Effect of Two Decades Aging on the Ultrasonic and Electrical Properties of Polymer Composite Materials

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Abstract*: The effect of aging, type and concentration of filler (Alumina trihydrate (ATH) and silica (SiO_2)) on the mechanical and electrical properties of polyester composite as a high voltage insulating materials, were investigated by means of ultrasonic and electrical techniques. Ultrasonic wave velocities (both longitudinal and shear) were measured at frequencies of 4 MHz at room temperature. Results of density, ultrasonic wave velocities, mechanical properties and electrical loss showed the improvement of the polymer composite network with aging and type of filler. This behavior may be due to the change in cross-link density and average stretching force of bonds with aging.*

Keywords*: Polymer composite, dissipation factor, ultrasonic measurements, aging effect.*

Introduction:

Polymers has been used in many electrical applications, especially polyester, it provides an excellent combination of mechanical, chemical and dielectric properties and process-ability. The degree of reliability of electrical energy is to a great extent dependent on the insulation used in power system. It is important to understand the effect of aging on the high voltage polymer insulators. Not only must the material be capable of with studying the effects on the polymer surface, but also the material must remain stable to these effects during the course of ageing in order to insure a long useful insulator life(1). Polyester resins are the most widely used resin systems. Filler materials are used extensively with polyester resin for a variety of reasons, such as cost reduction, and more importantly, to enhance some physical and/or mechanical properties. Through the present work several types of inorganic fillers (Alumina trihydrate and silica) were incorporated into the polyester resin. Also, a comparison between two groups of samples were investigated, one of these groups prepared from about 20 years ago with the same types of filler and same percentages and the other group prepared recently. The effects of type and percentage of filler and aging on the mechanical and electrical properties were investigated. Quantitative measurements and qualitative observations were made to recognize the different aspects related to their employment in an attempt to find an appropriate means to enhance a prescribed property. Test results indicated that although a pronounced enhancement of the mechanical properties was achieved, a specific filler type may not have the same effect on each mechanical property. Therefore, in real applications where only some of the properties are of concern, the proper filler type and content should be specified accordingly. In any case, employing a combination of filler types (mixed fillers) is an efficient way to utilize the benefits of each of the employed fillers.

Nondestructive testing methods ore one of the most dynamically developing branches of science in general. The procedure of ultrasonic tests on objects comprises passing waves into objects, scanning objects by moving head over their surface and detecting signals caused by waves passed through objects. The basic rule in such tests is to know dependencies between the value of an ultrasonic parameters being measured (for example, ultrasonic longitudinal and shear velocities) and the tested property of internal structure of the polymer material under investigation. Dependencies between acoustic parameters and structural properties of polymer materials are usually determined empirically based on measurements of standard samples with precisely defined and known structural parameters (2, 3).

Some electric utilities have begun converting to polymer composite materials for some types of insulators. Composite insulators are less costly, lighter in weight, and excellent hydrophobic capability. This combination makes them ideal for service in polluted areas. However, these materials do not yet have the long-term proven service life of glass and porcelain. It has been discussed in former researches that aging and pollution performance of a composite insulator is closely linked to the properties of the material (4,5). It is well known that most polymers are inherently electrically insulating by nature. The ability of polymers to behave as insulators is one of the main reasons for their extensive use in the electrical and electronics area. To increase the electrical resistivity of polymers is to incorporate inorganic particles such as organic filler.

Experimental Procedure:

1- Ultrasonic Technique

The ultrasonic wave velocities (longitudinal V_L and shear V_S) at room temperature were obtained using the pulse-echo method. In this method, x-cut and y-cut transducers (KARL DEUTSCH) operated at frequency 4 MHz and a digital ultrasonic flaw detector (KrautKramer USIP20) was used. The uncertainty in the measurements of ultrasonic wave velocities is $\pm 13 ms^{-1}$for longitudinal wave velocity and ± 9 ms^{-1} for shear wave velocity. The two velocities with the density measurements with accuracy 1 kgm^{-3}, were used in determining two independent second-order elastic constants (SOECs), namely, the longitudinal (L) and shear (G) moduli. L and G described the elastic strain produced by a small stress in an isotropic amorphous elastic solid. For pure longitudinal waves $L = \rho V_L{}^2$ and for pure transverse waves $G = \rho V_S{}^2$. The elastic bulk modulus (B), Young's modulus (E), micro-hardness (H) and Poisson's ratio (σ) can be determined from L and G using the standard relations adopted (6, 7). The uncertainty values in the elastic moduli were ± 0.5, ± 0.2, ± 0.1, ± 0.2 GPa and ± 0.008 for (B), (E), (G), (H) and (σ) respectively.

$E = (1+\sigma)\, 2G$, $\sigma = [(L-2G)/2(L-G)]$

$H = (1-2\sigma)E/(6(1+\sigma))$

2- Dielectric Technique

The dissipation factor for sets of polyester and composite samples has been evaluated according to ASTM D150-64T.

Results and discussion:

Experimental values of density, ultrasonic wave velocities (longitudinal and shear), elastic moduli and Poisson's ratio of the investigated samples are listed in Table (1). First of all, Table 1 shows the result of pure polyester samples, aging improves the elastic moduli for pure polyester samples.

Table1, also shows the experimental estimated values of the elastic moduli of the samples, longitudinal modulus L, shear modulus G, Bulk modulus B, Poisson's ratio σ , Young's modulus E and the micro-hardness H. As seen from the table, the elastic moduli values of L, G, B, E increases as the filler percentage increases and this may be due to the increase in the average number of bonds per unit volume and cross link density which is related to increasing of hardness and rigidity of the sample material.

Figure 1, Illustrates the density of pure new sample is 1195.3 kg/m^3 and 1225.16 kg/m^3 for old sample. In addition the values of densities of samples are increased with increasing the ATH filler percentage. It was 1508.63 kg/m^3 for 40% ATH and 1752.89 kg/m^3 for 70% ATH filler percentage for the new samples and ranging from 1516.26 kg/m^3 with40% ATH filler to 1766.86 kg/m^3 with 70% ATH filler for the old samples.

The increase of densities for new and old samples with both types of fillers is due to the direct addition of the ATH. We notice that the densities of the old samples with the same concentrations of ATH behaves with the same manner but the densities of the old ATH filled Polyester-styrene group is higher than that the densities of the new group of samples and this may be due the improvement of the dimensionality of the polyester structure by aging.

The density values behave the same way in the polyester/styrene new and old samples filled by silica with the same percentages. It increased from 1554.9 kg/m^3 with 40% silica filler to 1851.27 kg/m^3 with 70% percentage for the new samples and from 1547.58 kg/m^3 to 1903.55 kg/m^3 for the old samples.

Figures 2, shows the values of longitudinal and shear ultrasonic wave velocities increased as the ATH and Silica fillers percentage increases respectively.

Table (1): Density, ultrasonic wave velocities, elastic moduli and Poisson's ratio of the investigated samples

F/PE %	Density (kg/m^{3})	V_L (m/s)	V_S (m/s)	L(Gpa)	G (GPa)	B (Gpa)	Σ	E (Gpa)	H (Gpa)
					ATH NEW				
0	1195.30	2500.00	1250.00	7.471	1.868	4.980	0.3333	4.980	0.2075
40	1508.63	2790.70	1470.59	11.749	3.263	7.399	0.3078	8.534	0.4181
50	1587.56	3045.68	1580.11	14.726	3.964	9.441	0.3159	10.431	0.4866
60	1689.54	3172.77	1714.29	17.008	4.965	10.387	0.2938	12.848	0.6824
70	1752.89	3240.64	1875.00	18.408	6.163	10.192	0.2484	15.386	1.0337
					ATH old				
0	1225.16	2571.43	1282.05	8.101	2.014	5.416	0.3346	5.375	0.2221
40	1516.26	2840.30	1428.57	12.232	3.094	8.106	0.3307	8.235	0.3493
50	1623.34	2964.43	1515.15	14.266	3.727	9.297	0.3232	9.862	0.4393
60	1707.23	3177.59	1666.67	17.238	4.742	10.915	0.3102	12.427	0.5999
70	1766.86	3309.89	1828.15	19.357	5.905	11.483	0.2805	15.123	0.8641
					Silica New				
40	1554.90	2890.47	1500.00	12.991	3.499	8.326	0.3157	9.206	0.4298
50	1618.29	2927.54	1600.00	13.870	4.143	8.346	0.2870	10.664	0.5882
60	1712.22	3125.65	1739.13	16.728	5.179	9.823	0.2758	13.214	0.7741
70	1851.27	3385.48	1960.78	21.218	7.118	11.728	0.2476	17.760	1.1975
					Silica Old				
40	1547.58	2808.63	1399.25	12.208	3.030	8.168	0.3349	8.090	0.3334
50	1612.95	2890.71	1500.00	13.478	3.629	8.639	0.3158	9.550	0.4458
60	1688.13	3087.33	1720.05	16.091	4.994	9.431	0.2749	12.735	0.7493
70	1803.55	3344.64	1953.13	20.176	6.880	11.002	0.2413	17.080	1.1867

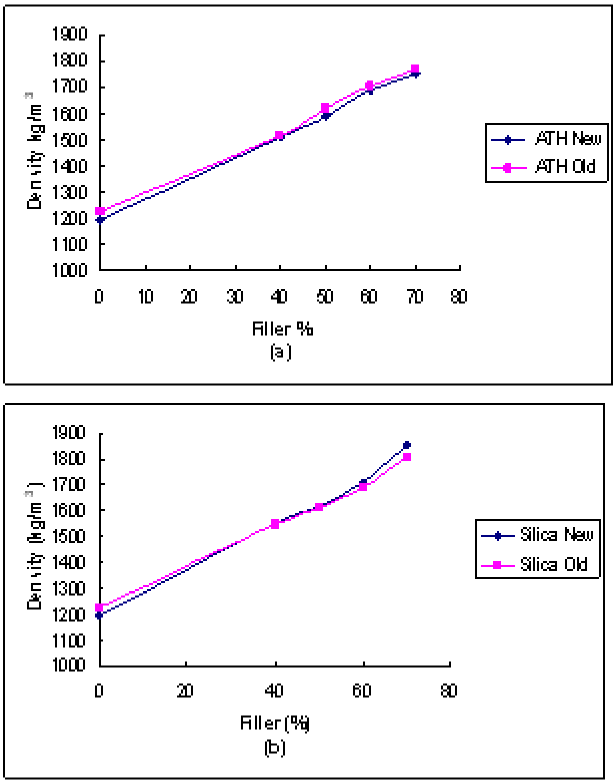

Fig. 1 Variation of Density of the Polyester composite filled wit (a) ATH and (b) Silica Fillers with the Filler Percentage for both new and old samples

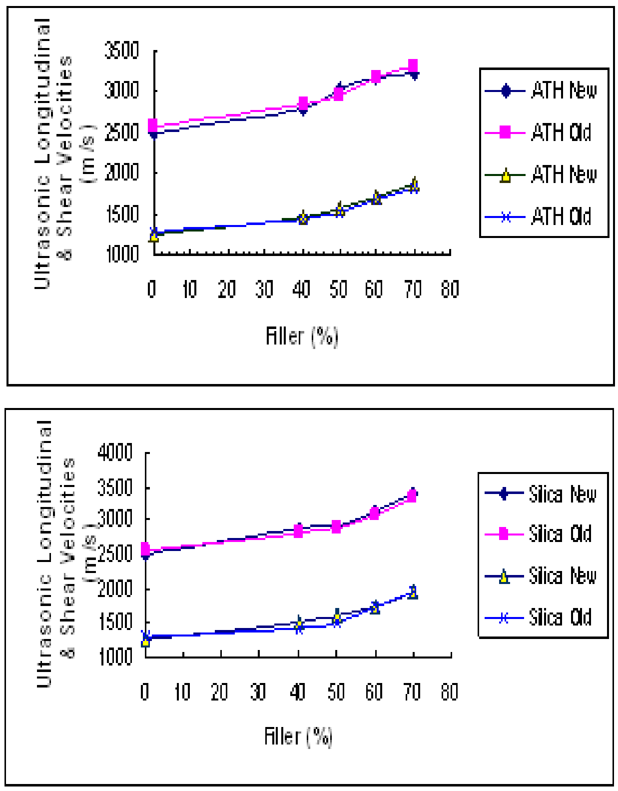

Fig. 2 Ultrasonic Longitudinal & Shear Velocities for the Polymer Composite filled with ATH filler and Silica filler and the filler Percentages for new and old samples

For longitudinal ultrasonic wave velocities, the values increased from 2500 m/s for pure polyester samples and 2790.9 m/s for 40% ATH filler to 3240.64 m/s for 70% ATH filler, in the new samples (first group) and in the second group (old samples) the longitudinal ultrasonic wave velocity increased from 2571.43 m/s in the pure polyester sample to 2840.3 m/s for 40% ATH to 3309.0 m/s for 70% ATH filler. In silica filled styrene-polyester samples, the ultrasonic velocity increased by increasing the concentration of the silica filler. It was 2890.47 m/s for the 40% silica and 3385.48 m/s for 70% filler for the new samples where it was 2808.63 m/s for 40% silica and 3344.64 m/s for 70% silica for the old samples.

In general, the increase of ultrasonic wave velocities is related to the decrease in the inter-atomic spacing of the material (increase in density or decrease in molar volume). This means that the structure of polyester samples improved with increasing the filler ATH or SiO2 percentage and aging. Also, the increase in longitudinal and shear ultrasonic wave velocities may be attributed to the increase of connectivity of the polyester network.

Figure 3, shows the variation of bulk modulus (B) and Young's modulus (E) with the fillers percentage. It is noticed that the bulk modulus (B) is 4.980 GPa for pure polyester/styrene new sample and 5.416 GPa for aged pure sample. Also as ATH filler percentage increase the bulk modulus (B) increase from 7.399 GPa for 40% to 10.192 GPa for 70% for new samples and from 8.106 GPa for 40% to 11.483 GPa for 70% filler percentage old samples. Also the values of Young's modulus were 4.98 GPa for pure polyester/styrene new samples and 5.375 GPA for the old sample. As the ATH filler added to the polyester samples, Young's modulus ranging from 8.534 GPa for 40% ATH filler to 15.386 GPa for 70% filler percentage for new samples and from 8.235 GPa for 40% ATH filler samples to 15.123 GPa for 70% filler percentage for old ATH samples. The same trend for the polyester samples with silica filler, figure 4, the bulk modulus (B) and Young modulus (E) increase by increasing the silica filler as in figure 5. Bulk modulus (B) increased from 8.326 GPa at 40% filler to 11.728 GPa for 70% filler percent for the new samples while the values of (B) increase from 8.168 GPa for 40% to 11.002 GPa for 70% filler percent. Also, Young's modulus increase from 9.206 GPa with 40% silica filler to 17.760 GPa and from 8.090 GPa at 40% filler percent to 17.080 GPa at 70% filler percent for the new samples while it increased from 8.090 GPa at 40% filler percent to 17.080 GPa at 70% filler percent.

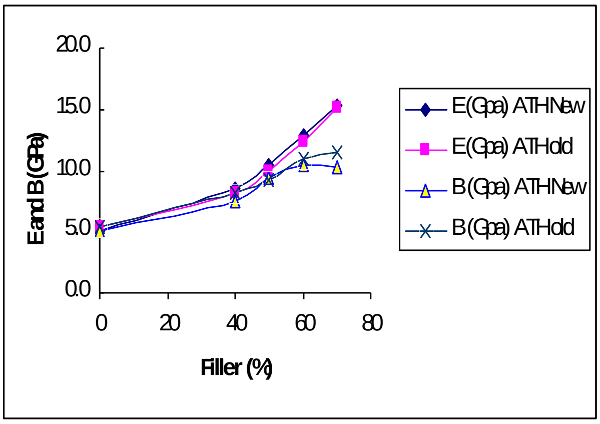

Fig. 3 Relation between Bulk (B) and Young's (E) Moduli for new and old samples of Polyester filled with different percentages of ATH filler

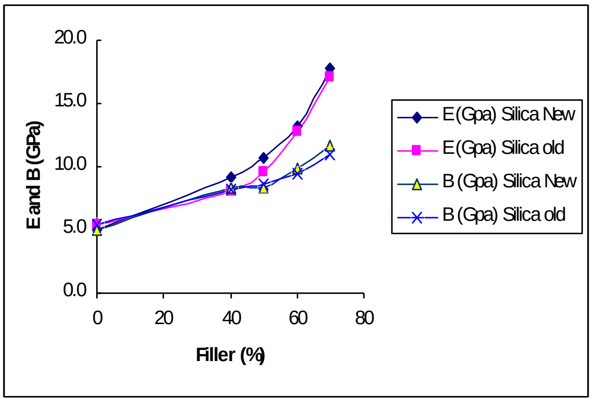

Fig. 4 Relation between Bulk and Young's Moduli for new and old samples of Polyester filled with different percentages of Silica filler

It is clear that from the above results that the type of bonding in the network structure plays a dominant role in deciding the rigidity of the sample structures. It is believe that the behavior of both bulk and Young's moduli are associated with the change in cross linkage coordination of the structure of the samples network (8).

Figure 5, illustrates the relation between the Poisson ratio and filler Percentage. In pure new samples of polyester it was 0.3333 and for old pure sample was 0.3346. Poisson's ratio decreased with increasing the filler percentage in both ATH and silica fillers as in table 1.The decease in σ is due to the increase in the cross link density of the samples.

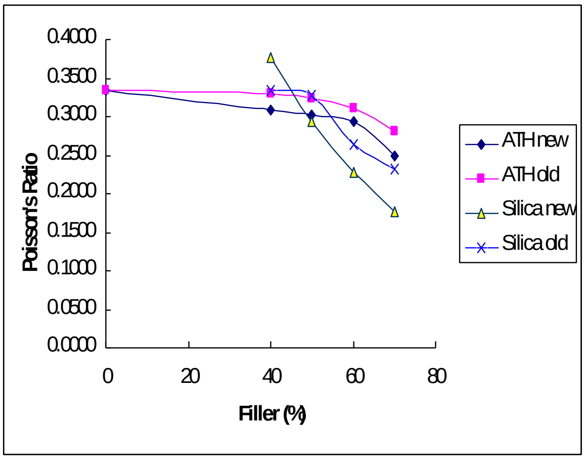

Fig. 5 Poisson's Ratio for new and old samples filled wit ATH and Silica fillers vs. filler percentages

It can be seen from table (1) that, the micro-hardness measured ultrasonically has the same trend as the elastic moduli, hence the observed increase in (H) is related to increase the rigidity of the samples.

Dielectric Property

The dielectric property of polyester samples was characterized in term of dissipation factor (tan δ) at different frequencies, ranging from 100 Hz to 0.1 MHz. The dissipation factor (tan δ) is the degree of electrical energy loss in insulation and is a key factor to evaluate its performance as insulator (9, 10). The relationship between the filler percentage (%) and the dissipation factor at frequency 100 Hz for old and new samples is shown in figure 6. From this figure it can be noticed that, the dissipation factor decreases with increasing the percentage of both ATH and Silica fillers for all samples (old and new).

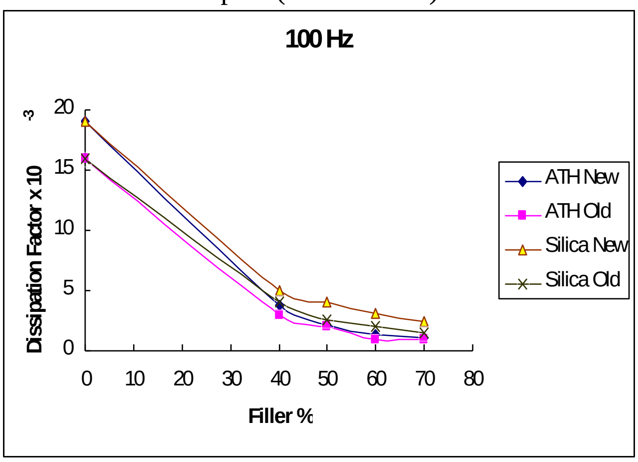

Fig. 6 Variation of the Dissipation Factor in the new and old samples of polyester filled with different percentages of ATH and Silica fillers at frequency 100Hz

For example, at new samples with silica filler, the dissipation factor (tan δ) is 0.019, 0.005, 0.004, 0.0031 and 0.0025 for 0, 40, 50, 60 and 70 % filler respectively. The values of dissipation factor (tan δ) for old samples with both ATH and silica are less than that of the new samples. At 70% ATH filler old sample, the dissipation factor is less than that of the new sample by about 9% while with the same percentage of silica filler the dissipation factor for the old sample is less than that the new one by about 40%.

Figure 7, illustrates the dissipation factor (tan δ) at frequency 0.1 MHz against the filler percentage (%) for old and new samples. It can be observed from this figure that, for all samples of ATH and silica fillers old and new, the values of the dissipation factor (tan δ) decreased as the filler percentage (%) decreases.

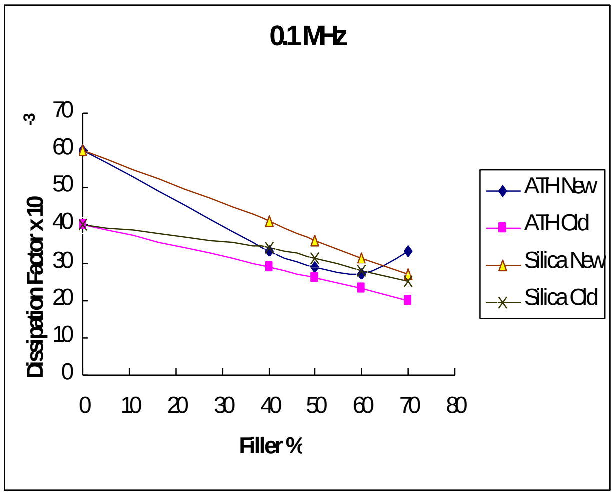

Fig. 7 Variation of the Dissipation Factor in the new and old samples of polyester filled with different percentages of ATH and Silica fillers at frequency

I.e., the values of dissipation factor (tan δ), for old samples with ATH filler, are 0.04, 0.029, 0.026, 0.023 and 0.02 for samples with filler percentage (%), 0, 40, 50, 60 and 70 respectively.

Same trend for values of dissipation factor (tan δ) old and new samples for both ATH and Silica fillers at frequency 0.1 MHz, the dissipation factor (tan δ) at frequency 100 Hz.

Also it is noticed that, for old samples, the dissipation factor (tan δ) less than that the new samples by 13% for 70% filler percentage ATH filler and less by 7.4% for the same percentage for the silica fillers.

Figure 8, shows that the dissipation factor (tan δ) for samples with both ATH and Silica Fillers (new and old) of various frequencies (1k, 30k, 60k and 80k) Hz under constant filler percentage 70%.

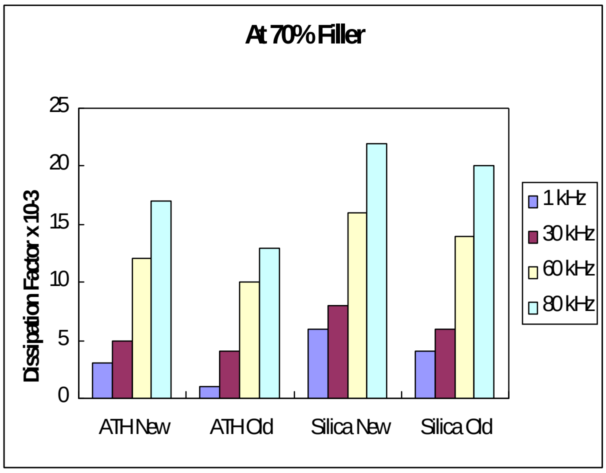

Fig. 8 Dissipation factor of new and old samples of polyester with 70% of ATH and Silica filler at frequencies 1, 30, 60 and 80 kHz

It can be seen from this figure that, the dissipation factor (tan δ) increase as the frequency increase for all types of samples. Old samples with Silica filler reach values of dissipation factor 4, 6, 14 and 20 x 10^{-3} at 1 kHz, 30 kHz, 60 kHz and 80 kHz. Also one can notice that the dissipation factor (tan δ) for old samples with both ATH and Silica fillers is less than that for the new samples. Same trend can be observed at all frequencies under investigation (1 k, 30 k, 60 k and 80 k) Hz. The reduction of the dissipation factor for the ATH samples is less than that for the silica filler samples so one can say that the polyester with ATH filler is better than that of silica filler samples for both old and new samples [(9)]. For example, at frequency 60 kHz, the values of the dissipation factor are 10 x 10^{-3} and 12 x 10^{-3} for old and new samples with ATH filler respectively, while, it was 14 x 10^{-3} and 16 x 10^{-3} for old and new samples with silica filler samples respectively. From the results, it can be conclude that, type and percentage of filler play important rule on the values of the dissipation factor (tan δ). Old samples (aging 20 years) have good dielectric properties as insulating material and this may be due to the increasing in the cross-link density of the polyester network.

Conclusion

The density, ultrasonic velocities, elastic properties and electrical dissipation factor studies on the network structure of polyester filled with ATH and silica fillers reveal the following conclusions: The density of samples under investigation increases with increasing of the two types of fillers percentages. Aging affect the densities of the old samples with ATH filler while it is nearly not change in the samples filled with silica. Aging has no remarkable effect on the ultrasonic velocities for both ATH and silica groups of samples. Velocities increase with increasing the fillers percentage which is interpreted as due to the increase in the connectivity of the network structure. Elastic moduli increase with increasing both types of fillers ATH and silica percentage in the samples while it slightly decreases with aging. Poisson's ratio decreases as both fillers percentages increases. Poisson's ratio of aged samples slightly higher than that of recent samples the may be due to the percentage of filler increases the cross-link density of the network structure. The reduction of the dissipation factor for the ATH samples is less than that for the silica filler samples so one can say that the polyester with ATH filler is better than that of silica filler samples for both old (prepared from 20 years) and new samples.

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