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Poly(dicyclopentadiene) Coatings for the Mitigation of Surface Flashover in Gas Switch Housings

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Abstract- **Surface flashover is a significant issue impacting the reliability of high voltage, high current gas switches. The goal of this work is to determine if poly(dicyclopentadiene) (pDCPD) coatings can be used to mitigate surface flashover on insulators compared to crosslinked polystyrene (Rexolite), cast poly(methylmethacrylate) (PMMA), and extruded PMMA. The pDCPD coating is expected to have a higher flashover voltage threshold to an initial flashover due to the oxidation of the polymer, creating trap sites for any free electrons that would otherwise serve as primary electrons in a surface electron avalanche. This is tested by measuring the flashover threshold for different extents of oxidation caused by thermally treating the samples for different durations. For subsequent flashover events the pDCPD coating is also expected to have a higher flashover threshold due to its high oxygen/hydrogen to carbon ratio, which is expected to preferentially create gaseous products, such as CO_2 after a flashover event, rather than conductive carbon deposits. The control and pDCPD-coated test coupons are repeatedly subjected to increasing voltage stresses until flashover occurs to determine both the initial and subsequent flashover thresholds.**

I. INTRODUCTION

The insulator material for high voltage compressed gas switches is an important consideration for reliable operation, as flashover on the housing is one of the leading causes of switch failure [1]. A variety of methods have been employed to increase the flashover threshold for insulators including changing the geometry [2], modifying the surface roughness [3], and modifying the surface to introduce trap sites on the polymer for emitted secondary electrons [4-6]. These trap sites can be created by various surface treatments such as doping the surface with nanoparticles or metal oxides [7], fluorinating the surface [8], or oxidizing the surface by ozone treatment [9].

We propose coating a gas switch housing with a novel polymer, poly(dicyclopentadiene) (pDCPD) as a potential method to improve the flashover performance of the gas switch. Poly(DCPD) has been chosen due to the ability to vary the amount of oxygen incorporated into the polymer. This is achieved by the monomer initially undergoing ring-opening metathesis polymerization (ROMP), which leaves many unreacted double bonds (Fig. 1). The double bonds in p(DCPD) oxidize at room temperature and this process can be accelerated at higher temperatures, introducing more oxygen into the polymer structure [10]. It is hypothesized that this oxygen will act as trap sites similarly to the ozone treated surfaces in [9]. With higher oxygen content, it is also hypothesized that more gaseous byproducts, such as CO_2, will be produced during flashover, reducing graphitic deposition on the surface and potentially leading to improved long-term flashover withstand.

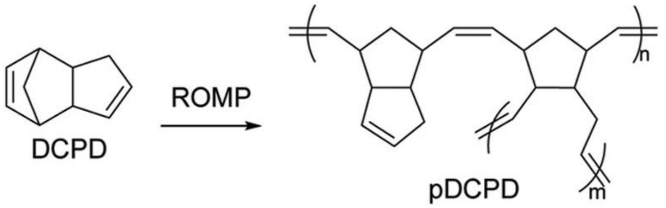

Fig. 1. Schematic of DCPD undergoing ring-opening metathesis polymerization (ROMP) to create pDCPD. The remaining double bonds are potential sites for oxidation to occur.

In this work, the flashover withstand voltage of coupons of standard gas switch housing materials Rexolite and poly(methylmethacrylate) (PMMA) are compared to pDCPD coated onto cast PMMA.

II. EXPERIMENTAL METHODS

A. Materials

Rexolite and PMMA samples were purchased from McMaster Carr. In addition to testing the as-received materials, polished samples were prepared using a mechanical polisher.

To create the pDCPD coatings, a 95:5 weight percent mixture of DCPD and ethylidene norbornene is mixed at 40–50°C. Next a 1:2:2 weight ratio of isopropylthioxanthone (photosensitizer), ethyl dimethylaminobenzoate (photo-cinitiator) and HeatMet, (a ruthenium-based ROMP catalyst) is dissolved in a minimum amount of dichloromethane. The DCPD mixture is then added to the catalyst mixture at a weight ratio of 1000:1 to create the final DCPD resin. This resin is coated onto cast PMMA sheets to a thickness of 0.25 mm using a doctor blade. The resulting film is then exposed to 365 nm ultraviolet light at an intensity of 60 mW/cm^2 for 90 to 270 s to initiate ring-opening metathesis polymerization (ROMP) to yield the pDCPD coating [11]. Films were thermally treated in an oven at 100°C in atmospheric pressure air for various times to induce further oxidation of the polymer.

B. Material Characterization

Differential scanning calorimetry (DSC) was conducted using a Q200 calorimeter (TA Instruments), ramping from 30°C to 200°C at 3°C/min. Atomic force microscopy (AFM) was conducted using a Bruker Dimension Icon Atomic Force Microscope with a ScanAsyst-Air probe (2 nm nominal tip

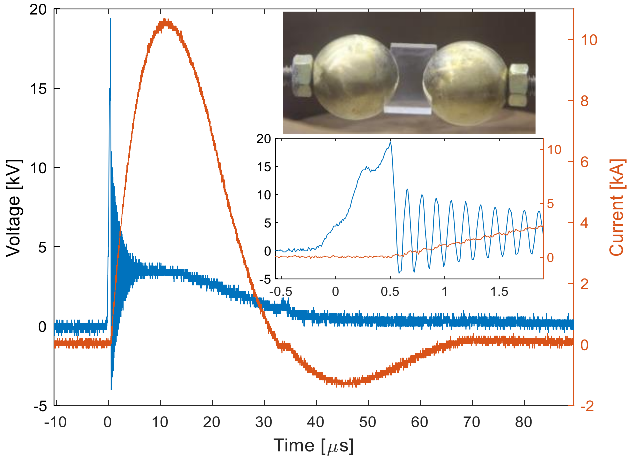

Fig. 2. Example voltage and current trace of a flashover event. Upper inset shows the experimental setup of a polymer sample inserted between brass electrodes for flashover testing; lower inset shows a zoom of the initial 2.5 µs in the voltage and current trace.

radius). A Keyence VK-X150 laser scanning confocal microscope (LSCM) with a 50x standard WD objective was used to image the as-received Rexolite sample.

C. Electrical Characterization

Flashover testing was performed using a PG 24-2500 (HILO-Test GmbH.) power supply, supplying a 24 kV voltage pulse with a 1.2 µs front time and 50 µs full-width, half maximum. The test setup is shown in the inset in Fig. 2, where the 0.3175 cm thick polymer samples are cut down to coupons 14 mm by 25.4 mm and inserted into slots in 2.54 cm diameter spherical brass electrodes. A Tektronix 6015 high voltage probe and Pearson 110A current transformer are used to measure the voltage and current, respectively. A characteristic pulse is shown in Fig. 2. Shots were taken in ambient air at a rate of approximately 1 shot per minute.

Three to six samples of each polymer are tested for 20 flashover events each; in addition, a few samples were tested for 40 flashover events to see if additional shots resulted in changes to the flashover withstand voltage.

III. RESULTS AND DISCUSSION

A. Material Preparation and Characterization

After casting and photocuring, the pDCPD samples were either tested as is (photocure only) or subjected to a further thermal treatment. Previous work [10] has shown that thermal treatment of pDCPD films accelerates oxidation of the polymer. However, thermal treatment can also increase the extent of cure if the photocure does not result in complete reaction. To determine the extent of cure, DSC was conducted on the samples. The enthalpy of residual cure was 93 J/g for the film that was only photocured and decreased to 7 J/g after a 16 hr thermal treatment at 100°C. This shows that the extent of cure increased significantly in thermally treated films compared to the film that was only photocured, indicating that the photocured film may contain unreacted monomer and may not be as fully crosslinked as thermally treated films. Further experiments are planned to fully characterize the variation in the extent cure and extent of oxidation in the pDCPD films before and after thermal cure.

The surface roughness (Sa values) of the pDCPD samples and the commercial materials was characterized by AFM or LSCM (as-received Rexolite samples only). Results are shown in Fig. 3 and summarized in Table 1, where averages are from at least 3 measurement locations. Since the as-received Rexolite samples were so much rougher, polished samples of Rexolte and PMMA were also prepared, so that flashover voltages for samples with comparable surface roughness could be compared.

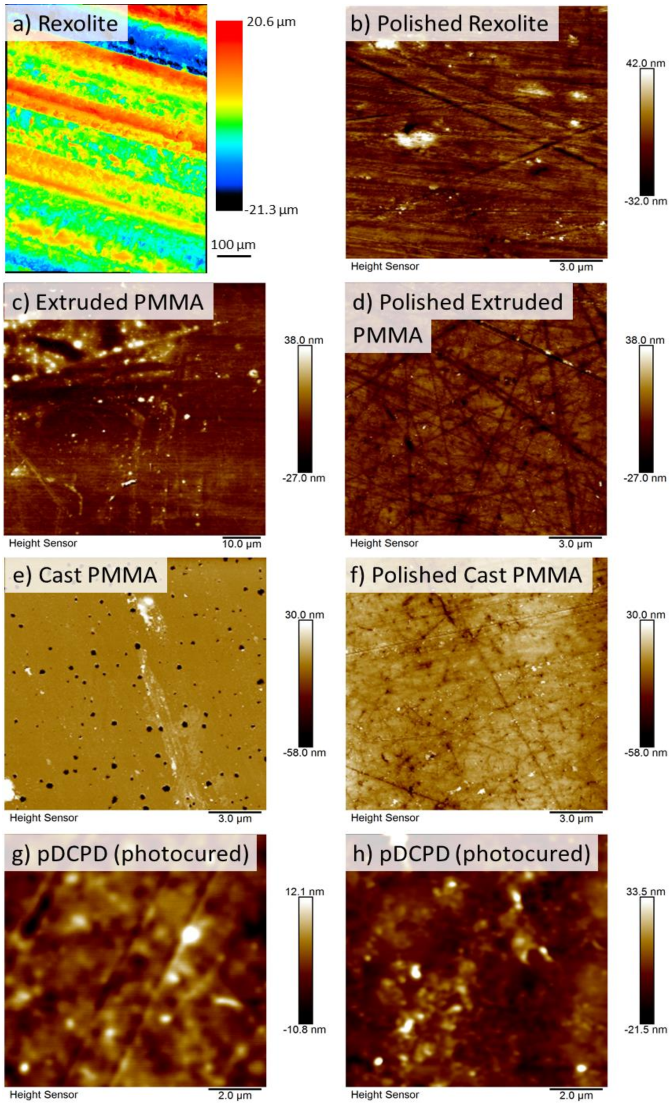

Fig. 3. LSCM (a) and AFM (b-h) of the polymer samples showing the as-received (a, c, e), polished (b, d, f) and pDCPD (g, h) samples.

Table 1. Surface roughness values (Sa) of the raw and polished polymer samples measured by AFM and LSCM with noted standard deviation

Material	Raw Sa (nm)	Polished Sa (nm)
Rexolite	1,910 ± 760[a]	5.0 ± 0.90
Extruded PMMA	7.6 ± 5.3	4.3 ± 0.27
Cast PMMA	3.0 ± 1.4	5.5 ± 0.40
pDCPD (photocured)	3.1 ± 1.7	-

[a] LSCM measured value, not AFM

B. Electrical Characterization

The flashover voltage for each discharge event for each sample material type is shown in Fig. 4 to Fig. 6. Three samples (two Rexolite and one pDCPD (photocure only)) were tested for 40 discharge events rather than 20. No substantial change in the flashover withstand voltage was noted with the additional shots (40 shot data not shown). Box plots showing the summary for each sample material are shown in Fig. 7. Results of fitting the data to a Weibull distribution are shown in Fig. 8 and summarized in Table 2. For some samples, partial voltage reflection occurred, resulting in flashover voltages above the supplied 24 kV pulse.

Both as-received and polished Rexolite were noted to be comparable to other materials for the initial flashover event; however, subsequent flashovers occurred at a lower voltage (Fig. 7). In contrast, PMMA and pDCPD samples showed no strong increasing or decreasing trends. The variation in flashover voltage decreased with increasing thermal treatment time for the pDCPD samples. This could be due to the additional oxidation resulting in a more homogeneous surface chemistry, or to further crosslinking and reaction or evaporation of residual monomer resulting in a more homogeneous composition throughout the pDCPD film.

Interestingly the flashover voltage of the polished Rexolite did not differ greatly from the high surface-roughness as-received Rexolite, suggesting that surface roughness is not the dominant factor in the comparatively poor flashover withstand of Rexolite (see Fig. 4(a) and Fig. 5(a)). The polished PMMA samples, however, generally greatly outperformed their as-received counterparts as is demonstrated by a higher mean flashover voltage in and Fig. 5(b-c) vs. Fig. 4(b-c), with numerous shots not flashing over at the power supply's maximum voltage. It is unclear what is causing the improvement of these samples. Further studies will focus on characterizing the polished samples, to determine if polishing debris may act as surface trap sites, and on controlling environmental variables (e.g., humidity, which has been shown to affect flashover voltages [12]) during testing to ensure that variations in ambient conditions are not impacting the results.

Though Rexolite has been shown to have superior flashover withstand performance in vacuum [13], that performance has been shown to not extend to oil environments [14]. Based on these results, Rexolite is inferior to PMMA and pDCDP in atmospheric pressure air as well.

The hypothesized trend of greater oxidation of pDCPD yielding improved flashover withstand was not observed (Fig. 6). It is not known at this time if this is because the extent of oxidation was smaller in thermally treated films than anticipated or if the oxidation does not, in fact, significantly effect the flashover mechanism and threshold voltage. Further studies to quantitatively characterize the extent of oxidation before and after thermal treatment are ongoing.

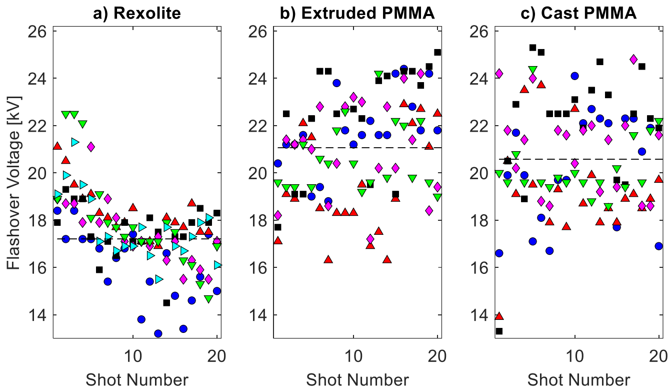

Fig. 4. Flashover events for as-received Rexolite (N=6) and PMMA samples (N=5). Each symbol represents a different coupon. The average for each material is shown as a dashed line.

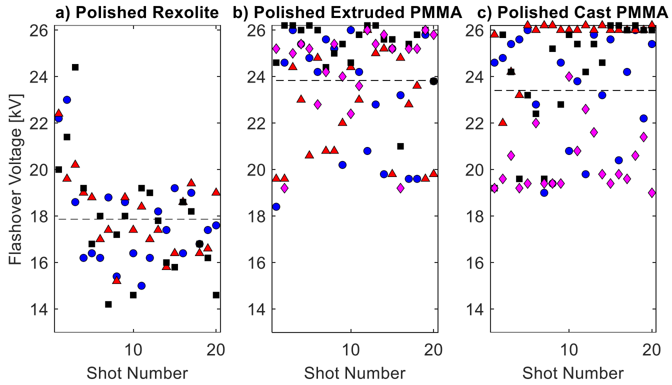

Fig. 5. Flashover events for polished Rexolite (N=3) and PMMA samples (N=4). Each symbol represents a different coupon. The average for each material is shown as a dashed line.

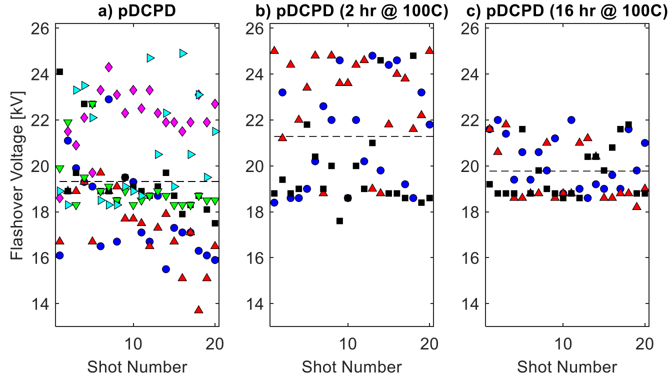

Fig. 6. Flashover events for pDCPD samples on cast PMMA (N=6, 3, and 3 for photocured only pDCPD, 2 hr thermal cure, and 16 hr thermal cure, respectively). Each symbol represents a different coupon. The average for each material is shown as a dashed line.

IV. CONCLUSIONS

Rexolite was shown to have comparable flashover withstand to PMMA and pDCPD for initial flashovers; however, its flashover withstand decreased significantly with additional shots. In contrast, PMMA and pDCPD flashover thresholds remained relatively constant up to 20 flashovers. Thermally treating the pDCPD coating did not result in a statistically significant change in flashover voltage, though there was a reduction in the variance of the flashover voltages for samples thermally treated for 16 hrs.

Further work is ongoing to better characterize the extent of polymer oxidation before and after thermal treatments as well

Table 2. Weibull parameters for each material

Material	**Number of Samples**	**Weibull Scale, α (kV)**	**Weibull Shape, β**	**Initial Flashover Voltage ± Std. Dev. (kV)**	**Mean Flashover Voltage ± Std. Dev. (kV)**
Rexolite	6	18.0	10.1	19.1 ± 1.1	17.2 ± 1.6
Extruded PMMA	5	22.0	11.4	18.6 ± 1.4	21.1 ± 2.1
Cast PMMA	5	21.6	10.1	17.8 ± 4.7	20.6 ± 2.3
Polished Rexolite	3	18.8	8.2	21.5 ± 1.3	17.9 ± 2.1
Polished Extruded PMMA	4	25.0	12.4	22.0 ± 3.5	23.8 ± 2.3
Polished Cast PMMA	4	25.3	8.2	22.2 ± 3.5	23.4 ± 2.7
pDCPD (no thermal)	6	20.4	8.8	19.1 ± 2.9	19.3 ± 2.3
pDCPD (2 hr @ 100C)	3	22.4	9.4	20.7 ± 3.7	21.3 ± 2.4
pDCPD (16 hr @ 100C)	3	20.4	17.2	20.8 ± 1.4	19.8 ± 1.2

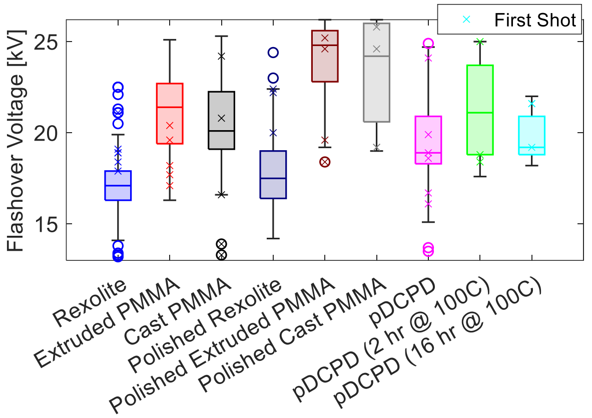

Fig. 7. Box plots of flashover voltage for each material type tested

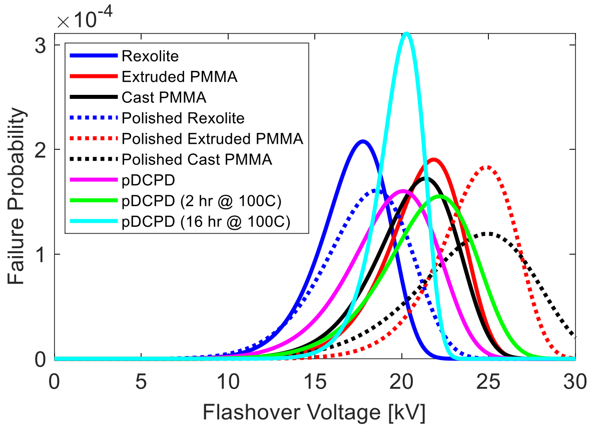

Fig. 8. Weibull plots of flashover voltage for each material type tested

as changing the electrical setup to a cylindrical dielectric geometry, exploring both DC and impulse voltages, implementing fixturing to enable better control of environmental factors such as humidity, and testing with varying gas atmospheres and pressures.

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REFERENCES

[1] K. LeChien, W. Stygar, M. Savage, R. McKee, D. Bliss, P. Wakeland, et al., "Performance Improvements of the 6.1-MV Laser Triggered Gas-Switch on the Refurbished Z," IEEE Pulsed Power Conference, 2009.

[2] A. Caulcrick, S. Olabisi, J. Zirnheld, H. Moore, and H. Singh, "Geometrical Effects on Hold-off Voltage in Polystyrene Insulator," IEEE International Power Modulator and High Voltage Conference, 2010.

[3] J. R. Laghari, "Spacer Flashover in Compressed Gases," *IEEE Transactions on Electrical Insulation*, Vol. 20, Issue 1, pp. 83-92, 1985.

[4] B. X. Du, H. C. Liang, J. Li, and C. Zhang, "Temperature Dependent Surface Potential Decay and Flashover Characteristics of Epoxy/SiC Composites," *IEEE Transactions on Dielectrics and Electrical Insulation*, Vol. 25, Issue 2, pp.631-638, 2018.

[5] J. Xue, Y. Li, J. Dong, J. Chen, W. Li, J. Deng, et al., "Surface Charge Transport Behavior and Flashover Mechanism on Alumina/Epoxy Spacers Coated by SiC/Epoxy Composites with Varied SiC Particle Size," *Journal of Physics D: Applied Physics*, Vol. 53, Issue 15, 2020.

[6] Y. Huang, D. Min, S. Li, Z. Li, D. Xie, X. Wang, et al., "Surface Flashover Performance of Epoxy Resin Microcomposites Improved by Electron Beam Irradiation," *Applied Surface Science*, Vol. 406, pp.39-45, 2017.

[7] J. Cross and T. Sudarshan, "The Effect of Cuprous Oxide Coatings on Surface Flashover of Dielectric Spacers in Vacuum," *IEEE Transactions on Electrical Insulation*, Vol. 9, Issue 4, pp.146-150, 1974.

[8] M. Z. Khan, A. Waleed, A. Khan, M. A. S. Hassan, Z. J. Paracha, and U. Farooq, "Significantly Improved Surface Flashover Characteristics of Epoxy Resin/Al2O3 Nanocomposites in Air, Vacuum and SF6 by Gas-Phase Fluorination," *Journal of Electronic Materials*, Vol. 49, Issue 5, pp.3400-3408, 2020.

[9] Y. Nie, X. Zhao, N. Zhao, S. Liu, S. Yu, and S. Li, "A New Surface Treatment Method for Improving Surface Flashover Performance of Polymers in Vacuum," IEEE International Conference on High Voltage Engineering and Application (ICHVE), 2020.

[10] J. Huang, A. David, P.-Y. Le Gac, C. Lorthioir, C. Coelho, and E. Richaud, "Thermal Oxidation of Poly(dicyclopentadiene)– Kinetic Modeling of Double Bond Consumption," *Polymer Degradation and Stability*, Vol. 166, pp.258-271, 2019.

[11] S. C. Leguizamon, A. W. Cook, and L. N. Appelhans, "Employing Photosensitizers for Rapid Olefin Metathesis Additive Manufacturing of Poly(dicyclopentadiene)," Chemistry of Materials, Vol. 33, Issue 24, pp. 9677-9689, 2021.

[12] K. Morales, J. Krile, A. Neuber, and H. Krompholz, "Dielectric Surface Flashover at Atmospheric Conditions with Unipolar Pulsed Voltage Excitation," *IEEE Transactions on Dielectrics and Electrical Insulation*, Vol. 14, Issue 4, pp.774-782, 2007.

[13] W. A. Stygar, J. A. Lott, T. C. Wagoner, V. Anaya, H. C. Harjes, H. C. Ives, et al., "Improved Design of a High-Voltage Vacuum-Insulator Interface," *Physical Review Special Topics - Accelerators and Beams*, Vol. 8, Issue 5, 2005.

[14] M. Wilson, S. Macgregor, M. Given, I. Timoshkin, M. A. Sinclair, K. J. Thomas, et al., "Surface Flashover of Oil-Immersed Dielectric Materials in Uniform and Non-Uniform Fields," *IEEE Transactions on Dielectrics and Electrical Insulation*, Vol. 16, Issue 4, pp. 1028-1036, 2009.