Free-volume changes in EVA composites studied by positron annihilation lifetime technique

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ABSTRACT

The influence of different concentration (0 – 60 wt %) of carbon black (HAF) filler on macrostructure and microstructure of ethylene vinyl acetate (EVA) composites was studied through electrical, mechanical measurements and positron annihilation lifetime (PAL) . The electrical conductivity measurements showed an abrupt increase when the concentration of filler reaches 30 wt%. This increase indicates the tendency of conductivity chain formation through the aggregation of carbon black particles network.

The size and the fraction of free- volume holes in PAL measurements revealed that the free-volume properties were strongly affected by the amount of filler; in particular, the free-volume fraction was rapidly decreased with increasing filler content. Furthermore, correlations were made between the lifetime parameters and electrical properties

Keywords: composites, carbon black, PAL, free volume, EVA.

1. INTRODUCTION

Ethylene vinyl acetate (EVA) is a random copolymer consisting of ethylene and vinyl acetate (VA) as repeating units. VA content has two fundamental effects that influence the properties of EVA copolymers. The first effect is to disrupt the crystalline regions formed by the polyethylene segments of the copolymer. The second overriding effect of VA content results from the polar nature of the acetoxy side chain. [George 2009, Brogly 1997, Gospodinova 1998].

EVA is one of the important organic polymers, extensively used for electrical insulation, cable jacketing and repair, component encapsulation and water proofing,

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corrosion protection, and packaging of components. However, bulk EVA does not often fulfill the requirements in terms of its thermal stability and mechanical properties in some specific areas [George 2009].

In order to improve various properties of polymers introducing fillers like carbon black, carbon fiber and metal powder into the polymer matrix has a well and profound effect, especially, on the mechanical and electrical properties [Gkourmpis 2013]. Depending on the filler and the required conductivity level the materials can be designed, that are suitable for many applications in the field of electronics and in electrical industries such as for electrostatic charge dissipation, electromagnetic interference shielding, thermal resistors, automotive boards, power cable shielding, chemical vapour sensors and pipe applications [Gkourmpis 2013, Miyashita 1993].

However, changes in properties of the polymer materials are usually related to changes in the size and fraction of free –volume hole. Positron annihilation lifetime spectroscopy (PALS) is one of the most sensitive methods of studying the free-volume whole size, where it is widely used for polymer studies [Misheva 2000].
PALS is very useful for direct measurements of free-volume hole radii (R) ranging from 1 – 10 Å.

The object of our study is concerned on the mechanical, electrical and free-volume properties of ethylene vinyl acetate (EVA) composites filled with conductive carbon black (HAF).

2. MATERIALS

Ethylene-vinyl acetate copolymer (EVA, PA-430) having vinyl acetate content of 24% was supplied by Repsol YPF.

High abrasion furnace black (HAF) with specific gravity (1.78-1.82), pH value (8-9.3), particle size (40 m) and fine granules (HAF- N330), was supplied by Transport and Engineering Company, Alexandria, Egypt.
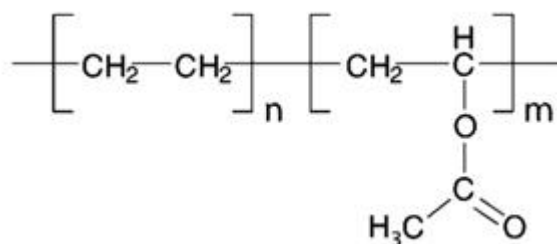
The chemical structure of EVA monomer

3. COMPOUND MIXING

EVA resin (100 grams) was mixed with different amounts of carbon black ranging from 0 to 60 wt% using a Barbender plastic order model (C.W. pra, instrument, INC. 50 Hackensack NJ 230 volt, 40 AMP) with an electrically heated mixer at constant

temperature of 120 ºC and at 30 rpm for 10 minutes to allow the torque to reach equilibrium. After mixing the compounds were compressed in mold under pressure of about 40 kg/cm^2 and a temperature of 120ºC, then cooled down to room temperature.

4. MECHANICAL MEASUREMENTS

The mechanical properties [tensile strength and elongation at break] were determined at room temperature using Zwick tensile testing machine (model-1425, Munchen, Germany) and at a crosshead speed of 50 mm/min according to ASTM D 412-98a. The samples were cut with a dumbbell shaped cutter. Cross-section areas of the dumbbell specimens were measured accurately with the aid of a thickness gauge. The mean of five readings were taking into consideration.

5. DILELECTRIC MEASUREMENTS

Dielectric constant test according to ASTM D150. Volume resistivity test according to ASTM D257-61. EVA samples with different carbon black percentages concentration by weight of sample are tested under room temperature, 50Hz, DC voltage 500 V. The samples are 5cm diameter and 1mm thickness.
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6. PAL MEASUREMENTS

Positron lifetime measurements were carried out at room temperature using a 11 µCi ^{22}Na source sealed between two kapton foils (thickness less than 1 mg/cm^2) with a small active diameter of l-2 mm in sandwich geometry with the pellets and a standard fast-fast coincidence lifetime spectrometer. Two identical plastic scintillator detectors fitted with Hamamatsu photomultiplier tubes [H3378-50] NO. BA0828 with a prompt resolution of about 250 ps (full width at half-maximum, FWHM) was used in the present study. With a channel constant of 6.5 ps, lifetime spectra were recorded for each sample with about 5 X 10^6 counts accumulated under the peak. After source correction was determined using a properly defect free Silicon sample, the lifetime spectra were analyzed in three components using the computer program LT [Kansy 1996] with the best fit χ^2 < 1.1. The two lifetime components 382 ps/7 % and 125 ps, which were attributed to annihilation in kapton and as para-positronium (p-Ps), were kept fixed during the analysis.

In lifetime analysis, the shortest component (τ_1 & I_1) is related to p-Ps annihilation, the intermediate (τ_2 & I_2) is the one indicating annihilation of free positron in the polymer matrix as well as amorphous-crystalline interfaces, and the longest one (τ_3 & I_3) represents pick-off annihilation of the ortho-positronium (o-Ps) in free volumes. Consequently, the o-Ps component will give information on free volume properties which markedly affect the microstructure changes.

The o-Ps lifetime, τ_3, can be correlated with the mean radius (R) of the free volume hole in the polymer material by the semi empirical equation [Tao 1972, Eldrup 1891]:

$$\tau_3 = 0.5[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin(\frac{2\pi R}{R+\Delta R})]^{-1} \qquad (1)$$

Where ΔR =0.1656 nm is the fitted empirical electron layer thickness.

On the other hand, positron lifetime measurements in polymers allow estimating the fractional free volume parameter, f, which is defined as:

$$f = (V - V_o)/V = V_f /V \qquad (2)$$

Where V is the total macroscopic volume of the polymer, V_o is the volume occupied by molecules, and V_f is the free volume of the polymer. Wang et al. [Wang 1990] proposed a semi-empirical equation which can be used to evaluate this parameter:

$$f = A\ I_3\ V_f \qquad (3)$$

Where I_3 is the relative intensity of the o-Ps lifetime component $V_f = \frac{4}{3}\pi R^3$ is the free volume of the single hole in nm^3, and the R value is taken from eq. (1). A is the normalization constant.

7. RESULTS AND DISCUSSION

EVA which is polymer containing polar acetate groups which can interact with HAF filler giving rise to composite formation. This interaction with conducted carbon black has major effects on the electrical conduction of composites.

7.1 MECHANICAL PROPERTIES

The tensile strength and elongation at break of EVA- HAF composites samples are plotted against the HAF content in Fig.1. It was observed that by increasing the filler loading up to 30 wt%, the tensile strength and elongation at break of EVA composites increase. This increase in both tensile strength and elongation at break is due to filler interaction cause by closer distance between aggregates in the polymer system and a better filler-filler interaction. However, both the tensile strength and elongation at breach have a significant decrement when HAF content is increased from 30 to 60 wt %. The drop can be related to the decrease of the polymer content in the composite as more filler is introduced. The presence of HAF in the polymer matrix restricts the mobility of polymer chains and reduces the ability of the sample to deform. As a, it is difficult for the segments of the material to easily slip past.

The maximum improvement in tensile strength and elongation at 30 wt% HAF may be because of the easy dispersion of filler in the rubbery phase and hence the vinyl acetate grades disperse the fillers well.
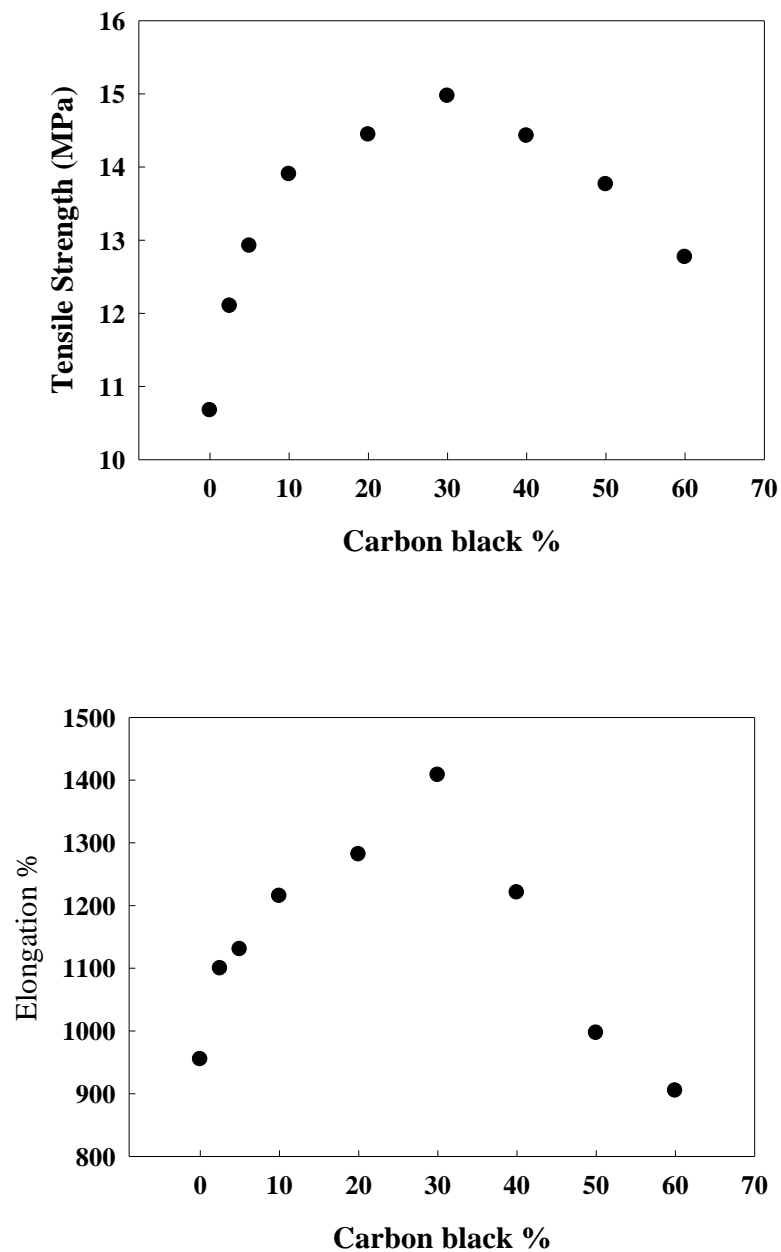
Fig. 1 Variation of tensile strength and elongation at break as
a function of HAF content of EVA composite samples.

7. 2 DIELECTRIC PROPERTIES

Conductivity enhancement of polymer composites depends on a large extent on the conductivity of fillers and their structural properties. Carbon black is common filler

used in plastics to achieve conductivity. As the filler loading increases, there is a tendency of the formation of some conductive networks through the aggregation of filler particles. Thus, some continuous three-dimensional networks are formed at a certain critical concentration through particle–particle contact among filler aggregates distributed in the matrix and high electrical conductivity is achieved. This concentration is called the percolation threshold where the change in conductivity at percolation is abrupt and a transition in the matrix from electrically insulating to electrically conducting state takes place [Das 2003]. For EVA-HAF composite system, the limit is occurring after the addition of 30 wt% HAF as shown in Fig. 2. However, a further increase in HAF loading beyond the percolation limit does not increase the conductivity significantly because after percolation there is only increase in the number of conductive networks.

The formation of conductive networks at the percolation limit may be considered as a sudden formation of continuous conductive wires through the insulating matrix.

The increased filler concentration beyond percolation may be considered as a simple increase in the diameter of that wire. Consequently, an increase in the diameter will increase the conductivity [Das 2003].

On the other hand, it is observed from the figure that the dielectric constant was increasing with the increase in filler loading for composites. Actually, the fillers particles present in the polymer matrix may be considered as micro/nano capacitors [Sohi 2011]. The increase in filler loading in the polymer matrix decreases the number of such capacitors, which in turn leads to the decrease in dielectric constant values as shown in Fig. 2.
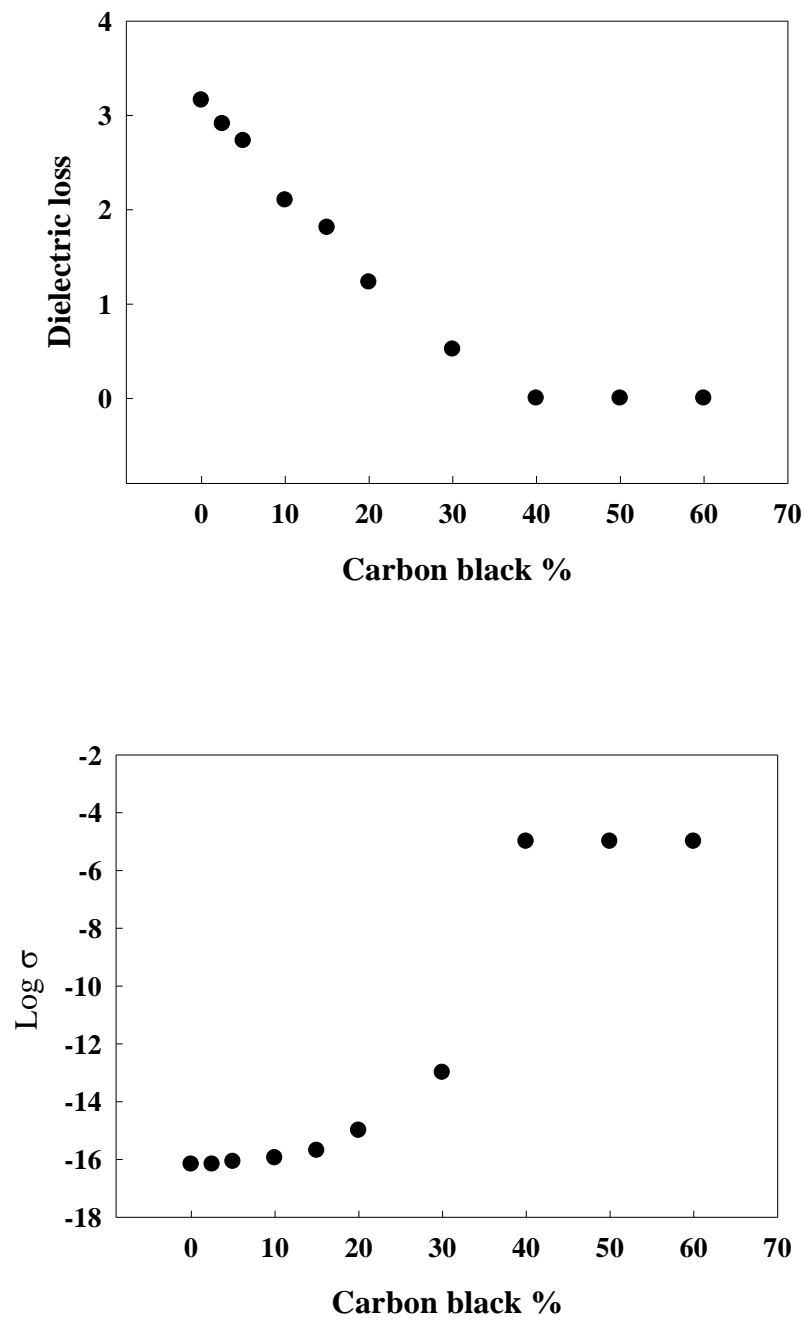
Fig. 2 Dielectric constant and electrical conductivity versus HAF content of EVA composite samples.

7.3 POSITRON LIFETIME

The o-Ps lifetime components (τ_3, I_3)), which are related to the size and fraction of free volume holes in virgin EVA is 2.7980 ± 0.0190 ns and is 22.0 ± 0.3600.%, respectively.

The variations of o-Ps lifetime components ($\tau 3$, I_3) and the intermediate lifetime components (τ_2, I_2) as a function of HAF content are shown in Figs. 3, 4.
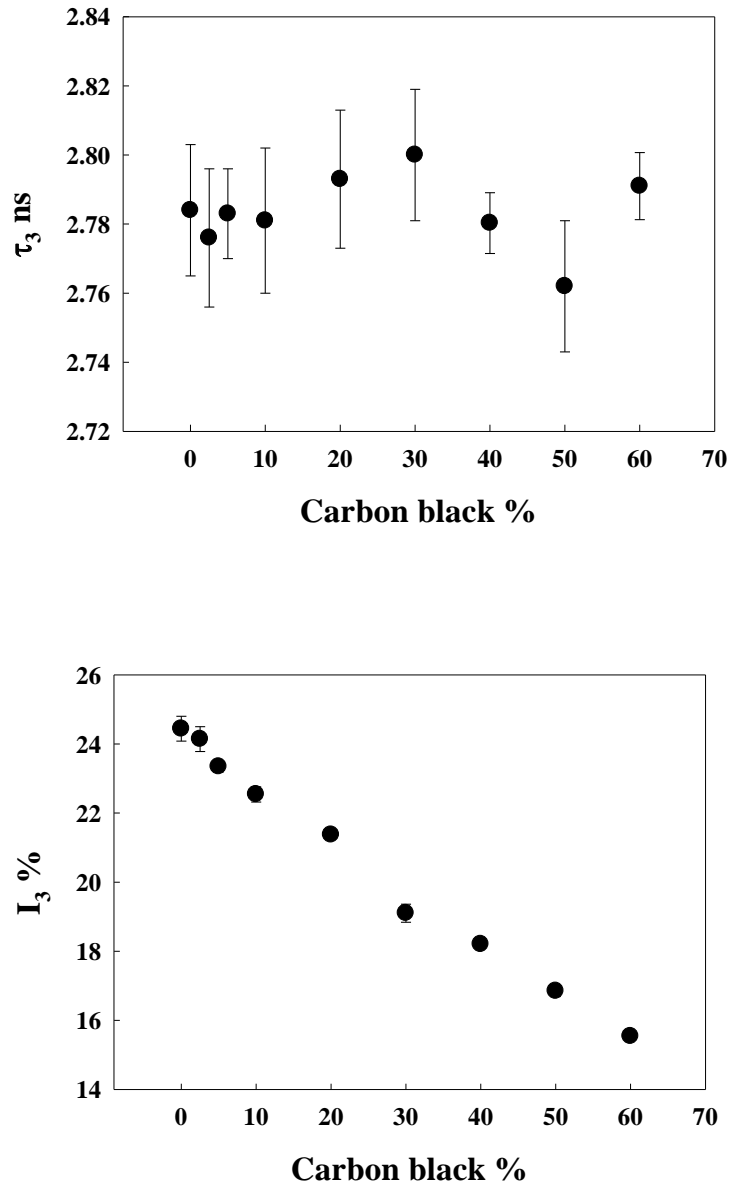

Fig. 3 Variation of o-Ps lifetime components (τ_3 and I_3) as a function of HAF content of EVA composite samples.

From these figures, one can observed that τ_2 and I_3 decrease sharply with increasing HAF content while τ_3 increases in the range from 2.5 to 25 % HAF follows by a decrease. The behaviors of τ_3 are due to the following reasons: i) the increase in τ_3 in the range from 2.5 to 25% HAF is due to vinyl acetate introduce some chain branching in EVA which leads to increase of size of free-volume holes (τ_3). ii) the decrease in τ_3 with increasing HAF contents is due to concentration of VA is 24% which leading to aggregation of filler and decrease in the size of free-volume holes (τ_3), where carbon black particles already have aggregating tendency [Balcaen 2000].

In the case of semicrystalline polymers like EVA, it is, moreover, presumed that most of the carbon black aggregates are located in the amorphous region, interspersed by spherulites of polymer crystals [Sircar 1981]. Spherulites, however, consist of crystalline and amorphous regions and it is possible that some black aggregates can penetrate and place themselves between the lamellae which lead to a decrease in free volume whole size and fractions.

Fig. 4, shows a decrease in τ_2 with increasing HAF content. This may be explained by increasing in electron negativity which leads to formation of some regions with high electron density in polymer composites, where the positron can annihilated within a short lifetime (τ_2) as shown in Fig. 4.
On the other hand, an increasing in I_2 is observed with increasing of HAF filler content in EVA which leads to reduction in the orientation and create of defects with small size (τ_2) and large fraction (I_2).
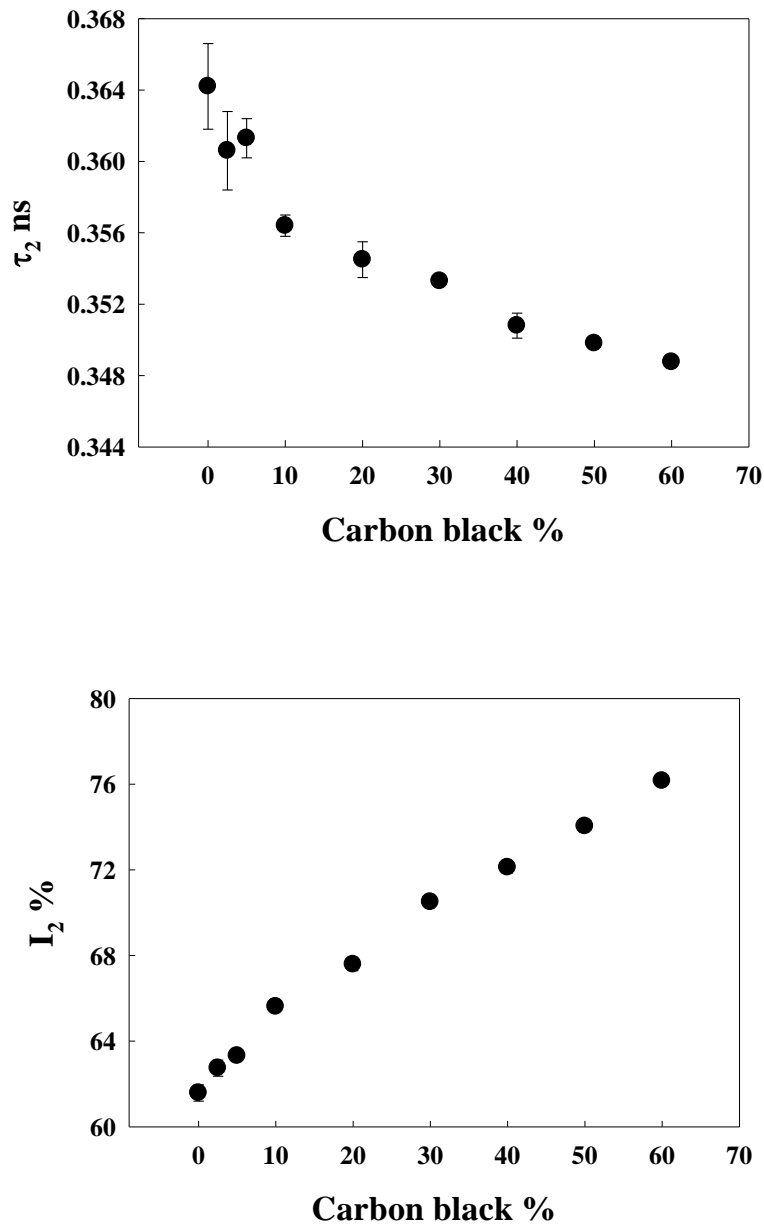
Fig. 4 Variation of o-Ps lifetime components (τ_2 and I_2) as a function of HAF content of EVA composite samples.

Fig. 5, shows the size distribution in pure and filled EVA samples. In pure EVA, the average size of nano-scale free-volume holes (V_h) is 177.57 Å^3. Upon addition of fillers the distributions shift to smaller free-volume holes sizes as a function in filler content, which are ranging from 175.72 Å^3 to 172.61 Å^3. The observed trends are consistent with the results obtained by the finite lifetime analysis (Fig. 3).

All these facts indicate that Ps atoms formed from positron–electron pairs with large initial separations are sensitively affected by positron trapping on the acetate group of EVA [Sircar 1981].
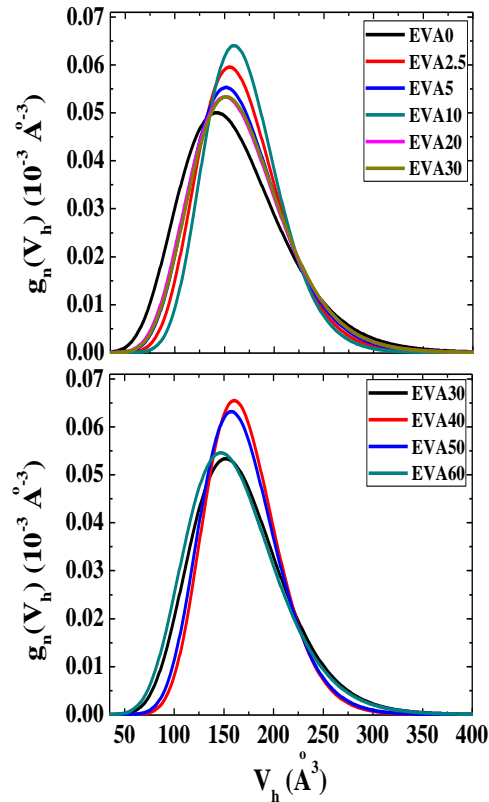

Fig. 5   Free-volume whole size distributions of EVA composite samples.

8. CORRELATION

The higher level of conductivity beyond the transition from insulator to conductor implies that the particles in the network be either closer together or have more contacts per particle or both [Sohi 2011]. As the concentration of the filler increases in a composite both situations occur. The electric conductivity (σ) of pure EVA was of the 10^{-16} Ω^{-1} cm^{-1} at room temperature. However, in EVA composites, it was found that σ rises by more than four orders of magnitude.

In Fig. 6, the conductivity is plotted versus the intensity of intermediate lifetime component, I_2, as a function of HAF content. A clear positive relation between σ and I_2 is observed. Assigning this lifetime component to the interface region between filler and polymer matrix, it follows that the formation of large amounts of micro-crystalline boundaries (high value of I_2) leads to a better conductivity and thus an increase in conducting path [Wang 1992].

Addition of filler leads to an increase in the negatively charged region and consequently, an increase in I_2 (conducting path). Increasing HAF content increases the number of mobile charge carrier consequently, increasing the conductivity.
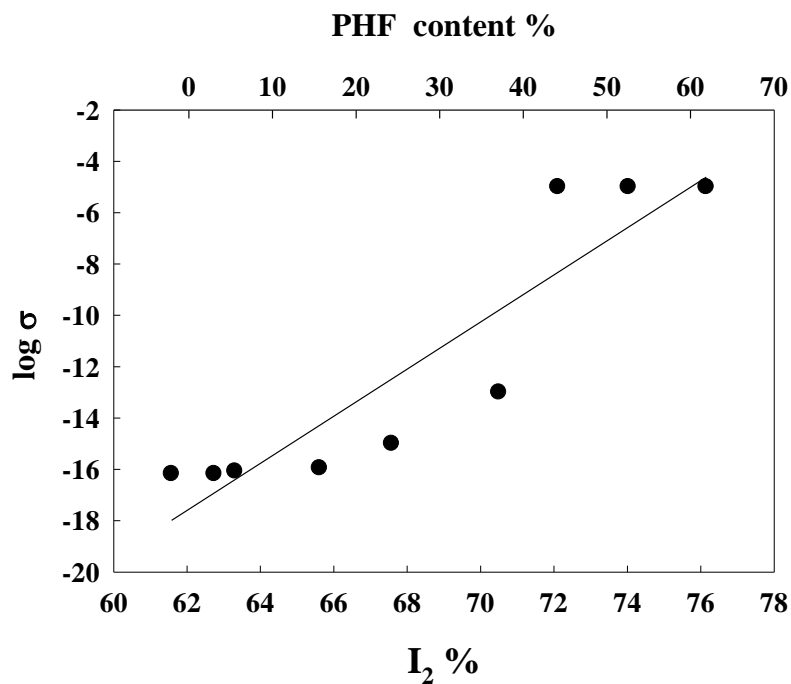

Fig. 6 Correlation between σ, HAF content and I_2, of EVA
composites samples. The line is drawn to guide the eye

8. CONCLUSION

The following conclusions are made based on results obtained.
- The incorporation of HAF strongly affects the properties of EVA-HAF composites.
- A critical limit of filler loading is 30 wt% HAF where mechanical, electrical and free volume properties were strongly positively affected.
- The tensile strength and elongation at break of EVA composites increase up to 30%.

- Conductivity, mechanical properties of EVA composites depend on the amount of HAF loading in the polymer matrix. A sharp increase in conductivity is observed at percolation limit.
- Correlation between conductivity and I_2 indicated that the electrical properties are improved by adding of HAF filler in EVA.

REFERENCES

Balcaen, N., de Baerdemaeker, J., Dauwe, C., Cosaert, K., Goethals, E., du Prez, F., (2000), "Composition and self- irradiation effects on the positron annihilation lifetime properties of poly (ethylene- co- vinyl acetate)", *Rad. Phys. Chem., * **58**, 497- 501.

Brogly, M., Nardin, M., Schultz, J., (1997), "Effect of vinylacetate content on crystallinity and second- order transitions in ethylene- vinylacetate copolymers", *J. Appl. Polym. Sci.*, **64**, 1903 – 1912.

Das, N.C., T. K. Chaki, D. Khastgir, (2003), "Effect of Filler Treatment and Crosslinking on Mechanical and Dynamic Mechanical Properties and Electrical Conductivity of Carbon Black-Filled Ethylene–Vinyl Acetate Copolymer Composites", *J. Appl. Poly. Sci.,* **90**, 2073–2082.

Eldrup, M.; Lightbody, D.; Sherwood, J. N., (1981), "The temperature dependence of positronium lifetimes in solid pivalic acid", *Chem. Phys*, **63**, 51 - 58.

George, J. J., Anil, A. E., Bhowmick, K., (2009), "Influence of Matrix Polarity on the Properties of Ethylene Vinyl Acetate–Carbon Nanofiller Nanocomposites", *Nanoscale. Res. Lett.*, **4**:655–664.

Gkourmpis, T., Svanberg, C., Senthil K. Kaliappan, Schaffer, W., Obadal, M., Kandioller, G., Tranchida, D., (2013), " Improved electrical and flow properties of conductive polyolefin blends: Modification of poly (ethylene vinyl acetate) copolymer/ carbon black with ethylene–propylene copolymer", *European Polymer Journal*. **49**, 1975–1983.

Gospodinova, N., Zlatkov, T., Terlemezyan, L., (1998), "Relationship between microstructure and phaseand relaxation transitions in ethylene- vinyl acetate copolymers prepared by emulsion copolymerization." *Polymer*, **39**, 2583- 2588.

Kansy, J., (1996), "Microcomputer program for analysis of positron annihilation lifetime spectra, *Nucl. Instrument. Methods Phys. Res., Sect.* **A 374**, 235 - 244.

Misheva, M., Mihaylova, M., Djouelov, N., Kresteva, M., Krestev, V., Nedkov, E., (2000), " Positron annihilation lifetime spectroscopy studies of irradiated poly(propylene- ethylene)/ poly(ethylene- co- vinyl acetate) blends", *Rad Phys Chem*, **58**, 39- 47.

Miyashita Y, Makishi Y, Kato H., (1993) *"* New approach to elucidate the properties of carbon black- filled semiconducting materials for high voltage power cables", *Annual report – Conference on electrical insulation and dielectric phenomena*, 678 - 687.

Sircar, A. K. and Wells, J. L., (1981) "Electrothermal Study of Carbon Loaded Ethylene-Vinylacetate Copolymer, *Polymer Engineering and Science,* **27 (13)**, 809 – 815.

Sohi, N.J.S., Rahaman, M., Khastgir, D., (2011),   "Dielectric Property and Electromagnetic Interference Shielding Effectiveness of Ethylene Vinyl Acetate-Based Conductive Composites: Effect of Different Type of Carbon Fillers", *Polymer Composites*, **32 (7),** 1148-1154.

Tao, S. J., (1972), "Positronium annihilation in molecular substances", *Chem Phys*, **56,** 5499 - 5510.

Wang, Y.; Nakanishi, H.; Jean, Y. C.; Sandreczki, T., (1990), "Positron annihilation in amine- cured epoxy polymers- pressure dependence", J. *Polymer Sci (B) Polym Phys*, **28**, 1431- 1.

Wang, Y. Y, Yang, Y. H., (1992), "The relations between positron annihilation and conductivity of non-metal conductors", *Mater. Sci. Forums,* **105- 110**, 1795 - 1803.