Vulcanizing System Dependence of the Rubbery Swelling, Dielectric and Doppler Shift Characteristics of IIR/EPDM Blends.

F. Abd El-Salam, M.H.Abd-El Salam and M. I. Mohamed

Physics Department, Faculty of Education, Ain Shams University, Cairo, Egypt

Effect of the vulcanizing system on the rubbery swelling, dielectric and Doppler shift characteristics of IIR/EPDM -carbon black (GPF) blends have been studied. Three different vulcanizing systems were used in this study namely, elemental sulphur (S-system), TMTD (T-system) and elemental sulphur + TMTD (M-system). The dielectric behaviour of the tested blends has been studied in the frequency range from 1KHz to 100KHz and in the temperature range from 40°C to 140°C. It has been observed that samples vulcanized with (T-system) give a higher dielectric permittivity values compared with those crosslinked with (S-system) or (M-system). The presence of the polar group C=S in the TMTD molecules is the most effective factor on the dielectric properties of the tested blends. The swelling behaviour and the positron annihilation characteristics by means of Doppler Broadening parameters for the tested blends have been investigated. The positron annihilation characteristics supported the swelling and dielectric measurements obtained.

1. Introduction.

The raw rubber – elastic product must be converted into the final product by means of a vulcanization process. Vulcanization [1] is the process which links the macromolecular chains with each other at their reactive sites. As a result of this process, plastic rubber is converted into elastic rubber vulcanizates [2]. However, the term vulcanization covers not only the actual crosslinking process, but also the methods by which the crosslinking is produced [3]. Vulcanizing agents are substances, which bring about the actual crosslinking process. Choice of vulcanizing or crosslinking agent depends on the rubber type and to a lesser extent on the combination of properties required for the product. Elemental sulphur is the predominant vulcanizing agent for general-purpose rubbers. It is used in combination with one or more accelerators

and an activator system comprising zinc oxide and a fatty acid (normally stearic acid). The most popular accelerators are delayed-action sulphenamides, thiazoles, thiuram sulphides, dithocarbamates and guanidines. Part or all of the sulphur may be replaced by a sulphur donor such as a thiuram disulphide.

The degree of swelling Q% of any polymer placed in solvent can be determined by applying the gravimetric method from the formula

$$Q\% = (\frac{M - M_d}{M_d}) \times 100$$

where M_d and M are the weight of the dry and the swollen polymer sample, respectively. According to the diffusion theory in elastomers [4,5], the swelling behaviour of any polymer is governed by two parameters, i)the penetration rate, P, given by the equation [6,7].

$$P = (\frac{S}{2M_e}) \frac{dM_t}{dt^{1/2}}$$

where S is the thickness of the sample, M_e and M_t are the weight uptake of liquid at equilibrium and after time t, respectively, and the average diffusion coefficient, D, which is expressed in terms of the penetration rate expressed as[8].

$$D = \frac{\pi P^2}{4}$$

The dielectric properties of polymer – conductive polymer composites have been extensivly reported[9-12] wheras, the dependence of electrical properties on the type of vulcanizing system has been studied in a small part of early works [13,14].

Recently, positron annihilation spectroscopy (PAS) has been applied to polymers[15-18]. This microscopic study provides a basic insight into the swelling measurements of polymer blends. The utility of positrons in polymer derives from the fact that they can combine with an electron to form positronium (Ps), which is preferentially localized in the free volume holes. Doppler broadening profiles of the annihilation radiation (DPAR) give the electron momentum distribution at the site of annihilation. The positron annihilation technique gives information about open spaces in amorphous polymers [15] as the free volume can be probed by the detection of a positronium atoms[18]. Since positrons are annihilated with core or valence electrons, the annihilation energy distribution varies with the fractional contribution of the core and the valence electrons in the annihilation process. In practice, the Doppler broadening profile is characterized by the line shape parameter 'S' and the wing parameter 'W' corresponding to annihilation with

valence and core electrons, respectively. In this paper, it is aimed to investigate the effect of the vulcanizing system on the rubbery swelling, dielectric and Doppler shift characteristics of IIR/EPDM -carbon black (GPF) blends.

2. Materials and Techniques:

2.1. Materials

All concentrations in this work were expressed by phr (part per hundred part of rubber by weight). The blend formulation containing (IIR, 90phr, EPDM, 10phr, ZnO, 5phr, Stearic acid, 2phr,Processing oil, 10phr, different content of GPF black up to 80 phr, N-cyclohexyl-2-benzthiozyle sulphenamide (CBS), 1.5 phr and vulcanized separately with a constant ratio equal to 3 phr of the following vulcanizing systems:
  a) Elemental sulpher (S), (S-system)
  b) Tetramethylthiuram disulfide (TMTD), (T-system)
  c) Elemental sulpher + Tetramethylthiuram disulfide (S +TMTD),
     (M-system).

The prepared compounded rubber was left for at least 48 hours before vulcanization. The vulcanization process was conducted at 160±2°C under a pressure of 40 kg/cm^2 for 20 min.

2.2. Measurements
(i) Swelling measurements

The test sample in the form of disc of radius 5mm and thickness of about 1mm was weighed by using a balance sensitive to 10^{-5} gm and then immersed in stoppered-glass bottle containing benzene. The sample was removed from the solvent after different periods 5, 10, 15, ...min. The excess solvent on the surface of the test sample was removed by blotting with filter paper then the sample was weighed again.

(ii) Dielectric properties measurements

Samples used in dielectric properties measurements have the form of discs of radius 5 mm and thickness of about 1 mm. The electrodes were made from silver paste covering the two major surfaces of the sample. Measurements concerning the frequency and temperature dependence of the dielectric properties of samples of the different vulcanizing systems S, M and T were obtained by *PM 6304, PHILIPS, Automatic RCL Meter*. The dielectric constant, ε' was recorded under varying temperatures 40-140°C and frequencies ranging from 10^3-10^5 Hz. The dielectric constant $\varepsilon^{\backslash}$ (real part of the dielectric constant)

of the sample was calculated by using the relation[19] $\varepsilon' = C_x d / \varepsilon_0 A$, where C_x is the capacitance of the sample, d thickness of the sample, A the cross-sectional area of each of the parallel surface of the sample and ε_0 the permittivity of free space ($\varepsilon_0 = 8.85 \times 10^{-12}$ F/m.).

(iii) Doppler Broadening of Annihilation Radiation (DBAR)

The energy distribution measurements were performed using, a high resolution Hyper-Pure Germanium (HPGe) Detector System having an energy resolution of 1.24 KeV was achieved for the 1.33 MeV γ- ray line of the ^{60}Co isotope. The calibration factor was 57.3 eV channel. 5μci of ^{22}Na source, deposited on Kapton foil from a ^{22}NaCI solution was used as a positron source. This source was sandwiched between two specimens. The detection of the annihilation peak was attained by putting the source-specimens sandwich directly into the active area of the detector which gave good statistics within a two - hours run. All the measurements were made at room temperature.

3. Results and Discussion

3.1. Swelling Behaviour

3.1.1. The Degree of Swelling

The dependence of the degree of maximum swelling, $Q_m\%$, in benzene on the **GPF**-carbon black content in different vulcanizing systems is represented in Fig.(1). It is clear that $Q_m\%$ decreases with the increasing carbon black content. This may be attributed to the tendency of **GPF**-carbon black to form aggregates[4] which impede the solvent penetration into the rubber matrix. Also, the increased number of chemical and physical bonds created between carbon black and macromolecules contributes markedly to the observed decrease of $Q_m\%$. The higher values of $Q_m\%$ for the T-system over those of both the S- and M- systems may be ascribed to the different types of crosslinks[3] resulting from these systems. It is assumed [20] that the T-vulcanizing system creates small amount of the mono and disulphide (-S-, -S-S-) crosslinks types in the rubber vulcanizates. Also, dithiocarbamate compound is formed and its molecules become attached to the rubber hydrocarbon chain, thus forming polymer composites molecules of higher molecular weight and decreased crosslinking density. On the other hand, the S and M systems create mixed crosslinks of the mono, di and polysulphide types, but in different ratios. The excess amount of sulphur in S-system increases the probability of formation of polysulphide crosslinks. This leads to a relative increase of the separation distance between rubber chains. The presence of sulphur (1.5 phr) which is the first component of the M-system leads to the

formation of mono, di and small amount of polysulphide crosslinks [21] which are less than those in the S-system. The contribution of the second component in the M-system, TMTD molecules, is the cereation of mono and disulphide. So, the crosslinking of *(*IIR/EPDM) composites is more affected by the mixed system *(*S+TMTD) than by either the sulphur or the TMTD systems.
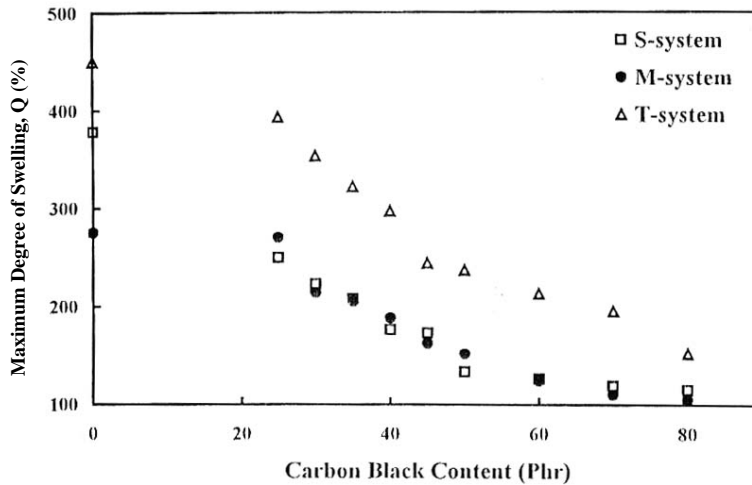

Fig. (1): The dependence of the degree of maximum swelling, Q_m %, of (IIR / EPDM) composited in benzene on the GPF black content for different vulcanizing systems.

3.1.2. Penetration and Diffusion of Solvent

Diffusion theory in elastomers [22,23] is based on the assumption that the swelling starts by the sorption of the liquid at the surface of the sample to a certain concentration equal to that attained by the whole sample at equilibrium; then the swelling proceeds by increasing the depth of the swollen layers. The penetration rate, P and the diffusion coefficient, D, were calculated using the slopes of the early stage in the plots of the increase in weight, due to swelling in benzene, with the square root of time for the investigated composites[6-8]. Fig. (2) shows the dependence of P and D for solvent molecules in the vulcanized (IIR/EPDM) composites on the GPF-black content for the different vulcanizing systems. From this figure, it is clear that P and D decrease with increasing carbon black content. This decrease, might be the result of the physical crosslinking action induced by carbon black aggregates. These aggregates which exist at different plate lamellae and act as screens, reduce the penetration rate of the solvent [24] molecules into the bulk of the rubber mix. Rubber reinforcement caused by the addition of carbon black restricts the equilibrium swelling. Again, The higher values of both P and D for the

T-system over those of the S and M-systems, can be attributed to the different types of crosslinks created by these systems, as mentioned before.
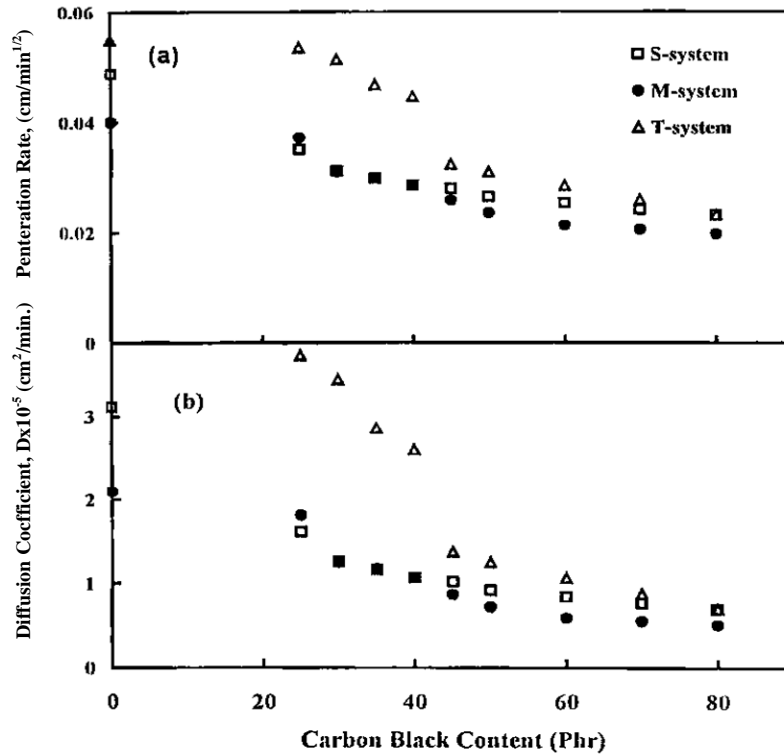

Fig. (2): The dependence of the penetration rate, P, and the diffusion coefficient, D, for solvent molecules in the (IIR / EPDM) composites on the GPF black content for different vulcanizing systems

3.2. Dielectric permittivity ε′

Fig. (3) depicts the frequency dependence of dielectric permittivity ε′ of the samples at 40°C. From this figure, it is observed that ε′ decreases with increasing frequency, while it increases with increasing carbon black content. The addition of carbon black, stabilizers, and other ingredients to the polymer matrix makes the polymeric material to be heterogeneous media consist of different phases with different dielectric permittivities and conductivities. The accumulation of electric charges on the interfaces of these different phases exhibits an interfacial polarization which is known as *Maxwell-Wagner-Sillars (MWS)* effect [25]. The observed decrease of the dielectric permittivity with increasing frequency might therefore be due to the interfacial polarization which dominates in the low frequency region, then gradually diminishes at high

frequency. Increasing carbon black content makes the matrix more conductive and this leads to the higher values of the dielectric permittivity observed for samples of different vulcanizing systems which have higher carbon black content.
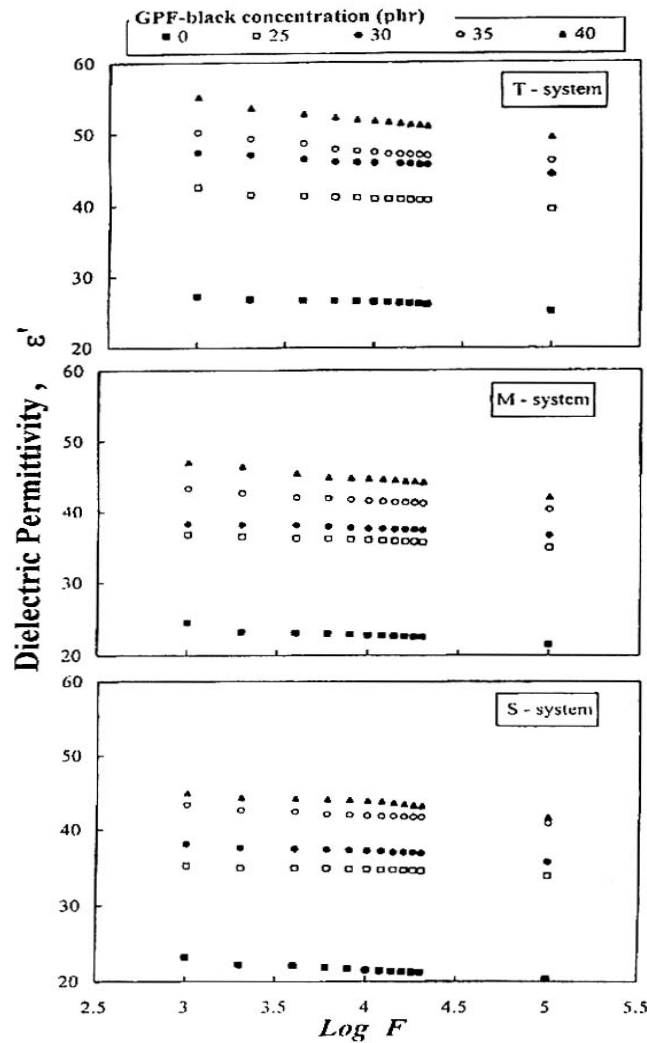

Fig. (3): The frequency dependence of dielectric permittivity for (IIR / EPDM) composites having different vulcanizing systems and/or different concentrations of GPF black at 40°C.

Figs (4 and 5) represent the temperature dependence of the dielectric permittivity ε' of *(IIR/EPDM)* composites having the same GPF black content 30 phr (Fig. 4) and 40 phr (Fig. 5) and vulcanized with the T, M and S vulcanizing systems as measured at three frequencies namely 10, 20 and 100KHz, respectively. From

these figures it can be noticed that the level of the dielectric permittivity values of the T-system is higher than that of the M system and the S system. This might be due to the presence of the polar group C=S, in the *TMTD* molecules. The polar group plays an important role in the electrical properties of the dielectric because the probabilities of the bonding electrons being, which exist in the field of the nuclei of the different atoms are unequal, makes the atoms differ in electron affinity. The electron affinity of S atoms is greater than that of C atom and therefore, the average density of the electron cloud around the S atom is higher than that around the C atom. So, if a polymer containing polar group is placed in an electric field, the orientation of both its segments and its lower kinetic energy units will be observed until a definite relaxation frequency. This gives rise to definite values of dielectric constant and dielectric loss[26]. The role of the polar group is more pronounced for samples containing higher amounts of carbon black (see Fig.5), where a remarkable increase in the dielectric permittivity in the case of *(M and T systems)* is observed.
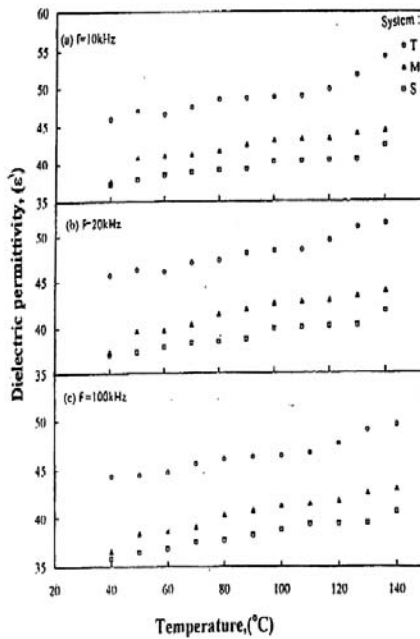

Fig. (4): Temperature dependence of the dielectric permittivity of (II / EPDM) composites having the same GPF black content (30 phr) with different vulcanizing systems.
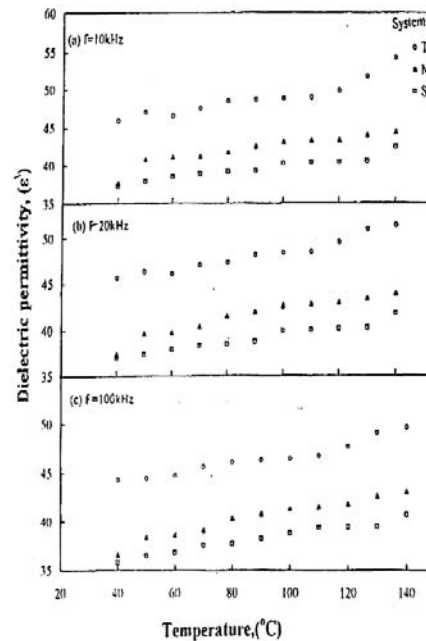
Fig. (5): Temperature dependence of the dielectric permittivity of (IIR / EPDM) composites having the same GPF black content (40 phr) with different vulcanizing systems.

(iii) Doppler broadening of the Annihilation Radiation

The observed Doppler broadening profiles are characterized by the existence of the S and W parameters. The S-parameter mainly characterizes the fraction of the annihilation of positron with valence (free) electrons. The

W-parameter characterizes positron annihilation with core electrons. This agrees with the fact that in amorphous polymers, the S-parameter is very sensitive to the annihilation probability of para-Ps (p-Ps) while the W-parameter can be related to the annihilation characteristics of ortho- Ps (o-Ps) [27]. The dependence of the S-parameter on carbon black content for different vulcanizing systems is shown in Fig. (6-a). It is noticed that the S-parameter increases with increasing carbon black content. This might be ascribed to the increase of the valence (free) electron density by adding the conductive carbon black inclusions, which raises the probability of trapping the free positrons in the polymer [28]. Also, the higher level of the S-parameter for M- system than that for both the S and T systems, might be explained in view of the high crosslinking density in the M system, which leads to a complicated network structure with very small free volumes [29] and lower probability for o-Ps formation. Accordingly, the contribution of the free Ps to the annihilation process will be more pronounced with the M- system in view of its higher level of the S-parameter, Fig. (6-a). On the other hand, the dependence of the W-parameter on carbon black content given in Fig. (6-b) shows that the W-parameter decreases with increasing carbon black content. This can be attributed to the physical and chemical crosslinking role of the carbon black. Besides, the higher level of the W- parameter in the T-system than that for of the S and M systems might be due to the fact that the W-parameter is very sensitive to the degree of order in the microstructure of polymers. In the T-system, with the lowest crosslinking density, the fractional free volume is high [30]. Thus, the probability of the o- Ps formation is very high and the pick off annihilation with the core electrons might therefore be the dominant process. This leads to the increase of the W-parameter on the expense of the decrease in the S-parameter. The measurements of the S-parameter for a certain composite at different conditions enable to predict the variations of the mechanical properties of this composite as discussed in a previous article [31].
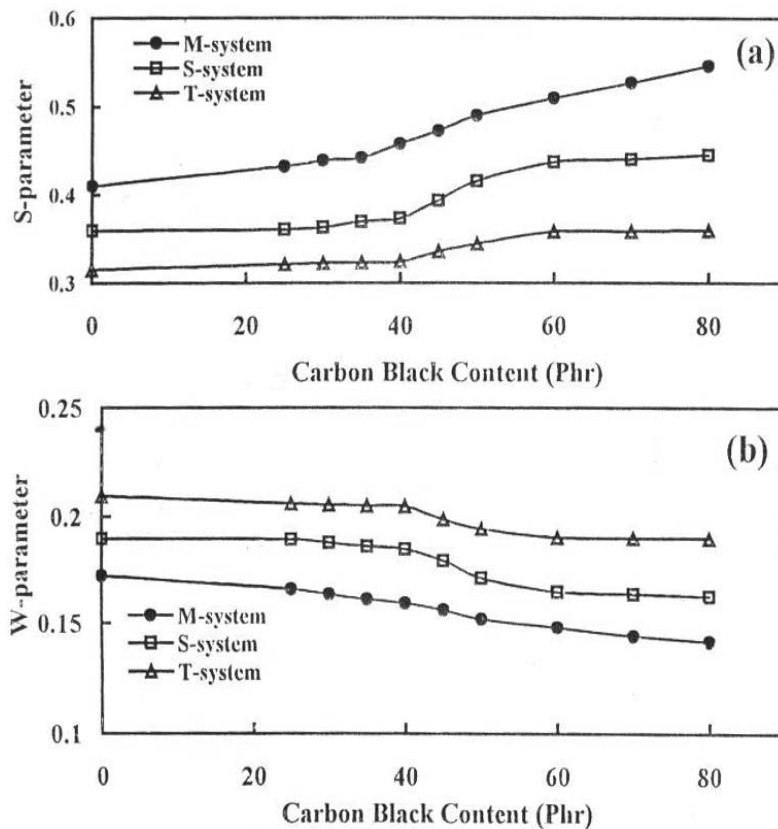
Fig. (6): The dependence of S-parameter (a) and W-parameter (b) for (IIR / EPDM) composites on the GPF black content for different vulcanizing systems.

Finally, from the above discussions, it is clear that the obtained information about the swelling and dielectric measurements are consistent with those concluded according to positron annihilation characteristics with an exception for the highest dielectric permittivity values of T-system vulcanizates which was ascribed to the presence of polar group (C=S) in this system.

4. Conclusion:

The results showed that the increased crosslinks density of M-system than that of both the S and T systems caused the higher decrease for the degree of swelling. The dielectric permittivity decreases with increasing frequency while it increases with increasing either temperature and/or carbon black content. The dielectric permittivity for the T-system was found to be higher than

those for the M & S systems, due to the presence of the polar group C=S in the TMTD molecules. The observed Doppler broadening profiles showed that positron annihilation with valence (free) electrons or the S-parameter increased with increasing carbon black content, while annihilation caused by core electrons or the W-parameter showed an opposite behaviour. Finally, the positron annihilation characteristics supported the swelling and dielectric measurements obtained.

References:

1. "*Encyclopedia of Polymer Science and Technolgy*", Vol. 12, p. 280, & 294, Inter science publishers, John Wiely and Sons Inc. New York (1970).
2. Morton Mourics "*Introduction to Rubber Technology*", Reinhold Publishing Corporation, New York, (1959).
3. W. Hoffman, "*Vulcanization and Vulcanizing Agents*", p.17, 80, 92, 98 & 104 Farbenfabriken Bayer AG, Lever Kusen (1965).
4. S. N. Lawandy and F. H. Helaly, *J. Appl. Poly. Sci*., **32**, 5279 (1986).
5. N. Lawandy and M. T. Wassef; *J. Appl. Polymer Sci*., Vol. **40**, p. 323, (1990).
6. P. Mason, Polymer, Vol. 5, p. 625, (1964), *Polym. Sci*., **46**, 909, (1992).
7. Z. Y. Ding, J.J Aklonis; *J. polym. Sci . Polym. Phys. Ed*., **29**, 1035 (1991).
8. S. N. Lawandy and M. T. Wassef; *J. Appl. Polymer Sci*., **40**, 323, (1990).
9. L. Benguigui, J. Yacuowicz and M. Narkis, *J. Polym. Sci.: Polym. Phys*., 25, 127, (1987).
10. C. Brosseau, F. Boulic, P. Queffelec and A. Beroual, *J. App. Phys*., 81, 882 (1997).
11. S. Abd-EL Ghany, M.H. Abd-EL Salam, G.M. Nasr, *J. App. Polym. Sci*., 77, 1816 (2000).
12. S.L. Abdel-Messieh and A.F. Younan, *J. App. Phys*., **62**, 805 (1996).
13. R.A. Brown, R. Abdel-Samad and Ben-Yahya, *J. Polym. Sci., Phys. Ed*, **23**, 451 (1985).
14. A.M. Abdel-Bary, H.H. Hassan, A.M. El-Lawendy, M.K. Abu- Assy and F.K. El-Tantawy, *Polym. Int*., **30**, 371 (1993).
15. Y. C. Jean, Microchem. J., **42**, 72 (1990).
16. W. Brandt and A. Dupasquier, "*Positron Solid State Phys.*", North Holland, Amesterdam, (1983).
17. R. Ramani, P. Ramachandra and G. Ramagopal, *phys. stat. sol*. (a), **158**, 3 (1996).
18. D.M. Schrader and Y.c Jean, "*Positron and Positronium Chemistry*" Elsavier, Amesterdam, (1988).
19. A. K. Sharma and K. L. Bahata, *J. Non cryst. Solids*, 95 (1989).
20. N. J. Morrison and M. Porter; *Rub. Chem. and Tech*. **57**, 63 (1983).

21. S.G. Kim. and S.H. Lee, Rub.Chem. and Tech. **67**, 649 (1994).
22. J. Crank, "*The mathematics of diffusion*" (Oxford University press, Oxford) (1956).
23. G. J. Van Amerogen, "*Rubber Chem. Technol.*", **34**, 1065 (1964).
24. M. Amin, G.M. Nasr, S.A. Khairy and E. Ateia, *J. App. Polym. Sci.*, **37**, 1209, (1989).
25. PATFIT package, purchaced from Riso. Nat. Lab. Denmark, (1989).
26. Tager, "*Physical Chemistry of Polymer*", Mir Pub., Moscow p.44 (1972).
27. S. WU, *Polymer Inter.*, **29**, 229 (1992).
28. M. Kosterzewa, Z. Michno and T. Majcherczyk, "*Act. Phys. Poly.*", **18**, 8 (1995).
29. Y. Ito in Positron and Positronium Chemistry, Y. C. Jean and D.M. Schrader, Eds., Elsevier, Amsterdam (1988).
30. P. E. Mallon and W. J. Mc Gill, *J. Appl. Polym. Sci.*, **74**, 2143, (1999).
31. F. Abd-EL Salam, M.H. Abd-EL Salam, M.T. Mostafa, M.R. Nagy, M.I. Mohamed, *J. App. Polym. Sci.*, **90**, 1539 (2003).