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Publisher's version / Version de l'éditeur:

<https://doi.org/10.1109/CEIDP.2005.1560647>

2005 Annual Report Conference on Electrical Insulation and Dielectric Phenomena, pp. 166-170, 2005-10-16

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Fig 4 shows the space charge distribution obtained by the PEA technique in PP, containing 0, 2, and 4% by weight of nanoparticles, when charged at ac fields of 2, 20, and 30 kV/mm. To minimize the capacitive charge the space

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Conclusions

Dielectric properties of PP with and without organoclay are reported. PP-2% had the highest dc breakdown strength of the three materials. The results of the EL intensity and space charge distribution indicate that under ac voltage less charge is injected into PP-2% than PP-0% or PP-4%. This suggests that the electrode-polymer interface plays a dominant role during the application of ac voltage to the insulation. Phase resolved PEA technique showed that the reversal of the PEA output peak at the electrodes corresponded to the field at which charge injection into the polymeric insulation was initiated. This work has shown that PP containing 2% by weight of dispersed organosilicate has better dielectric properties, such as higher dc BD strength, less EL intensity and space charge, than pure PP.

References

- [1] M. Rabuffi and G. Picci, "Status quo and future prospects for metalized polypropylene energy storage capacitors", *IEEE Trans. on Plasma Science*, vol.3, pp. 1939-1942, 2002.
- [2] E. Ildstad and T. Haave, "Conduction and partial discharge activity in HVDC cable insulation of lapped polypropylene films", *IEEE 7th Intl. Conference on Solid Dielectrics*, June 25-29, 2001, pp. 137-140.
- [3] K. Tohyama, S.S. Bamji, and A.T. Bulinski, "Simultaneous measurement of electroluminescence and dissipation current in cable insulation", *Proc. of 7th Intl. Conf. on Properties and Applications of Dielectric Materials*, June 1-5, 2003, pp. 1051-1054.
- [4] L. A. Utracki, "Clay-containing Polymeric Nanocomposites", Publisher: RAPRA Tech Ltd., Shawbury, Shrewsbury, Shropshire UK, (2004).
- [5] C. Laurent, "Optical pre-breakdown warnings in insulating polymers", *IEEE Intl. Conference on Conduction and Breakdown in Solid Dielectrics*, June 22-25, 1998, pp. 1-12.
- [6] C. Laurent, G. Teyssedre, and G. C. Montanari, "Time-resolved space charge and electroluminescence measurements in polyethylene under ac stress", *IEEE Trans. on Dielect. and Electrical Insulation*, vol. 11, pp. 554-560, 2004.

Acknowledgments: Mrs. Y. Chen and Mr. D. McIntyre provided technical assistance to this project. Mr. D. St-Jean machined various test-cells and other experimental setup components and Dr. Jianming. Li (from NRCC/IMI) provided the nanocomposite samples. Their assistance is very much appreciated.

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minimum (for hole injection) or maximum (for electron injection). However, EL emission reaches its maxima prior to the peaks of the positive and negative half-cycles of the ac voltage. This is because the local electric field due presence of space charge in the polymer is always in advance of the applied field [3]. Further experimental work is required to verify this initial finding that the reversal of the PEA output voltage peak at the electrodes corresponds to the initiation of charge injection in the material. Organoclay added to PP could increase the electric field for charge injection into the polymer.

Conclusions

Dielectric properties of PP with and without organoclay are reported. PP-2% had the highest dc breakdown strength of the three materials. The results of the EL intensity and space charge distribution indicate that under ac voltage less charge is injected into PP-2% than PP-0% or PP-4%. This suggests that the electrode-polymer interface plays a dominant role during the application of ac voltage to the insulation. Phase resolved PEA technique showed that the reversal of the PEA output peak at the electrodes corresponded to the field at which charge injection into the polymeric insulation was initiated. This work has shown that PP containing 2% by weight of dispersed organosilicate has better dielectric properties, such as higher dc BD strength, less EL intensity and space charge, than pure PP.

References

- [1] M. Rabuffi and G. Picci, "Status quo and future prospects for metalized polypropylene energy storage capacitors", IEEE Trans. on Plasma Science, vol.3, pp. 1939-1942, 2002.
- [2] E. Ildstad and T. Haave, "Conduction and partial discharge activity in HVDC cable insulation of lapped polypropylene films", IEEE 7th Intl. Conference on Solid Dielectrics, June 25-29, 2001, pp. 137-140.
- [3] K. Tohyama, S.S. Bamji, and A.T. Bulinski, "Simultaneous measurement of electroluminescence and dissipation current in cable insulation", Proc. of 7th Intl. Conf. on Properties and Applications of Dielectric Materials, June 1-5, 2003, pp. 1051-1054.
- [4] L. A. Utracki, "Clay-containing Polymeric Nanocomposites", Publisher: RAPRA Tech Ltd., Shawbury, Shrewsbury, Shropshire UK, (2004).
- [5] C. Laurent, "Optical pre-breakdown warnings in insulating polymers", IEEE Intl. Conference on Conduction and Breakdown in Solid Dielectrics, June 22-25, 1998, pp. 1-12.
- [6] C. Laurent, G. Teyssedre, and G. C. Montanari, "Time-resolved space charge and electroluminescence measurements in polyethylene under ac stress", IEEE Trans. on Diel. and Electrical Insulation, vol. 11, pp. 554-560, 2004.

Acknowledgments: Mrs. Y. Chen and Mr. D. McIntyre provided technical assistance to this project. Mr. D. St-Jean machined various test-cells and other experimental setup components and Dr. Jianming. Li (from NRCC/IMI) provided the nanocomposite samples. Their assistance is very much appreciated.

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