Laser ablation of silicone composites

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Abstract. Silicone rubber based composites are widely used to produce outdoor insulators. In adverse weather conditions these can be damaged by surface discharge activity resulting in deterioration of their dielectric properties and an eventual need for replacement. Inclined plane tracking tests are frequently used to determine the relative performance of different material formulations used in their construction. An alternative approach to characterisation is to use an infra-red laser to deposit known amounts of energy at a known rate to the sample’s surface allowing comparative ranking of different materials. In this paper several silicone based composites have been ranked using a laser ablation technique and the results were then compared to those obtained from tracking tests on the same materials. The comparison indicates that laser ablation ranks the materials in the same order as the tracking tests and may therefore constitute a quick and cost effective method for the routine characterisation of outdoor insulation components.

Introduction

Silicone rubber based composites are used widely for outdoor high voltage components such as bushings, cable strings and as weather resistant coatings. In adverse weather conditions, dry band discharges [1] can occur resulting in tracking and surface damage which can ultimately result in dielectric or mechanical failure. Traditionally these components are filled with either aluminium hydroxide (ATH), silica or a mixture of the two, to improve their tracking resistance and erosion performance and to reduce the amount of expensive silicone material [2-4]. It is important in designing such materials that good arc resistant composites are chosen in order to maximize lifetime and minimize downtime and maintenance costs. Inclined plane tracking tests [2] have proved useful in determining the relative resistance of different material formulations to surface damage and have indicated that materials having a high filler loading are beneficial up to the point where a good dispersion of the filler can be maintained [3]. An alternative test method is to use a high power laser to apply a known amount of energy at a known power to a localized region of the sample [4-6]. Significantly, it has been demonstrated that laser ablation can give the same ranking as inclined plane tracking tests [4] and is considered superior to traditional FTIR analysis [5].

In the current investigation we have considered the role of the filler content and composition on the ablation resistance of several silicone rubber based composites. A range of laser powers and energies was employed and the resulting surface damage was quantified by pit-depth and mass loss measurements supplemented by optical microscopy. The various samples were then ranked and the results were compared to those obtained from inclined plane tracking tests on the same materials.
1. Experimental

1.1. Materials

Table 1 provides a list of the six samples used in this investigation arranged in order of increasing silica content and overall filler content. All the samples, with the exception of L, employ a conventional high temperature vulcanized (HTV) silicone rubber as the polymeric matrix. Sample M employs ATH as filler, sample H is its silica filled analogue whereas sample I contains a mixture of the two fillers. Samples F and E are silica filled and both contain commercial fire retardants to ensure compliance of these materials with UL94 V-0 classification [3]. Sample L is described as an “unfilled liquid silicone rubber”.

Table 1: Samples used in this investigation, filler content is in parts per hundred rubber (phr)

| Designation | Filler content                                      |
|-------------|-----------------------------------------------------|
| Sample L    | None                                                |
| Sample M    | 100 phr aluminium hydroxide (ATH)                   |
| Sample I    | 75 phr aluminium hydroxide (ATH) and 25 phr silica  |
| Sample H    | 100 phr silica                                      |
| Sample F    | 100 phr silica and 15 phr melamine cyanurate (MCA)  |
| Sample E    | 100 phr silica and 30 phr ammonium polyphosphate (APP) |

1.2. Sample characterisation

A carbon dioxide laser (Synrad) operating at a wavelength of 10.5 – 10.6 μm was used to irradiate the samples [6]. The power output of the laser was controlled by a PWM controller over the range 2 to 28 W. For safety, the laser was completely enclosed in a metal interlocked cabinet and the system was used under a fume extractor vented externally. At the sample (~20 cm away from the laser aperture), which was mounted horizontally to minimize any flow effects, the laser spot diameter was 3 mm. Each sample was weighed on a digital balance (accuracy 0.1 mg) before and after irradiation, to determine the mass loss after knocking out any loose filler. The pit depths were measured on bisected holes using a magnified hand graticule (accuracy 0.1 mm). Thermogravimetric analysis (TGA) was performed on ~ 30 mg samples using a Mettler Toledo TGA/DSC 1 scanning at 10 K/min under either dry nitrogen or an “air mixture” composed of 40 % oxygen and 60 % nitrogen.

2. Results

2.1. Thermogravimetric analysis (TGA)

The TGA results are shown in Figure 1. Sample L undergoes a gradual decomposition in nitrogen but rapidly combusts in the air mixture upon reaching 500 °C. Samples M and I show a behavior which is consistent with the decomposition of ATH (~380 °C), followed by the polymeric matrix [6] under both atmospheres. Whilst sample H heated under nitrogen indicates a slow decomposition of the polymeric matrix, the same sample under the air mixture undergoes rapid combustion at ~500 °C. The results confirm that ATH is an effective combustion retardant whilst silica is not [3]. The final two samples F and E behave similarly in both atmospheres confirming that both MCA and APP are performing as effective combustion retardants. For sample E the traces are consistent with decomposition of the polymeric matrix followed by the APP which decomposes into ammonia (NH₃), water (H₂O) and polyphosphoric acid [7]. In sample F the MCA appears to decompose first, into gaseous products such as nitrogen and ammonia [8] followed by the polymer. The mass losses due to the decomposition of the APP and MCA (12 % and 8 % respectively) are in line with the volume concentrations indicated in Table 1 and indicate that any polyphosphoric acid is eventually lost from sample E. In the analogous reaction ATH (Al(OH)₃) is converted to alumina (Al₂O₃) and water resulting in an overall mass loss of 34 %. The corresponding mass loss during the ATH decomposition in samples M and I respectively is
15 and 12% indicating an initial ATH content of 47 and 35% which is again consistent with the data shown in Table 1.

2.2. Laser ablation results

Typical examples of the “as collected” data are shown in Figures 2 and 3 along with fitted exponential curves. Sample L, as an unfilled material, was found to offer the least resistance to ablation giving a maximum pit depth of 3.2 mm and a relatively high mass loss (Figure 2). By comparison, the filled materials (Figure 3) offered a greater resistance to ablation and gave lower pit depths and reduced mass loss. For all samples, the pit depth and mass loss are non-linear functions of energy, this primarily comes about through the formation of an ashy layer (Figure 6b) which serves to protect the underlying material from damage. At laser powers of 15 and 28 W the ablation behavior for any given energy is identical and more importantly, is independent of laser power, whereas at 3 W the pit depth and mass loss are lessened, presumably through the effects of lateral heat losses [6].

2.3. Ranking

To rank the various materials both the pit depth and mass loss were compared at fixed laser power. Whilst the results at 3 W indicated smaller differences between samples (Figure 4) than higher laser powers (Figure 5) all the results indicated a common ranking scheme, from the worst to the best – L E
M I F H. These broadly follow the order established in Table 1 with one dramatic exception, sample E - despite the high filler loading of this sample and the addition of APP, this sample appears to behave much worse than expected. Considering samples M, I and H, it is clear that silica provides a composite with a better degree of ablation resistance than ATH. Finally sample F appears to perform somewhat worse than sample H in ablation tests despite the presence of the MCA fire retardant. The current results would indicate that APP, and to a lesser extent MCA, appear to degrade the ablation performance of the silica based composites.

Figure 4: Comparison of materials at 3 W power (a) pit depth, (b) mass loss

Figure 5: Comparison of materials at 28 W power (a) pit depth, (b) mass loss

2.4. Morphology
Figure 6 shows the effect of laser power on pit profile, at low laser power (Figure 6a) a small, shallow pit (~0.5 mm deep) is formed whereas at high laser power and the same energy (Figure 6b) a much deeper (~2.2 mm) and wider pit is formed. In the majority of the samples the pits are hemispherical in shape and are ashy which are the characteristics previously associated with filled composites as opposed to the “V” shaped profiles which are characteristic of unfilled materials [6].

Figure 6: Comparison of pit profiles at different laser powers in Sample I (a) 3 W, 1600 s (b) 28 W, 160 s

Figure 7 shows a series of images of bisected pits formed at 15 W for 320 s comparing the effects of the different materials. Sample L shows broad, deep pits with little evidence of filler formation after irradiation, as expected (Figure 6a); the pit is partially filled with “broken” slabs of material giving an
irregular hole profile. The remaining samples, by comparison, show a hemispherical profile with evidence of ash inside the ablated pits. Sample E assumes broad, deep pits (Figure 6b), whereas samples M, I, F and H in turn assume increasingly narrow and shallower pits. These samples contain a high filler loading (100 phr or above) which doubtless contributes to the ashing seen after ablation. It is not clear from the photographs why sample E should behave in such an unexpected way which suggests that the reason is chemical rather than physical in origin. The TGA data of sample E indicates that the polymeric matrix is degrading at a much lower temperature than any of the other composites considered; i.e. that the APP may be catalyzing its degradation in some way.

![Figure 7: Images of pits formed at 15 W for 320 s, (a) Sample L, (b) Sample E, (c) Sample M, (d) Sample F.](image)

2.5. Comparison to tracking tests
Table 2 shows the tracking test and breakdown results [3] arranged in order of decreasing track depth (i.e. improved performance). The tracking depth measurements do appear to correlate to the general ranking scheme established from ablation testing [4] with the exception of samples H and F which are reversed. However, both the tracking and ablation measurements from these samples are very close so experimental uncertainties could be the origin of this minor discrepancy. The correlation between the two sets of data suggests that laser ablation is a reliable way to rank different materials and may provide a quicker and more cost effective alternative to tracking tests.

| Designation | UL94 class | Failed at 4.5 kV | Average track depth |
|-------------|------------|-----------------|---------------------|
| Sample L    | Failed     | 0/20 (0 %)      | 3.8 mm              |
| Sample E    | V0         | 5/5 (100 %)     | 3.5 mm              |
| Sample M    | V0         | 3/15 (20 %)*    | 2.6 mm              |
| Sample I    | V0         | 5/15 (33 %)     | 2.1 mm              |
| Sample H    | Failed     | 5/15 (33 %)     | 1.3 mm              |
| Sample F    | V0         | 0/15 (0 %)      | 0.9 mm              |

*all samples passed 3.5 kV test with track depths of <0.5 mm
Significantly, composites utilizing silica in place of ATH perform much better in ablation and tracking tests but at the cost of reduced breakdown performance and loss of UL94 compliance. Silica based composites therefore require the addition of a suitable fire retardant to meet UL94 requirements. The presence of APP (Sample E) appears to be particularly deleterious in terms of all three test methods and should therefore be avoided; the TGA data suggests that it may be promoting the degradation of the polymeric matrix material. Finally, it is of no surprise, given the TGA data (Figure 1b), that both samples L and H fail the UL94 tests.

3. Conclusions
Comparisons between tracking and ablation tests reveal a good correlation, with all the filled samples behaving better than an unfilled LSR (liquid silicone rubber). In one case, where discrepancies do occur, the ablation and tracking test results were very similar indicating that experimental uncertainties may be a factor.

Composites employing silica, as opposed to ATH, appear to provide better resistance to tracking and ablation but at the expense of reduced breakdown performance and loss of UL94 compliance. Fire retardants are added to overcome this disadvantage but appear to reduce the tracking and ablation resistance, particularly APP (ammonium polyphosphate) which appears to promote the degradation of the polymeric matrix. A composite containing 100 phr silica in isolation provided the best resistance to tracking and with the addition of MCA (melamine cyanurate) to ensure UL94 compliance, would provide a useful composite material despite the MCA leading to slightly reduced tracking and ablation resistance.

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