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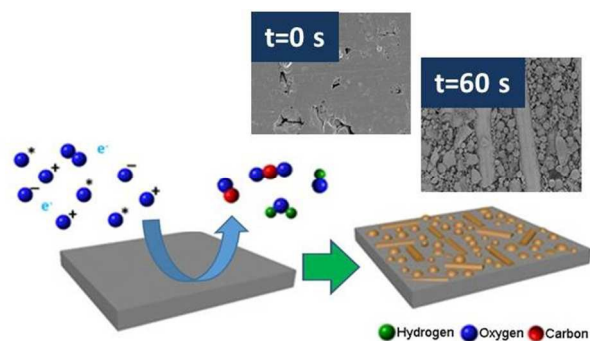
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**Colour abstract:**



**Novelty of the work:**

A novel method for improving the CTI performance level of polyphenol composites by oxygen plasma selective etching.

## ARTICLE

## Plasma as a tool for enhancing insulation properties of polymer composites

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Performance of electrical insulating polymers measured by comparative tracking index can be improved by flame retardant fillers in the polymer-matrix, but is not necessary effective due to persisting surface layers. We demonstrated a method for selective etching of polyphenol-matrix composites which leads to improvement of the tracking properties. Selective etching was performed by low pressure inductively coupled oxygen plasma generated at 35 Pa. Species created in discharge were monitored in-situ during the treatment by Optical emission spectroscopy (OES). Their surface reactions were established indirectly from X-ray photoelectron spectroscopy (XPS) and Energy dispersive X-ray spectroscopy (EDXS) after plasma treatment. The effective etching was done by oxygen species which removed off surface polymer layer within 10 to 15 s during plasma pulse operation to prevent surface overheating. The selective polymer removal improved tracking properties of the 70% glass filler reinforced composites up to 56%, whereas the performance level decreased with the decrease in filler content. This technology provides an important enhancement of polymer-matrix composites' tracking properties and resistance of composites to electrical short-circuit fire.

### 1 Introduction

Degradation and stability of polymer materials under various physical and chemical environments was an interesting subject of studies in last few decades. The most frequent is thermal degradation which refers to the unfavorable changes in physical, mechanical or electrical properties of materials in contact with heat. Generally, above the degradation temperature, polymers breakdown into chemical fragments. The lighter fragments such as CO, CO<sub>2</sub>, etc., desorb from the surface, whereas the heavier fragments remain in a condensed phase.<sup>1</sup>

Carbonization by high voltage arcing is a major disadvantage of polymer materials, when they are used as electrical insulators since it forms a conductive path.<sup>2</sup> Comparative tracking index (CTI) is a common test for materials used in electrical insulation applications. CTI represents a maximum voltage at which no tracking occurs, when 50 drops of ammonium chloride solution are added to the surface of the material as per IEC 60112 standards. This is an important test that determines the performance level of materials, which are used in electrical insulation applications.<sup>3,4</sup> There were attempts to correlate the tracking of various materials at high voltage arcing with the chemical structure as well as the binding energy of the insulating material, but this approach was applicable only for pure polymer materials. The problem is that in composites the

additives vary the stability of polymeric materials.<sup>5</sup> On the other hand, CTI performance of various polymers could be enhanced by mixing suitable fillers with polymers. Glass reinforced fillers along with phosphorous or brominated fire retardants were found to be effective in improving the CTI performance of various polyesters and polyamides.<sup>6</sup> For example, addition of 1-2.5 wt% nanoclay into the epoxy matrix made them more resistant to tracking, since the exfoliated clay acted as a barrier and limited tracking, while the pure polymer burnt vigorously during the tests.<sup>7</sup> Similar effects on the tracking properties were reported for various flame retardants in poly(butylene terephthalate).<sup>4</sup> The flammability and CTI tests also confirmed that diethylphosphinic acid aluminum salt which forms condensed form of char enhances the flame retardant properties. On the other hand, melamine polyphosphate which burns completely, improved the CTI performances. Among various polymeric materials, polyphenol composites are important in various electrical insulation applications. Glass filled polyphenols have higher temperature resistance than the alternative polyamide materials filled with melamine salts. However, lower CTI performance makes them unfit for applications in warm and damp conditions.<sup>8</sup>

Use of plasma for the improvement of bulk or surface properties of polymer-matrix composites was reported before.<sup>9</sup> Surface modification of various polymers by means of plasma treatment was reported to improve the adhesion between fillers and matrix in the bulk. Kafi *et.al.*,<sup>10</sup> found that the atmospheric pressure plasma

treatment on jute fibers significantly improved surface characteristics, which improved the flexural and shear strength of the composite when incorporated into the polyester matrix because the mechanical properties of composites are affected by extend of interfacial adhesion between the matrix and the fillers. Oxygen plasma treatment was reported to improve the interfacial compatibility and thereby makes an easy route for the stress transfer at the interfaces between the matrix and the fibre.<sup>11</sup> Moreover both low pressure and atmospheric pressure plasma pretreatments were reported to improve the adhesion between various nanoparticles and polymer substrates, and thus enhance thermal, mechanical and flame retardant properties.<sup>12-15</sup>

Physical surface modifications of polymeric material and possible chemical changes during plasma treatment significantly depend on various plasma discharge parameters including the used gas as well as connected plasma parameters.<sup>16-19</sup> Weakly ionized and highly dissociated plasma generated at low pressure, especially oxygen plasma is known for the selective removal of polymer materials from the composite surfaces. In this process, the reactive oxygen radicals from plasma react with surface atoms including the polymer chains already at room temperature.<sup>20,21</sup> At first, plasma species (neutral atoms, ions) physically adsorb to the surface, and then chemically react with the surface layer of atoms. Result of these reactions is formation of small volatile molecules (e.g. OH, CO, etc.), which finally desorb away. Etching rate of various components in plasma depends on their binding energy and chemical stability. Many of the commonly used fillers such as glasses, ceramics, metals or graphite are not etched easily in oxygen plasma compared to carbon polymers.<sup>20-22</sup> This makes it possible to remove the polymer from the surface without affecting the bulk or fillers.

Fillers are added to polymer-matrix composites that are used in electrical appliances to further improve the tracking properties. However, even the very thin surface polymer layer still makes an adverse effect on the CTI performance. To the best of our knowledge, there are no reports on the surface modification of composite materials by plasma selective etching for improving the track resistant properties of materials. Herein, we report a novel method for the improvement of CTI performances of glass filled polyphenol composite by the time-resolved selective removal of surface polymer layer by reactive oxygen plasma treatment.

## 2 Experimental section

### 2.1 Plasma treatment

Polyphenol composite with glass fibres and glass beads were prepared by injection molding process. The temperature in tool cavity was 160 – 170 °C. After molding, the plates were cured, 2 h at 160 °C, 4 h at 180 °C and 4 h at 210 °C. The samples with dimensions 2.2cm × 2.2cm × 5mm (Ibh) were used for the experiments. The plasma was generated using AE-Dressler CESAR plasma generator using an inductively coupled RF discharge at pressure 35 Pa with power of 700 W and oxygen flow rate of 40 sccm. The frequency used for discharge 13.56 MHz, enabled generation of  $\sim 10^{22} \text{ m}^{-3}$  neutrals oxygen atoms and  $\sim 10^{17} \text{ m}^{-3}$ .

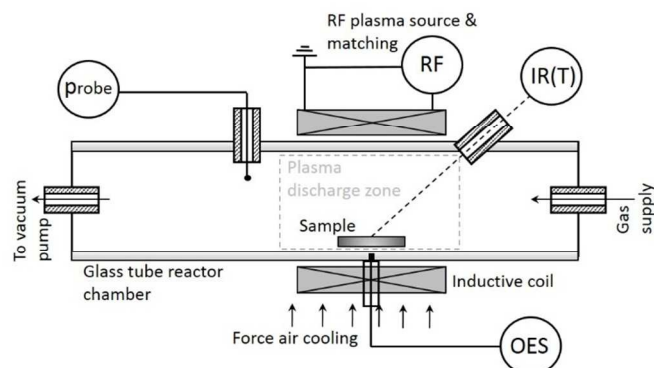


Fig. 1 Experimental setup schematic representation with plasma reactor and measurement systems.

A schematic of the experimental setup with reactor is presented in Figure 1. The coil was water cooled, whereas the reactor chamber was cooled with forced air to prevent reactor tube overheating. To prevent overheating of samples, they were treated in pulses of 3 s and sufficient time intervals were kept in between successive pulses for the sample to cool down. Qualitative optical emission spectroscopy (OES) measurements were performed with Avantes AvaSpec-3648, while the sample surface temperature was measured with infrared pyrometer Raytek Raynger MX4+ (IR(T)) during all treatments. Mass spectroscopy analysis of various species during the treatment process was carried out with Pfeifer PrismaPlus QMG 220 Residual Gas Analyser (RGA), 0-100 AMU.

### 2.2 CTI measurements

Comparative Tracking Index (CTI) as one of the fundamental standard pass/fail tests used to assess the suitability of the material for electrical insulation purpose was measured according to IEC 60112:2003 standard using PTL Tracking Test Apparatus M31.10.

### 2.3 Surface analysis

The X-ray photoelectron spectroscopy (XPS) analyses were carried out with the PHI-TFA XPS spectrometer. The analyzed area was 0.4 mm in diameter, at a depth about 3 - 5 nm. The accuracy of binding energies was  $\pm 0.3$  eV. The surface of the samples was imaged with a scanning electron microscope (SEM) FE-SEM Jeol JSM-7600F with electron beam energy 2kV. Contact angles were measured by imaging the water droplet ( $2\mu\text{l}$ ) on the surface by using wettability contact angle (WCA) measuring Advex Instruments system.

## Results and discussion

When polymer composites were exposed to reactive oxygen plasma created by RF discharge the interaction of various oxygen species started with polymer surface. Predominant interacting species were neutral O atoms and positive O ions, which caused surface etching. As a result of these interactions were different products released into plasma and many times disintegrated into smaller products. This etching process was seen from optical emission spectra and intensity of spectral

emission lines. The intensity of various species as

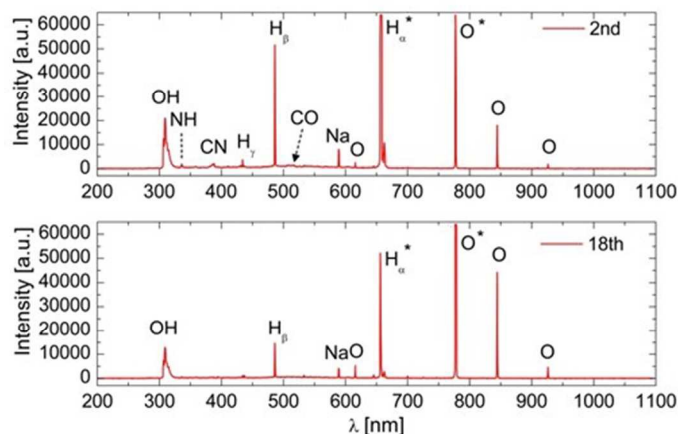


Fig. 2 OES spectra of plasma taken during the processing at the end of 2<sup>nd</sup> and 18<sup>th</sup> pulse.

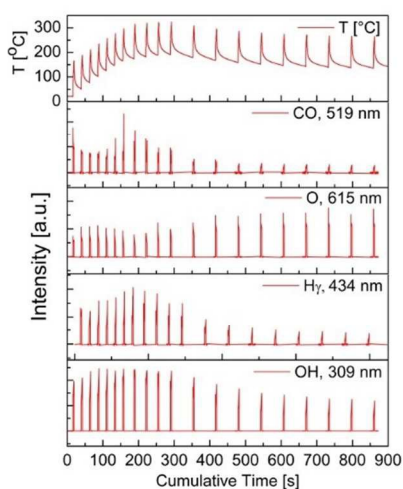


Fig. 3 Surface temperature measurements and corresponding OES spectra for selected emission lines presenting typical species during the treatment process.

measured by OES at the end of 2<sup>nd</sup> and 18<sup>th</sup> pulses is shown in Fig. 2. Observed spectral features such as O atom emission lines, hydrogen Balmer series and molecular OH band are typical for plasmas containing water vapor and also as a byproduct of reactions of oxygen species with the hydrogen from the polymer. In the beginning of the single-first pulse we have typically pure oxygen plasma with only oxygen species or sometimes evaporating water from reactor walls or sample surface as well as from polyphenol which results in molecular OH peak and H lines. Other spectral features like molecular CN, NH and CO or even Na are the result of sample etching, when reaction products are desorbed from surfaces into plasma. The species CN and NH are seen in the beginning of the treatment as an etching byproduct of the reaction between the polymers and nitrogen (air) desorbed from the surface of composite samples during degassing. When the etching is slowed down or almost over (seen from Fig. 2, 18<sup>th</sup> pulse), the spectra becomes similar to the initial – empty plasma conditions with only oxygen species and lower contents of OH

coming from under-layers of polyphenol or water vapor. By these means OES offers unique opportunity to efficiently monitor plasma etching process and reactions occurring on surface in real-time. This was clearly perceived from Fig. 3, where the time evolution of selected emission peaks are drawn.

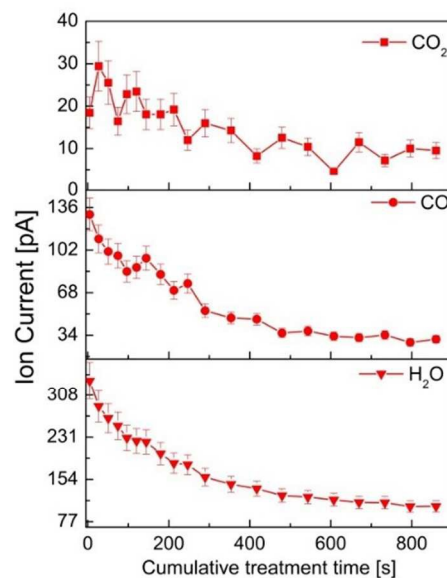


Fig. 4 Intensities of CO, CO<sub>2</sub> and H<sub>2</sub>O species as observed by mass spectroscopic measurement during the treatment

Later, there is significant decrease in CO peak intensity until it is almost vanished after prolonged treatment. On the other hand, the pretty rich OH emission at 309 nm ( $A^2 \Sigma^+ - X^2 \Pi$ ) still persists for the maximum treatment time of 60 s, and it is originated by the reaction between the polymer and the oxygen neutrals as well as the dissociation of water vapor inside the plasma chamber.<sup>25</sup> One of more important oxygen species recorded during our experiments was triplet atomic oxygen, at wavelength of 615 nm. The intensity of O is lower for the first few pulses and thereafter increases.<sup>26</sup> This is attributed to the higher consumption of oxygen species for interactions with surface and consequent etching. Secondly, the H $\alpha$  line at 434 nm and molecular OH band at 309 nm show same trends, increasing with surface temperatures and slowly decreasing with treatment times. During the treatment, the surface temperature increase also to up to around 300 °C, with steady increase for first 8 pulses, reaches saturation for next 4 pulses and then slowly decreases due to increased cooling time (Fig. 3). The surface temperature results from the exothermic carbon oxidation as well as the ion bombardment and neutral atom recombination on the composite surface. Such increase in the surface temperature can affect the overall bulk properties of the material. To prevent such adverse effects, the sample surface was allowed to cool down by keeping sufficient time intervals between successive pulses. Despite this, there was still accumulation of heat in the bulk which is seen as background temperature and would require longer cooling times between sequential pulses. Additionally, mass spectroscopy analysis of the residual gas was performed in a remote chamber at the end of plasma reactor on the way to vacuum pump, which allowed monitoring of the etching products, namely CO, CO<sub>2</sub> and H<sub>2</sub>O molecules, which reform into stable molecules upon exiting

plasma discharge. From all mass spectra, the gradual drop in the densities of oxidized carbon species CO and CO<sub>2</sub> as well as H<sub>2</sub>O is observed (Fig.4).

This is indication of the reduced carbon mass on the material surface due to etching of material from the surface, especially polymers. Similar holds for detected H<sub>2</sub>O species from the residual gas mixture, whose peak in mass spectra showed similar trend with the OH band intensity in observed OES spectra. However, it is important to mention that optical emission spectra doesn't overlap with mass spectroscopy measurements, since in OES we count only for excited plasma species which emit photons during deexcitations. This is seen in the first stages of etching, where not all species leaving the surface are excited with electron collisions.

significant increase happens between 5 and 10 pulses in accumulative time of 15 s to 30 s.

After this the trend slowly starts to reach saturation profile. Surprisingly the short treatment times lead to 56% improvement of CTI index, and better tracking performance. As seen from OES and mass spectra the etching occurs on the surface and leads to reduced carbon content. As a result the reduced amount of carbon on the surface lowers potential carbonization by electrical current and thereby increases the tracking voltage. To confirm the effect of glass fillers on the surface, the samples with different filler content were treated with plasma for 60 s and tested for CTI performances. The sample containing fillers ~20% showed only 13% of increase. But, as we increased the filler content by four times to ~70%, the tracking performance reached a value 56% more than that of the non-treated composite (Fig. 5b).

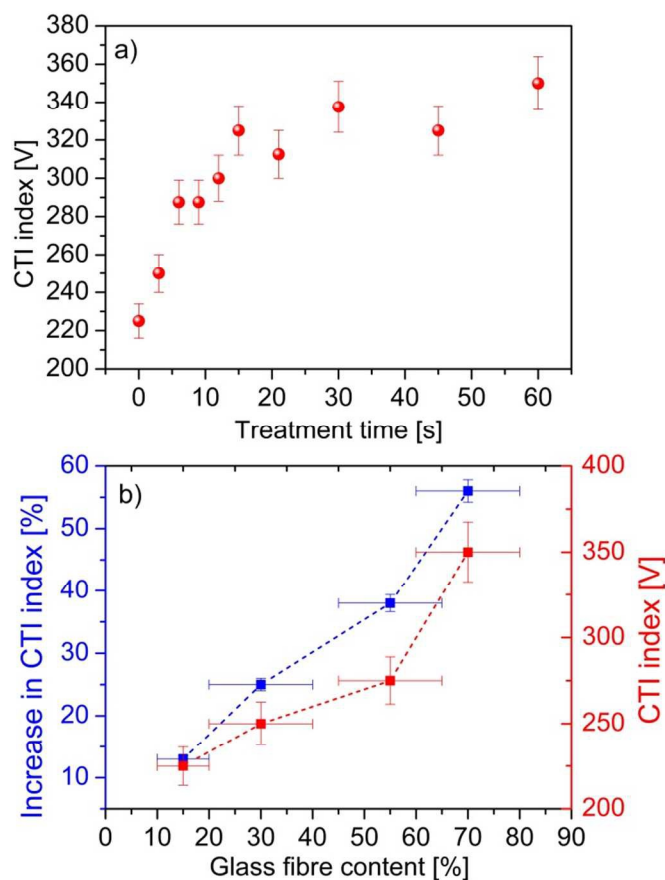


Fig. 5 a) Composite tracking properties (CTI) with respect to accumulated pulse treatment time; b) the CTI index of the composites with different glass filler content, when treated for 60 s.

After the surface treatment with plasma and consequent etching, the samples were subjected to CTI index testing. The average results of ten samples tested presented in Fig. 5a display significant increase in the CTI index values of the material with increasing plasma running time. The CTI performances were increased from 225 V to 350 V after an accumulative treatment of 60 s of 3 s pulses. The most

The reason behind the significant increase of CTI was due to selective removal of the polymer, which was confirmed by scanning electron microscopy of sample surfaces after different treatment times in Fig. 6, where exposure of composite fillers is observed. These glass fillers act as an additional insulating layer towards surface tracking measured by CTI index. Higher content of fillers therefore simply leads to more significant improvements of CTI. As seen from SEM images (Fig.6), the surface of the untreated sample composite is almost completely covered with polymer. By increasing the treatment time, the polymer covered on the surface is gradually removed and the fillers (glass fibers and spheres) become clearly visible. This process is schematically shown in Fig. 6e. Increasing the treatment times up to 20 pulses yields also etching of composite under surface layers where polymer is removed from the inner parts of composite and the fillers are further revealed. This results in gradual increase in the CTI performances and eventual decrease in the potential surface carbonization level enabling electrical current.

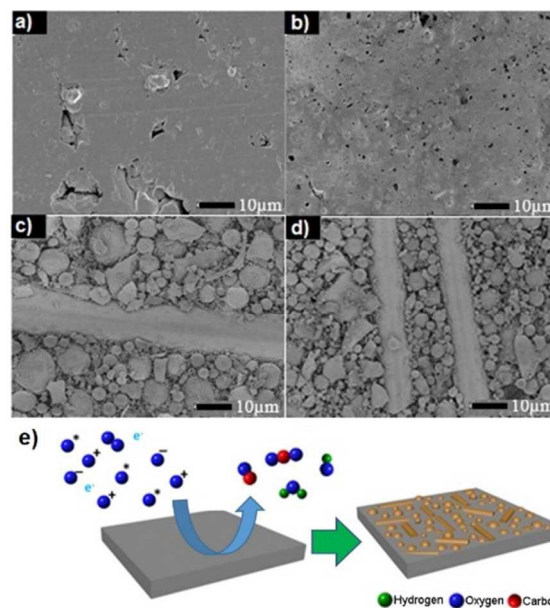


Fig. 6 SEM images of a) non-treated sample, plasma treated for b) 6 s (2 pulses), c) 15 s (5 pulses) and d) 60 s (20 pulses) as well as e) schematic representation of plasma etching with corresponding plasma species and resulted products.

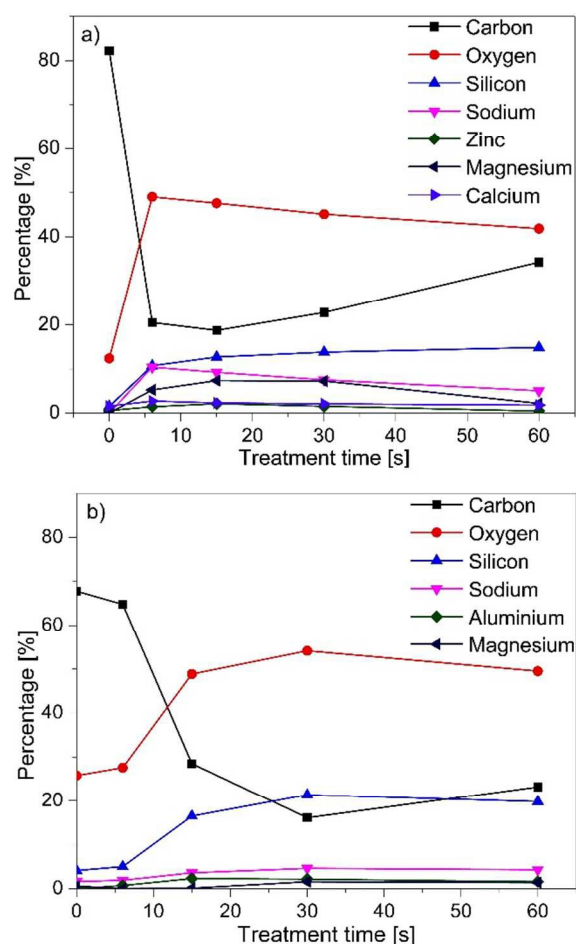


Fig. 7 Surface elemental composition analyzed with a) XPS measurements from survey spectra and b) from EDXS measurements.

To confirm visual observations of selective etching, the XPS and EDXS analyses of composite surfaces (Fig.7) were performed to monitor the surface chemistry changes and surface etching with respect to treatment time. Both methods gave almost identical results in the frame of measurement errors and restrictions of used analyses. On the surface, the gradual and selective removal of the surface polymer was observed from the carbon content. Whereas the exposed composition of elements such as Si, O, Mg, Na, Mg, etc. originated mostly from the fillers inside. The first selective removal occurred in 6 to 30 s of accumulative plasma treatment time. The oxygen content increases slightly more than silicon, due to combined effect of the functionalization of the surface carbon and exposition of the glass fillers from  $\text{SiO}_2$ . This is observed also from XPS high resolution peaks C1s and O1s, where primary rise of peaks is due to C-O, C=O and COO functional groups. However this functionalization starts to reduce due to heating effects and etching of polymer and after 15s C/O ratio tend to increase slowly.<sup>27</sup> Result of sample heating and increased surface tension is also the creeping of polymer to the surface, which is gotten from slight increase in carbon content at prolonged treatment times. The functionalization of surface with oxygen polar groups versus progressive etching of polymer and its selective removal is indirectly measured from surface wettability. Plasma treatment

itself enhances the surface energy of the composite, which results in decreased water contact angle. This is a simultaneous effect of polar group incorporation and roughening of the surface.<sup>28,29</sup> Surface roughening is a permanent change on the surface, while the functional groups will be moved into the bulk of the material, are degraded or/and removed by recombination with impinging air gas molecules with time. The surface functionalization and sequenced surface ageing are perceived from the water contact angle (WCA) for various time intervals of treatment (Fig. 8). The surface becomes superhydrophilic only after treating the surface for 9 s (3 pulses), which means that this is the optimal ratio between incorporation of polar O groups and surface etching. However, due to persisting polymer this is not a very lasting effect, since surface is pretty quickly influenced by polymer ageing. Longer lasting effects of this phenomena are achieved after 30 s or even 45 s treatments, when polymer is almost completely removed. In these cases, the surface is superhydrophilic even after a period of 8 day ageing, whereas for 60 sec treatments surface WCA turned into the value of  $27.8^\circ$  only after 30 days of ageing.

The results from the SEM, XPS, OES, TGA (see Supporting Information) and WCA confirmed that plasma is selectively removing carbon (polymers) from the surface and exposing the glass fillers. With less and less of carbon on the surface, insulating properties of the composite, depending on glass filler content, increased for up to 56%. Prolonged plasma treatment of the composite leads to stabilization of insulating properties of material, since the fillers homogenously dispersed throughout the composite volume persist in upper surface layer fully exposed and are not etched away. Whereas the polymer content gradually increases into inner layers, and is harder to reach and etch by plasma radicals due to upper glass layer.

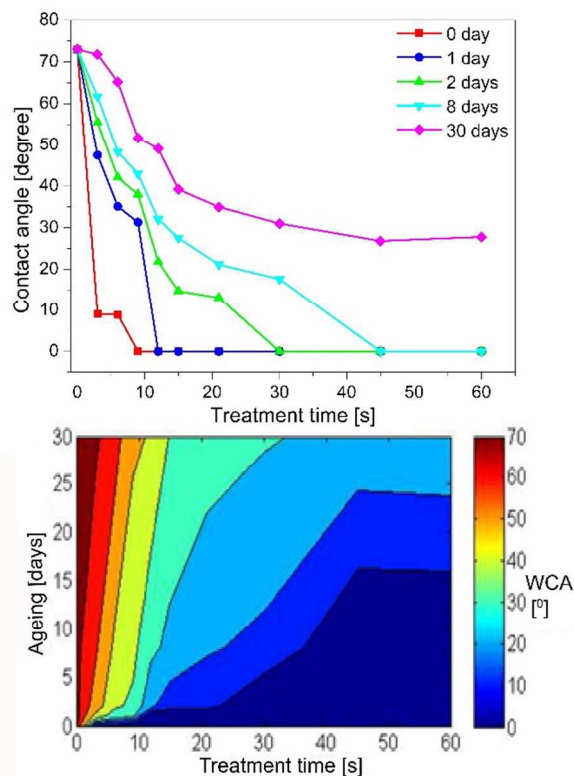


Fig. 8 Wettability of composites surfaces for different accumulative time treatments and time aging of those surfaces presented in x-y graph (top) and 2D contour plot (bottom).

## Conclusions

In this paper, a new method for improving the tracking performances of insulating composite materials was presented. This was achieved by the selective removal of the polymer layer from the surface by means of oxygen plasma treatment. During the plasma treatment, the carbon content on the polyphenolic composite surface is drastically decreased because of the etching by oxygen neutral atoms and ions. This decrease reduces the possibility of carbon layer oxidation and thereby tracking in the presence of high voltage arcing on the material surface. Furthermore, the exposed glass fibers on the surface, as observed by SEM after the oxygen plasma treatments, act as a protective surface layer against high voltage arcing. The repetition of the experiment with lower filler content further confirmed this argument. Thus, it was demonstrated that the tracking properties of composite materials could be improved simply by surface modifications. This proved that selective oxygen plasma etching is an effective and very fast surface processing method for achieving this goal, and that is a very valuable tool in designing novel cost-effective high-voltage electrical insulators.

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## Notes and references

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