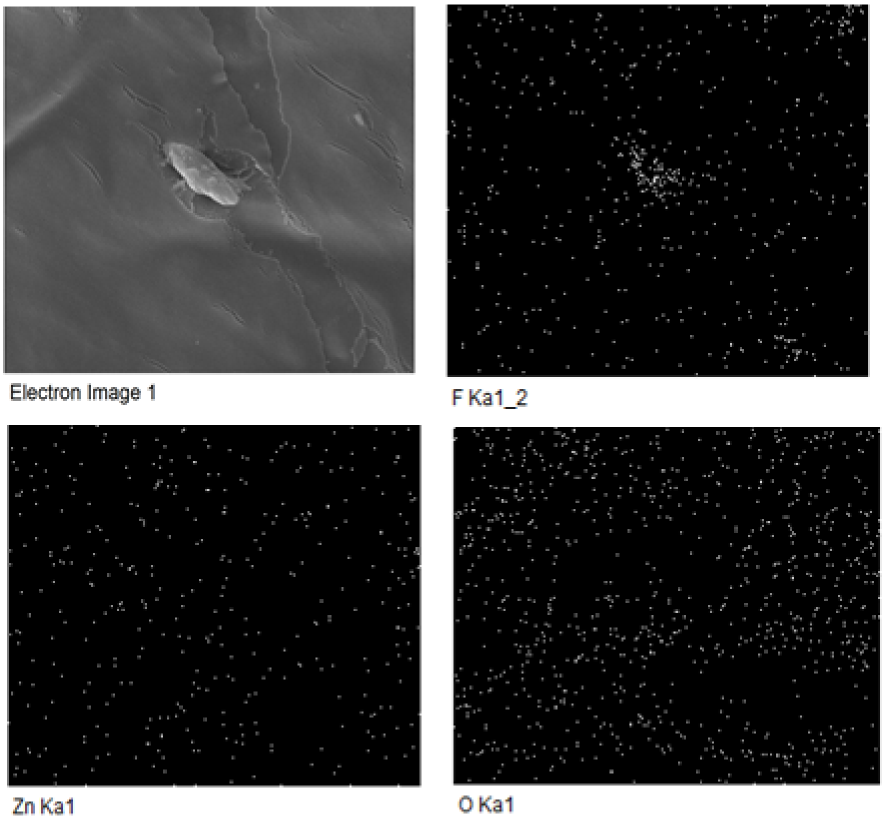

Figure 7: The SEM-EDX analysis of PTFE rubber blend with 8 phr ZnO a) Top-left: The PTFE particle traced by SEM-EDX b) Top-right: Distribution of fluorine element c) Bottom-left: Distribution of Zn element d) Bottom-right: Distribution of Oxygen element.

4. CONCLUSION

The effect of ZnO on the dispersion and homogeneity of PTFE micropowder in NR/NBR rubber matrices has been investigated. The findings from the rubber swelling analysis show that the PTFE-filled rubber blend with 8 phr ZnO shows an improvement in the resistance towards solvents. Further investigations on the microstructural image of the rubber compound blend with ZnO shows that the PTFE agglomerates reduced in sizes and were found to have enhanced dispersion and homogeneity in the rubber matrices compared to the rubber blend with no ZnO. The mixing of ZnO with PTFE during shear mixing of the rubber compound helps to reduce the PTFE agglomerates. Consequently, a uniformed distribution of the particles could be achieved, resulting in improved resistance towards solvents.

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