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Ageing Study on Glass Fiber Composite Rod of Silicone Rubber Insulators

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SUMMARY

Contribution of Silicone Rubber Insulators (SRI) also called as composite insulators is continuously increasing in transmission and distribution network. The load bearing component of composite insulator is Glass Fiber Reinforced (GFR) composite rod. The long term performance of SRI depends on the quality of composite rod which can vary depending on the material properties namely type of glass fibres and resin as well as the manufacturing process parameters. All these factors result in wide variation in quality of insulator composite rod. The conventional methods of composite rod analysis may not be adequate to filter out the poor quality rod which results in premature failure of insulators. In this paper, we report Dynamic Mechanical Analysis (DMA) of: 1) GFR composite rod samples removed from SRI with known service history and 2) chemically aged composite rod samples. DMA measurements carried out on composite samples with poor service history showed Tan δ (damping) peak with increased intensity and peak width. On the other hand composite sample removed from insulator with good service history showed increased glass transition (Tg) and Tan δ peak having low intensity and decreased peak width. To understand the changes in Tan δ at various states of degradation, accelerated ageing of GFR composite was carried out in a Nitric acid solution. The aged samples were periodically analysed using DMA and Scanning Electron Microscope (SEM). DMA analysis of the aged samples showed three distinct zones in growth of Full Width of Half Maximum (FWHM) of Tan δ peak. As per the degradation state, the width of Tan δ was observed to be growing. Additional shoulder on the Tan δ appeared for samples with longer ageing time. The Tan δ peak of DMA is the result of segmental motions of resin matrix chains during glass transition (Tg). The molecular motions involved in the glass transition depend on filler concentration and interfacial interactions between resin and glass fibers. Therefore, the shape and intensity of Tan δ peak changes depending on the glass fiber and resin interactions. For composites having better interfacial properties, the inter-phase is large where segmental motions are constraint resulting in higher Tg and smaller Tan δ values. The additional shoulder of Tan δ peak for composite rod samples with longer ageing time indicated weak interface between glass fiber and resin matrix. SEM images of the aged GFR composite sample after weakened interface also showed micro-cracks. This showed that the poor interfacial properties also results in growth of micro-crack which are susceptible to partial discharge and resulting in degradation of the insulator rod. The experimental results suggest that DMA will be good analytical technique for evaluation of composite rod.

KEYWORDS

Silicone Rubber Insulator, Composite insulator, DMA, glass fiber composite, degradation, glass transition, Tan δ

1.0 Introduction

Insulators have a long history of application in electricity distribution and transmission networks. Glass and porcelain insulators are in use for more than 100 years. They have outstanding insulating properties and good mechanical properties but they are heavy and easy to fracture and therefore susceptible to vandalism. Also, in polluted environment service life of glass and porcelain insulators is very low. To overcome these problems, insulators with composite rod and polymeric housing were developed in the 1970s [1]. Share of polymer insulators in transmission line started increasing from 1990s in the USA. Now, due to their low cost, very low weight and better pollution performance, Silicone Rubber Insulators (SRI) have captured large share of insulator market in India and rest of world. Failures in SRI are relatively lower but are not uncommon. Failures are costly due to downtime, repair costs and results in disruption in services. Therefore long term reliability of insulators is prime importance for any operator of the transmission line. Composite insulators are made up of Glass Fiber Reinforced (GFR) composite rod which is the load bearing component of the insulator. Silicone rubber housing is used for protecting the composite rod from external environment. A survey carried by EPRI in the USA is reported in CIGRE TB 481, it described the most common failure mechanisms in SRI. The survey results showed that the reason for failure of the SRI was brittle failure (44%), mechanical failure (9%) and destruction of rod due to discharge activity (10%) [2]. Altogether composite rod is responsible for approximately 63% of failure of composite insulators.

Such detailed survey is not available with us for India. However, our recent paper showed that the poor quality of composite rod along with increased electrical stresses can result in failure of SRI [3]. The poor quality (micro-cracks) of the composite rod was not detectable using dye penetration or water diffusion tests mentioned in IEC 62217/61109. However, the micro-cracks in the composite rod were visible in stereo microscopic observations. Microscopic observation is a qualitative and more localised test (covers small area) and it also depends on operator skill. Therefore, in this paper we report, Dynamic Mechanical Analysis (DMA) as a characterization method for composite rod analysis.

It is evident from EPRI study and our analysis of SRI failures that poor quality of composite rod can lead to insulator failures. The quality of the GFR composites may vary depending on type of glass fibers used, type of resin matrix along with manufacturing processes and parameters. This large variability in parameters can result in varying properties of the composite rod. The traditional methods for determining quality of composite rod may not be sufficient to account for issues arising from different mechanical and electrical stresses that the composites are subjected in an insulator. Therefore, it is important to develop new test methods which can predict long term properties of composite material in an insulator. For this purpose, composite rods from insulators were subjected to accelerated ageing in a chemical solution. The samples were periodically analysed using Dynamic Mechanical Analysis (DMA) and microscopic observations. Also, composite samples with known history was analysed using DMA. The DMA results show distinct features of composite materials which can be helpful in predicting long term properties of GFR composites in insulators.

2.0 Ageing and Characterization

Some composite samples for this work were removed from various insulators with known service history. The ageing experiments were carried out on samples from a new insulator with no service history (field performance of this insulator is nil because it was a new insulator). Sample details with their service history are listed in Table I. The three types of insulators listed in Table I are from three different manufactures therefore their glass content, resin system and manufacturing processes may have been different.

Table I. Composite insulator used for analysis

Sample Name	Service History
Type -1- Failed	Failed insulator after 10 years of service (Make-1)
Type -1 from store	Not in use insulator from same batch (Make-1)
Type - 2	Insulator with good service history (Make-2)
Type - 3	New insulator used for ageing study (Make-3)

2.1 Specimen Preparation

Composite rod was removed from the insulator by separating the silicone rubber sheath. Required dimension specimen were cut from the composite rod using precision saw. Specimen used for DMA had size of 50 mm x 4 mm x 2 mm, length, width and thickness, respectively. Samples used for DMA are shown in Figure 1.

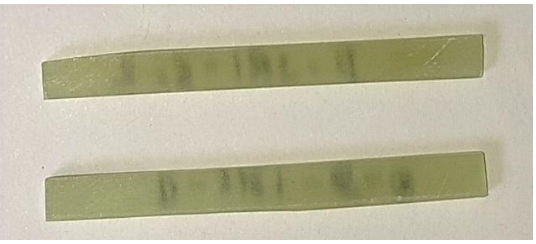

Figure 1. Specimen for DMA analysis cut from composite rod of insulator

2.2 Sample Ageing

Nitric acid is formed on insulators in presence of electrical discharges and moisture present in the air [4][5]. This mechanism of acid formation is known for brittle fracture of composite rod. Presence of Nitric acid can lead to degradation of the resin resulting in failure of composite insulation. Therefore, Nitric acid was used in this work to accelerate the degradation process of GFR composite. Nitric acid solution of different molarity (0.25 M, 0.5 M and 1 M) was used for chemical ageing of composites. The samples were immersed in Nitric acid solution and kept in closed glass bottles. Samples were removed for analysis after each 30 days cycle. Before DMA measurements, the samples were removed from ageing solution and dried in air circulation over for 1 hour at 80 °C.

2.3 Dynamic Mechanical Analysis (DMA)

DMA is a characterization method for evaluation of visco-elastic properties of polymers and composite materials. DMA measures material response as a function of applied small cyclic deformations. The measured properties are loss modulus (viscous response indicated by E'') and storage modulus (elastic response indicated by E'). The ratio of loss modulus to storage modulus gives damping factor 'Tan δ' also called mechanical damping or dissipation [6]. Typically, peak of loss modulus represents glass transition temperature (Tg) of a material. Compared to Differential Scanning Calorimetry (DSC) the Tg in DMA is observed at a higher temperature. However, DMA is more sensitive for Tg as compared to

DSC. Tg measurements are difficult and sometimes impossible using DSC for highly filled composites, for example glass fiber composites of insulator (core).

The DMA measurements described in this paper were carried out using Perkin Elmer DMA 8000, refer Figure 2a. Dual cantilever assembly was used for DMA analysis of composite samples, as shown in Figure 2b. Unless specified, all the DMA measurements were carried out at 1 Hz frequency and 0.05% strain.

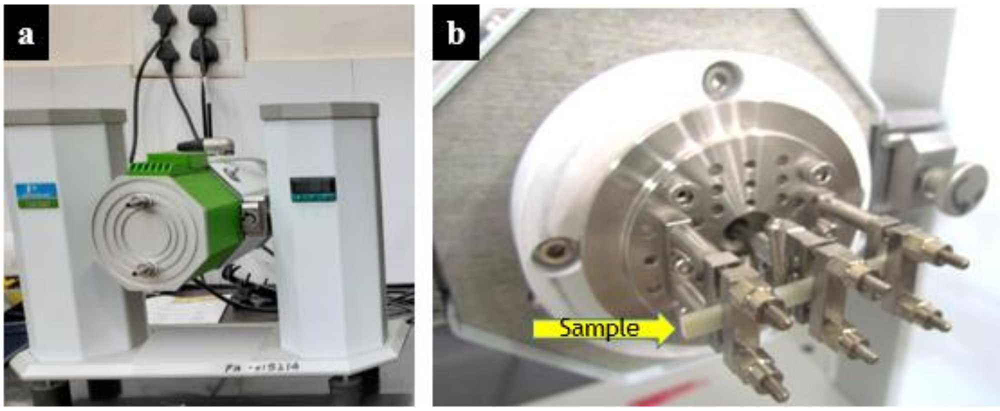

Figure 2. a) DMA instrument and b) Dual cantilever assembly with composite sample

3.0 Results and Discussion

3.1 DMA Measurements

Figure 3a shows the DMA results of Type-3 insulator, the storage modulus (E') decreases above 110 °C, simultaneously with decrease of E' the loss modulus (E") shows a peak at 125 °C which indicate Tg. The glass transition process in composite material is related to segmental motions of resin matrix, also referred as α-relaxation. During α-relaxation, the polymer chains are involved in large scale cooperative motions [7]. For composite materials only the polymeric chains from resin is responsible for the loss modulus peak observed in Figure 3a. The glass fibres, used as filler, in the composite are in solid state and does not contribute to the segmental motions responsible for Tg. Similarly the Tan δ or Mechanical damping is also related to resin matrix. Sometimes Tan δ peak is also referred as Tg. In this paper, DMA results are analysed with the help of Tan δ, therefore for simplicity Tan δ peak is considered as Tg of composite samples.

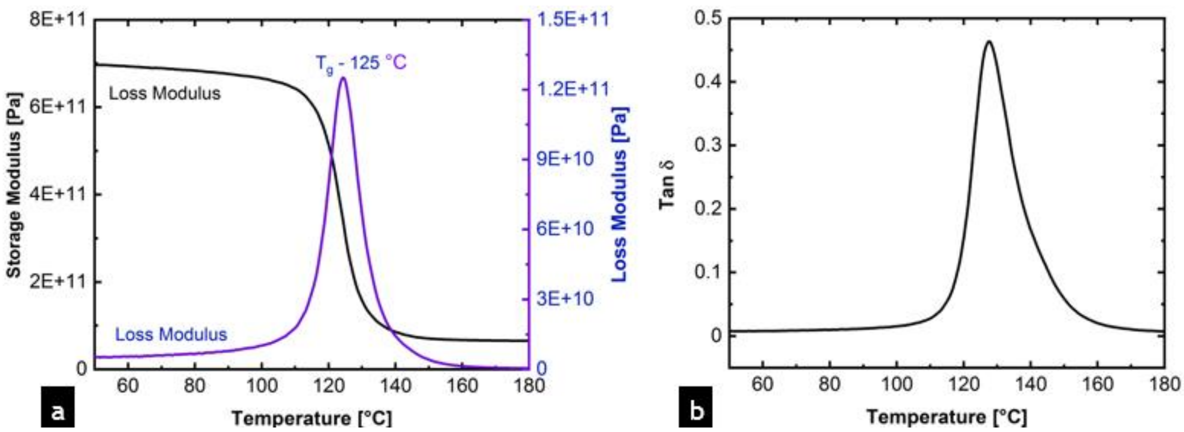

Figure 3: DMA results of composite sample of Type-3 insulator: a) Storage and loss modulus and b) Tan δ

Since the Tan δ peak is related to segmental motions of polymeric chains from resin, the shape and position of the Tan δ peak changes depending on the resin and filler interactions. Better resin and filler interactions lead to restricted motions of the polymer chains resulting in shifting the Tg to higher temperatures with simultaneous reduction in intensity of Tan δ peak [8]. Therefore, Tan δ values are also used to calculate interfacial shear strength (IFSS) in a composite materials [9]. IFSS quantifies the strength of interface between resin matrix and fillers. Interfacial strength affects most of the mechanical, chemical and thermal properties of composites. High interfacial strength indicate enhanced properties of composites. The interfacial strength in glass fiber composite is inversely proportional to Tan δ. This indicates that lower Tan δ value (peak intensity) is better indicator of quality of composite.

3.2 DMA Measurements of Samples with Known Service History

Composite samples were removed from two types of insulators installed on a 400 kV transmission line; these insulators were from two different manufacturers. Type-1 insulators had poor service history with many failures and Type-2 insulators were having good service history with zero failure, both installed on same transmission line, described in our earlier paper [3]. Tan δ measurements of both types of insulator are shown in Figure 4. The composite from poor service history shows Tan δ peak with larger width and height with lower peak temperature, showing Tg of 124 °C. Composite from Type-2 insulator shows smaller width and reduced height with higher peak temperature, showing increased Tg of 146 °C. The increased width of the Tan δ peak for Type-1 insulator indicates relaxation processes in the composite taking place on a wider temperature range. Type-1 failed insulator, after 10 years of service life, also shows a small shoulder/bump indicated by arrow in Figure 4. The shoulder in Tan δ peak indicates another relaxation process which does not appear prominently for the insulator sample which was un-used.

To resolve the shoulder visible in the Tan δ peak from sample of Type-1 failed insulator, DMA measurements were carried out at different frequencies as shown in Figure 5a. Tg being frequency dependent phase transition process, measurement at low frequency helps in separating the shoulder appeared on the Tan δ peak. Figure 5b shows Gauss multi-peak fit for Tan δ measured at 0.1 Hz. It appears that the resin matrix goes through two individual relaxation process resulting in two peaks of Tan δ. The low temperature relaxation process peak is at 112 °C and the high temperature relaxation process peak is at 141 °C. The ageing related degradation of GFR composite properties may be related to the appearance of second relaxation process contributing to the Tan δ peak. To understand the effects of ageing process on Tan δ peak, GFR composite samples were chemically aged to understand the degradation process.

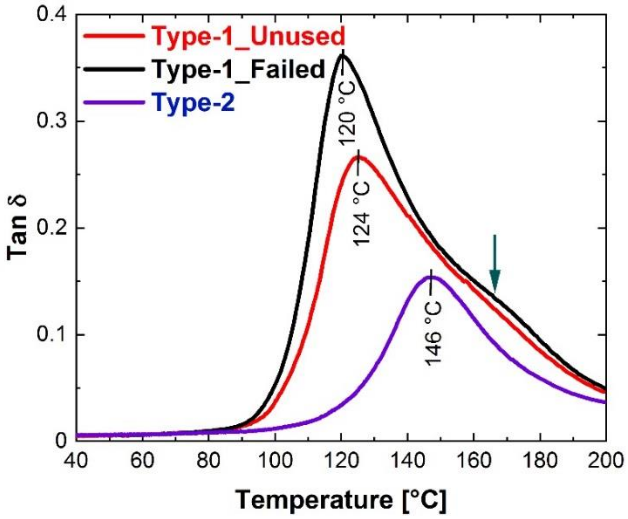

Figure 4: Tan δ graphs of composite samples having different service history. Peak temperatures indicating Tg is shown. The arrow indicate a shoulder/bump in the Tan δ peak for a failed insulator.

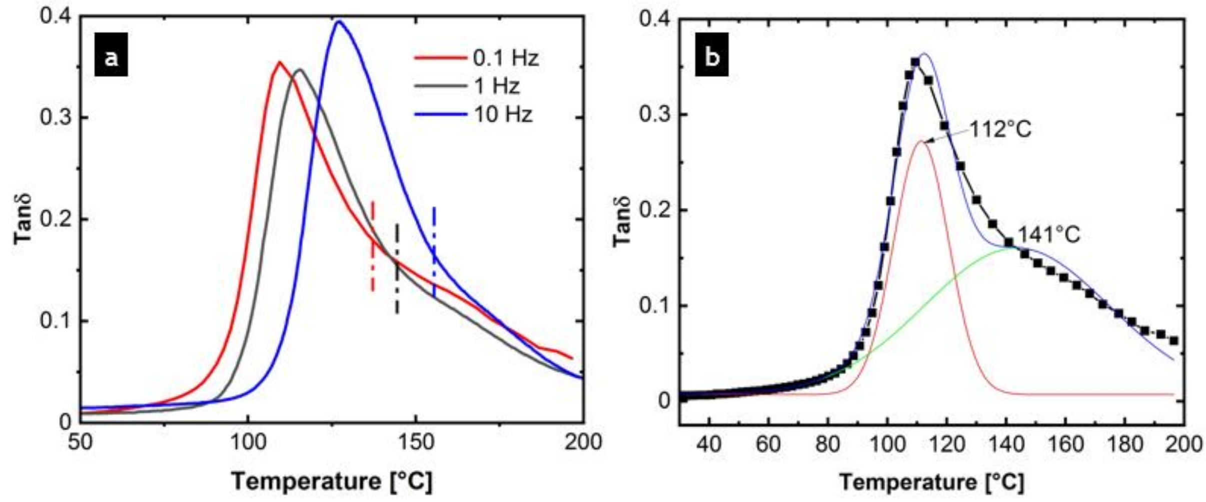

Figure 5: a) Tan δ measured at different frequencies (second peak starting point shown by broken line) and b) Gauss multi-fit for Tan δ measured with 0.1 Hz frequency, the measure data is indicated by black symbols with line. Fitting lines are thin solid.

3.3 DMA Measurements of Aged Samples

The composite samples from Type-3 insulators were chemically aged and after each 30 days interval DMA measurements were carried out. Figure 6 shows the waterfall plot of Tan δ against temperature and ageing time. The graph shows that as the ageing of the samples progresses the Tan δ peaks become broader and in late stages of ageing, a second peak appeared at around 145 ˚C. Similar phenomenon was observed for the field aged samples as described in section 3.2.

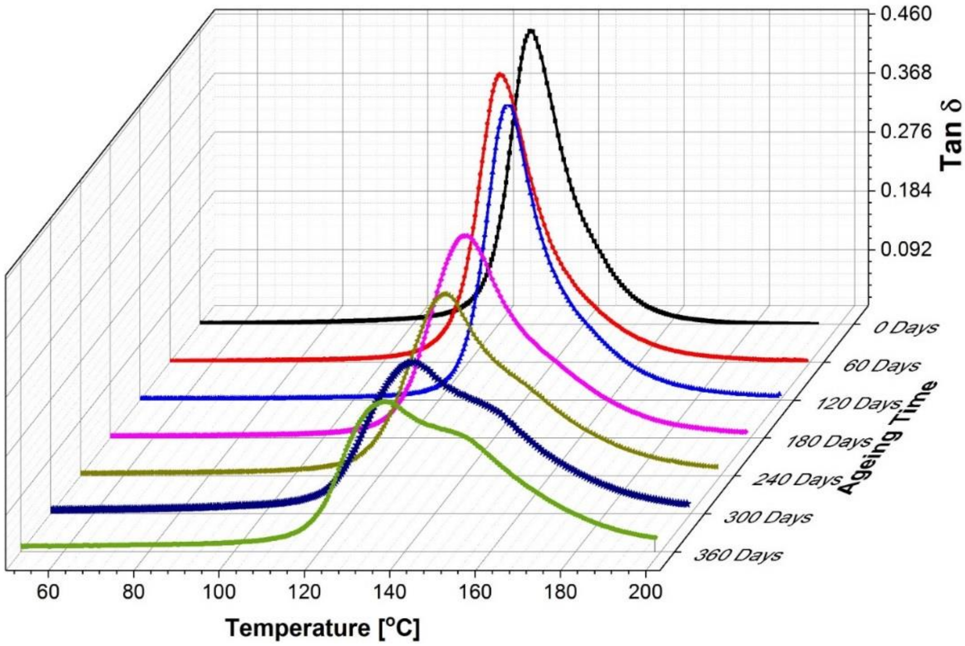

Figure 6: Waterfall plot of Tan δ of composite samples from Type-3 insulator. Periodic measurements of chemically aged samples over a period of 1 year

The broadening of Tan δ peak width was analysed by measuring the Full Width of Half Maximum (FWHM) for each peak. FWHM is plotted against ageing time in Figure 7, this plot shows three distinct zones:

- Zone – 1: the FWHM is almost constant for ageing time up to 120 days,
- Zone – 2: continuous increase in peak width for ageing time ranging from120 days to 270 days
- Zone – 3: above 270 days of ageing time there is sharp increase in slope because of prominent appearance of second Tan δ peak

Tan δ is related to glass transition, where a material changes its behaviour from solid and rigid, below Tg, to rubbery, above Tg. Onset of Tan δ peak indicates start of polymer segmental motions involved in cooperative motion of polymer chains between cross-linking points in a thermoset resin. If the cooperative motions of chain segments are constrained, the glass transition temperature (Tg) increases. The width of the Tan δ peak depends on number of chain segment taking part in the relaxation process at a particular temperature. Additional restrictions by filler particles or increase in crosslink density can result in increased width of Tan δ peak, with simultaneous decrease in intensity. It appears in zone-2 that the width is increasing with a constant rate with ageing time because of chemical cross-linking of the resin. Increase in tensile modulus due to chemical ageing is reported in literature, due to increased chemical cross-linking the tensile modulus increases because of better fiber - resin interactions [10]. However, in this case the storage modulus found to be decreased after 90 days of ageing time, as shown in Figure 7. Storage modulus does not indicate improved interfacial interactions between resin matrix and glass fibers. Therefore, the restricted segmental motions may be the result of increasing crosslinking density within the resin matrix. This results in increased width of Tan δ in zone-2 with simultaneous decrease in the height of peak. Leaching of the resin matrix in the acidic solution can not be ruled out, this results in less number of polymer chains taking part in the glass transition process thereby decreasing the height of Tan δ peak.

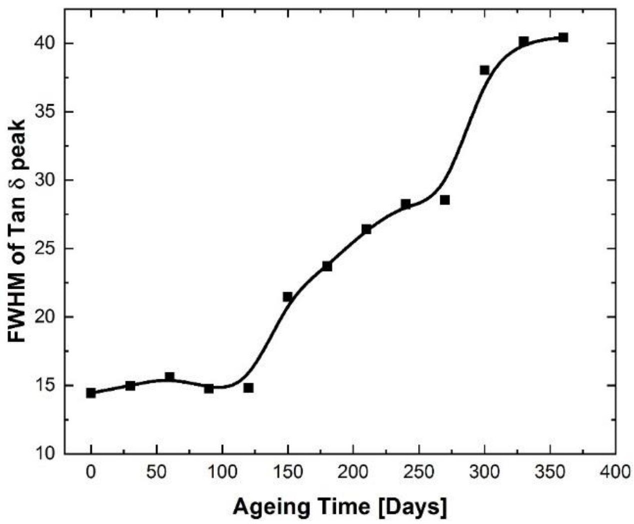

Figure 7. FWHM of Tan δ peak plotted against ageing time

In zone-3, the increased width of Tan δ peak is related to the appearance of second peak for ageing time above 250 days. The second relaxation peak can be related to weakening of the interface between glass fibers and resin matrix. Performance of glass fiber composite is strongly depended on adhesion between glass fibers and resin matrix (shown in SEM images in Figure 9a and 9b), stronger interfacial properties contribute towards larger inter-phase region. Inter-phase in polymer composites (refer Figure 9C) is a region between fiber and matrix having different chain mobility, density and chain conformation compared to the bulk matrix [11]. The polymer chains in inter-phase region are highly restricted due to additional crosslinking and decreased free volume therefore they do not contribute to Tan δ peak observed in composites. Inter-phase affects most of the mechanical properties including tensile and shear strength. To make this inter-phase region stronger and larger, usually the glass fibers are treated with chemicals and this treatment is called sizing. Weaker interface and therefore smaller inter-phase region in composite can result in poor mechanical properties making it more susceptible to early degradation and failure.

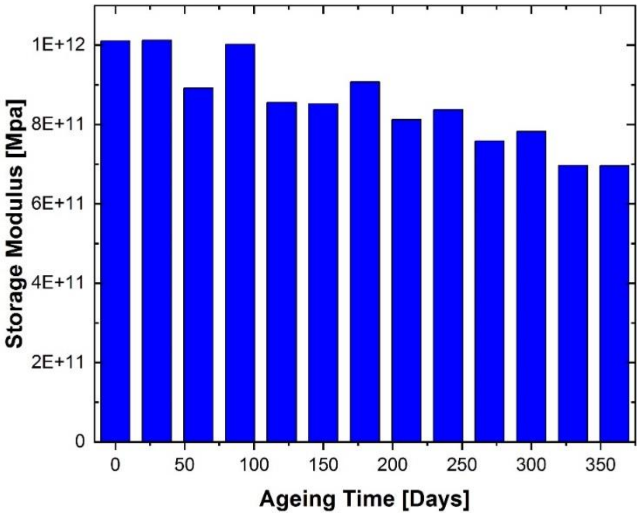

Figure 8. Storage modulus measured at 50 ˚C plotted against ageing time

In zone-3, the second Tan δ peak (shoulder) is related to weakening of the interfacial adhesion between glass fibers and resin matrix. Due to chemical degradation, the polymeric chains at the interface start separating from the glass fibers, making them mobile and visible in the form of second Tan δ peak. The second Tan δ peak is observed at higher temperature because the inter-phase is not completely dissociated from the glass fibers and chain mobility is still low as compared to the chain mobility in bulk matrix. The second Tan δ peak, can also be present in fresh composite samples having poor inter-phase due to inferior manufacturing processes.

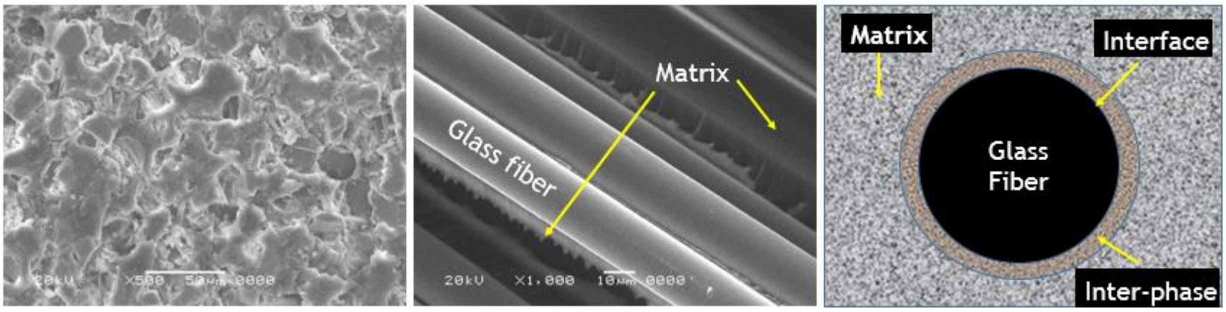

Figure 9: a) SEM image of glass fiber composites (top view), b) view from long axis direction after removal of outermost layer of composite and c) sketch of microscopic model of composite showing different regions of composite material

The weakening of the interfacial interactions can result in formation of micro-cracks in the composite material. Scanning Electron Microscope (SEM) observations of the samples before and after ageing (270 days) indicated growth of micro-cracks in the composite samples as shown in Figure 10. Presence of these micro-cracks in the composite rod of the insulator can lead to partial discharges and degradation of the composite insulator [3]. The micro-cracks visible in the SEM images indicate poor adhesion between glass fibers and resin matric, this confirms the DMA results indicating poor interfacial properties for composite samples chemically aged above 270 days.

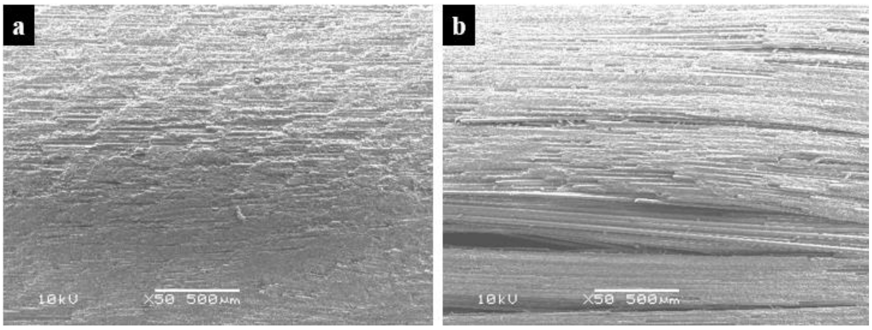

Figure 10: SEM images of sample for chemical ageing: a) Sample before chemical ageing and b) cracks developed after ageing of 270 days

4.0 Conclusion

Samples of GFR composite rod removed from silicone rubber insulators were analysed using Dynamic Mechanical Analysis (DMA). Analysis of the composite samples from insulators with known service history showed clear differences in the Tan δ peaks which can be correlated with their performance in field. Composite samples with poor service history showed broader and larger Tan δ peak with lower Tg along with an additional shoulder on the Tan δ peak. DMA results of composites samples with good service history showed smaller Tan δ peak with higher Tg.

Composite samples from a new insulator (with no service history) was aged in Nitric acid solution to study the degradation process. The aged samples were analysed using DMA, the results showed increasing width of Tan δ peaks with ageing time. The Tan δ peak FWHM showed three different zones indicating changes in the relaxation dynamics of polymer chains of the resin matrix. The additional shoulder to Tan δ peak appeared for samples with longer ageing time, indicating weakening of the interface between glass fibers and resin matrix. Good interfacial interactions between resin and glass fibers results in larger inter-phase region leading to enhanced mechanical properties of the composite material. Due to prolonged ageing, the interface becomes weaker resulting in additional segmental motions which appeared as shoulder to the Tan δ peak. The weak interface results in micro-cracks in the composite samples which are visible in SEM images, confirming the DMA results.

DMA can be a powerful method for analysis of composite rod of silicone rubber insulators. DMA has capability to evaluate the interfacial properties of composites which are better indicator of quality of composite materials. Therefore, use of DMA for quality evaluation of composite rod will be useful for selection of composite materials for better long term performance of silicone rubber insulators.

BIBLIOGRAPHY

[1] J. F. Hall, "History and bibliography of polymeric insulators for outdoor applications," *IEEE Trans. Power Deliv.*, vol. 8, no. 1, pp. 376–385, 1993.

[2] CIGRE TB 481, "Guide for the Assessment of Composite Insulators in the Laboratory after their Removal from Service," WG B2.21, 2011.

[3] N. R. Shingne *et al.*, "Analysis of 400 kV Failed Silicone Rubber Insulators: Role of Micro-Cracks in Glass Fiber Rod and Electric Field Distribution in Failure Mechanism – Case Study," in *Cigre e-Session 2020*, 2020, pp. 1–17.

[4] M. S. Kumosa, L. S. Kumosa, and D. L. Armentrout, "Failure analyses of nonceramic insulators

Part 1: Brittle fracture characteristics," *IEEE Electr. Insul. Mag.*, vol. 21, no. 3, pp. 14–27, 2005.

[5] A. R. Chughtai, D. M. Smith, and L. S. Kumosa, "FTIR Analysis of Non-ceramic Composite Insulators," vol. 11, no. 4, pp. 585–596, 2004.

[6] K. P. Menard, *Dynamic Mechanical Analysis A Practical Introduction*. CRC Press, 1999.

[7] E.-J. Donth, *The Glass Transition*, vol. 48. Berlin, Heidelberg: Springer Berlin Heidelberg, 2001.

[8] Y. S. Lipatov, *Polymer Reinforcement*. ChemTech Publishing, 1995.

[9] P. S. Chua, "Dynamic mechanical analysis studies of the interphase," *Polym. Compos.*, vol. 8, no. 5, pp. 308–313, 1987.

[10] K. Sindhu, K. Joseph, J. M. Joseph, and T. V. Mathew, "Degradation studies of coir fiber/polyester and glass fiber/polyester composites under different conditions," *J. Reinf. Plast. Compos.*, vol. 26, no. 15, pp. 1571–1585, 2007.

[11] Y. S. Lipatov, *Polymer Reiforcement*. ChemTech Publishing, 1995.