

Electrical Behavior of PET Films Coated with Nanostructured Organic–Inorganic Hybrids

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ABSTRACT: Hybrid coatings, based on poly(ethylene oxide) (PEO) or polycaprolactone (PCL) and silica (SiO₂), at different organic–inorganic compositions have been used to coat PET films employed in the electric industry to produce capacitors. The overall electrical behavior of the coated films has been investigated. The electrical strength of the coated films increases up to 10–15% of the uncoated ones regardless of polymer type (PEO/PCL) and amount of inorganic phase, as far as the thickness of the coating is below 5 μm. A systematic increase of surface electrical conductivity is found in all

coated samples which however still behave as insulators. Permittivity and loss factor also increase particularly at low frequencies (< 10 Hz) on account of the presence of ions deriving from the sol–gel process and on the presence of interfacial polarization probably related to the coatings nanostructured morphology which leads to phase separation. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4870–4877, 2006

Key words: organic–inorganic hybrids; PET films; electrical properties

INTRODUCTION

Polymers are widely used in electrical industry for their low conductivity and high electrical strength combined with flexibility and easy processing. For many applications, an improvement of the intrinsic electrical properties of the commonly used polymers is highly requested because it would allow improving performances of electrical devices. A possible way to improve some specific property of electrically insulating materials is the application of a coating onto their surface. This method has been already proposed through rather different techniques: for instance, polytetrafluoroethylene (PTFE) and poly(ethylene terephthalate) (PET) films have been coated with plasma polymerized films.¹ PET has been coated with *in situ* polymerized polyaniline (PANI) to increase its electrical strength² and antistatic films for polycarbonate (PC) minute electronic parts have been synthesized from radiation curable monomers.³

Organic–inorganic hybrids (also named *ceramers*) have recently attracted a strong interest in material science as confirmed by many reviews recently published.^{4,5} Indeed, ceramers combine flexibility of polymers with hardness and chemical resistance of inor-

ganic materials. They are transparent, due to the nanosize of domains, and can be easily applied as coatings to different materials by mild processes, opening new frontiers to the development of products with improved properties. Up to now, ceramers have been successfully applied onto metals and glasses^{6,7} and less frequently on polymer substrates. Hybrids are usually obtained through sol–gel process:⁸ this technology has a high appeal for polymeric substrates as it allows the formation of the inorganic network at temperatures that can be far below those of softening or degradation of the organic substrate. The chemical reactions involved in the process are the hydrolysis and the simultaneous condensation, acid or base catalyzed, of a metal alkoxide M(OR)₄, until formation of a metal oxide three-dimensional network. During the build-up of the inorganic network, organic compounds can be introduced and entrapped in the network structure. Alternatively, the organic component can be chemically modified so that it can be covalently bonded to inorganic domains, originating a network of organic–inorganic nanosized domains with high surface/volume ratio. Some nanocomposite hybrids have been recently used for the protection of some polymers.^{9–12} In particular, the scratch and flame resistance of PMMA^{13–14} and the barrier properties of PET¹⁵ and PVC¹⁶ have been significantly improved by ceramer coatings. The ability of ceramer coatings to improve at the same time resistance to oxygen diffusion, surface hardness, and scratch resistance led us to think that

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they can also be usefully applied to polymers to improve some electrical properties: for this purpose, we decided to study the effects of ceramer coatings on the electrical properties (performance) of PET, a polymer that combines a good balance of electrical, mechanical, and thermal properties with a low cost, and for these reasons is widely used as dielectric in the electric industry. Organic-inorganic materials have already attracted the interest of scientists in the formulation of optical devices and microelectronics.¹⁷⁻¹⁸ Consequently, in the present article organic-inorganic ceramer coatings of different compositions and thicknesses have been applied onto PET films and their effect on electrical properties such as electrical strength, permittivity, and surface conductivity has been investigated.

EXPERIMENTAL

Materials

High purity tetraethoxysilane (TEOS, Aldrich), poly(ethylene oxide) with $M_n = 1000$ g/mol (PEO, Aldrich), polycaprolactone diol with $M_n = 2000$ g/mol (PCL, Aldrich). 3-isocyanatopropyltriethoxysilane (ICPTES, Fluka), hydrochloric acid at 37% concentration (Carlo Erba), ethanol (EtOH, Carlo Erba), tetrahydrofuran (Aldrich) were used without further purification. Electrical grade PET films (Melinex[®] 401, DuPont) with thickness of 100 μm , commercially available for the production of capacitors, have been used as substrate without any preliminary surface treatment.

Preparation of PEO/silica and PCL/silica hybrids

α,ω -hydroxy terminated PCL with molecular weight 2000 and PEO with molecular weight 1000 have been triethoxysilane functionalized with ICPTES. ICPTES has been directly added to OH/ICPTES molar ratio of 1:1. The reaction has been carried out in bulk at 120°C for 1 h. The progress of the reaction has been monitored by means of ATR infrared spectroscopy (FTIR), performed with an Avatar 330 thermo Nicolet spectrometer: a minimum of 32 scans with a resolution of

4 cm^{-1} has been used. The broad absorption band of the hydroxyl groups of the oligomers (at about 3500 cm^{-1}) has been compared with the absorption band of the urethane groups (at about 3380 cm^{-1}) and following the disappearing of the absorption band related to isocyanate groups (at 2270 cm^{-1}). The expected structures have been also confirmed by the ¹H-NMR analysis of the reactant ICPTES and the final products as already reported.^{13,16} Hybrids have been obtained according to the following procedure: triethoxysilane functionalized polymer (PCL-Si or PEO-Si) and TEOS were dissolved in tetrahydrofuran (usually, 40% wt/vol) until a homogeneous solution was obtained. Then, EtOH, water, and hydrochloric acid have been added to the solution at the following molar ratios with respect to ethoxide groups: EtO—/EtOH/H₂O/HCl = 1/1/1/0.05. Afterwards, the solutions have been heated at 60°C for 1 h, to promote partial hydrolysis-condensation of the reactants.

Coatings application and characterization

After the above-described thermal treatments, the sol-gel solution has been used to coat both sides of transparent and uncolored PET films (5 × 5 cm^2 and 100 μm of thickness) by manual dip-coating. Afterwards, samples have been left at room temperature for 30 min, then annealed at 70°C for about 18 h, and postcured at 100°C for 2 h. Differential scanning calorimetry (Thermal Analysis Instruments, mod 2010) has been carried out on the coatings submitted to the previously described thermal treatment, at a scanning rate of 20°C/min from -150 to 100°C. Scanning electron microscopy (Philips, mod XL-40) has allowed to estimate the average thickness of the coatings, and to derive information about the adhesion of the coating to the PET substrate before and after the electrical strength tests. Electrical strength has been measured according to ASTM D 149 test, by means of two stainless steel spherical electrodes (Rogowsky type) with a 15 mm diameter. The whole system (sample plus electrodes) has been soaked in silicon oil at room temperature during the measurements. Voltage has been applied at an increasing rate of 50 kV/min, at a

TABLE I
Coating Compositions and Thickness

Sample	Organic/inorganic weight ratio	Coating thickness (μm)	Overall sample thickness (μm)
PEO-Si/SiO ₂ 1 : 2	1/2	1.5	103
PEO-Si/SiO ₂ 1 : 1	1/1	3.0	106
PEO-Si/SiO ₂ 2 : 1	2/1	2.5	105
PEO-Si/SiO ₂ 2 : 1 >	2/1	9.0	118
PCL-Si/SiO ₂ 1 : 2	1/2	2.5	105
PCL-Si/SiO ₂ 1 : 1	1/1	3.0	106
PCL-Si/SiO ₂ 2 : 1	2/1	4.5	109
PCL-Si/SiO ₂ 2 : 1 >	2/1	20	140

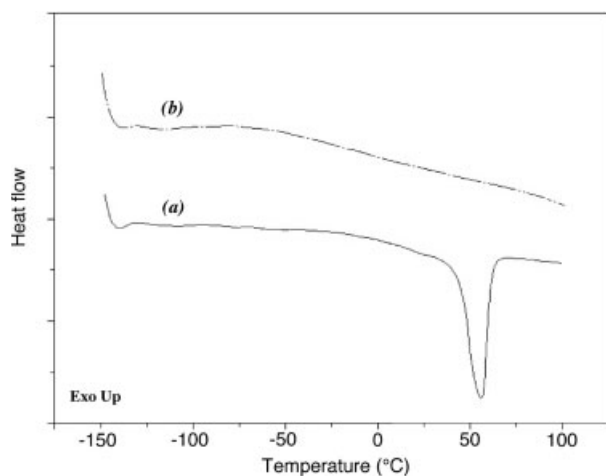


Figure 1 DSC thermograms of PCL homopolymer (a) and PCL-Si/SiO₂ 1 : 1 (b).

frequency of 50 Hz. Permittivity (ϵ') and loss factor (ϵ'') have been determined according to ASTM D 150, with a three-terminal electrode configuration obtained by gold evaporation *in vacuo* on the sample surfaces. Measurements have been carried out in air at room temperature, in the frequency range 10^{-2} – 10^6 Hz, by means of a Novocontrol Instrument (WinEta 3.1). Moreover, the surface electrical conductivity of the coatings has been measured according to ASTM D 257, through a volt-amperometric method, i.e., by determining the current flowing between two electrodes as a function of time after voltage set: again a three-terminal electrode configuration has been applied.

RESULTS AND DISCUSSION

Preparation, application, and characterization of the coatings

The preparation of PEO/silica^{16,19–21} and PCL/silica^{13,22–24} hybrid materials by sol-gel method has already been reported. It is widely accepted^{13,22,25} that the presence of alkoxy-silane groups on the polymeric chains increase the reactivity/miscibility with the metal alkoxide and promote a better interconnection between organic and inorganic phases. For this reason, in this work, α,ω -hydroxy terminated PEO and PCL were first reacted with ICP TES to obtain α,ω -triethoxy-silane terminated polymers (PEO-Si and PCL-Si). Table I lists all the organic-inorganic coatings that have been prepared and used as coatings of PET films. Two different oligomers (PCL and PEO) have been used as organic phases (the correspondent hybrids hereafter referred to as PCL-Si/SiO₂ and PEO-Si/SiO₂, respectively). Three different organic/inorganic ratios were used for the coatings (1 : 2, 1 : 1, and 2 : 1 wt/wt); all of them appeared transparent at visual inspection. DSC analyses disclosed the absence of any significant

melting transition due to PEO and PCL crystallites, as highlighted in Figure 1, where the thermograms relative to the unmodified PCL and the 1 : 1 PCL-Si/SiO₂ are reported as an example. Both evidences suggest the formation of nanocomposite hybrid structures where organic and silica domains are intimately interconnected with dimensions less than the wavelength of

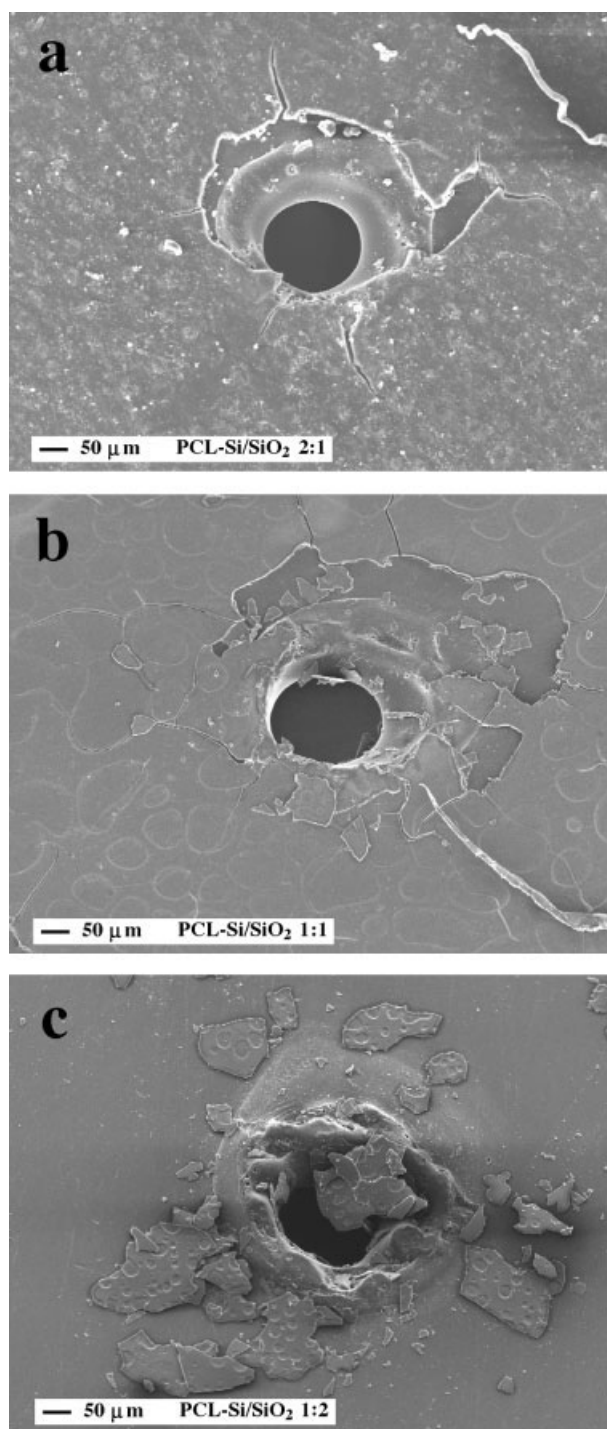


Figure 2 Scanning electron micrographs of PET film coated with PCL-based hybrids submitted to electrical strength tests: coated with PCL-Si/SiO₂ 2 : 1 (a); 1 : 1 (b); 1 : 2 (c).

the visible light and where organic chains bonded to silica domains are not able to organize themselves into crystalline structures of significant size: this hypothesis has been previously confirmed by several techniques both on coating samples of comparable thickness¹⁴ and on bulk materials.^{24,26}

Scanning electron micrographs have been taken for all samples of coated PET films (Fig. 2). Both the surfaces and the edge view of the fracture surface were examined. The films appear to be homogeneously coated by the ceramers and no significant defects have been detected. The edge view micrographs showed that coatings are quite uniform in thickness, which ranged from 2 to 5 μm for most of the samples (see data in Table I), with the higher values obtained by dipping PET films into more concentrated and viscous solutions. The edge view micrographs also indicated a good adhesion of the coatings to the PET substrate for both PEO- and PCL-based ceramers for all the investigated compositions. On the contrary, significant differences were detectable by observing samples after the electrical strength tests (Fig. 2): for both PEO- and PCL-based coatings, those with the highest organic content (2 : 1) show only a reduced extent of damage around the discharge hole; this damage progressively increases by decreasing organic/inorganic ratio with an almost complete coating removal for the more brittle samples 1 : 2. These different behaviors towards the electrical shock probably reflect the intrinsic brittleness and the adhesive properties of the coating to the substrate.

Electrical strength measurements

Electrical strength data (E_s) were treated according to the statistical relation, which is derived from the Weibull theory:

$$P(E_s) = 1 - e^{-\left(\frac{E_s}{\alpha}\right)^\beta}$$

where α corresponds to the value that provides a 63.2% probability of discharge, and β can be related to data dispersion and consequently to the reliability of the resulting material.

Figure 3 shows, for all the investigated systems, both the values of α (kV/mm) and β . All coatings with thickness below 5 μm provide an increase in the electrical strength up to about 10 kV/mm, approximately a 15% increase with respect to the PET value. It is noteworthy that this improvement has been obtained for coatings having a thickness that is just a small fraction of the overall thickness of the film, decreasing by increasing the thickness of the coating and that is not related to the composition of the coating (organic/inorganic ratio and chemical nature, PEO or PCL, of the organic component). This behavior suggests that the increase of the electrical strength has probably to be related to the characteristics of the very surface in contact with the electrodes rather than to a contribution due to the coating itself, because in this last case the electrical strength should depend on its bulk composition and should increase with coating thickness. In this respect, it is interesting to note that the surface composition may be different from the bulk composition. Indeed, previous studies^{13,14} evidenced a preferential surface segregation of silica at the coating-air interface, so that the compositions of the very surface were similar, even when the organic/inorganic ratios in the bulk were different and this phenomenon was used to explain the very similar flame resistance of PMMA coated with different PCL-based ceramers. A similar phenomenon of surface segregation may be assumed for the explanation of the similar increase of electrical strength observed for different coatings. If the above interpretation is accepted, it remains to elucidate why there is a strong reduction of electrical strength by increasing the thickness of the coating. The explanation can be derived from the observation that many of the coated samples have β values lower than those found for

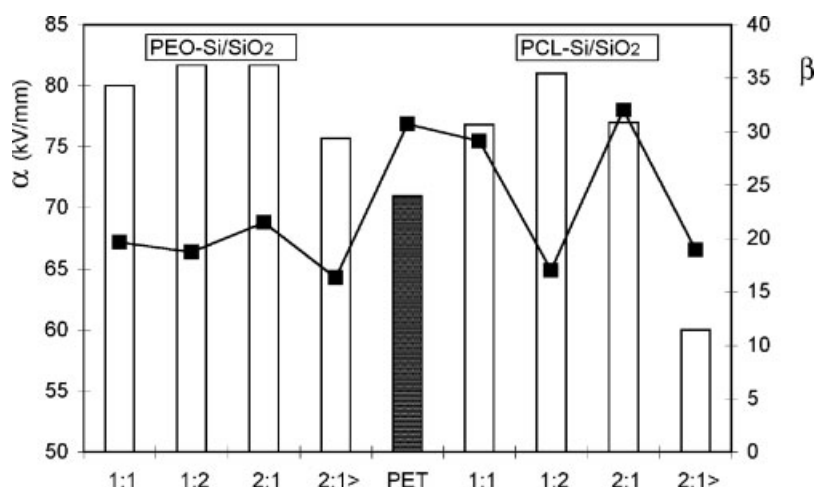


Figure 3 Electrical strength (bars) and β values (square symbol) of coated and uncoated PET films.

TABLE II
Surface Conductivity at 25°C and 50 ± 10 RH%

Sample	Surface conductivity, S_{sq} (10^{-16})
PET	1.0
PEO-Si/SiO ₂ 1 : 2	4.3
PEO-Si/SiO ₂ 1 : 1	1.4
PEO-Si/SiO ₂ 2 : 1	2.0
PEO-Si/SiO ₂ 2 : 1 >	19.2
PCL-Si/SiO ₂ 1 : 2	3.2
PCL-Si/SiO ₂ 1 : 1	2.5
PCL-Si/SiO ₂ 2 : 1	10.3
PCL-Si/SiO ₂ 2 : 1 >	17.1

uncoated PET films. In fact, the presence of defects in the coating may explain both the lowering of β values in many of the coated films with respect to PET sample and the lowest electrical strength for the thickest coating (PCL-Si/SiO₂ 2 : 1 >, 20 μ m), which have the highest probability of being defective. Even though SEM observations have shown a homogeneous surface of the coatings and a satisfactory adhesion to the substrate, a limited amount of defects (probably microvoids), not disclosed by the previous technique, may however be present in particular taking into account that coated films have been prepared by manual dipping and that microvoids can be more easily originated in thick samples, in which solvent evaporation is more difficult.

Permittivity and surface conductivity measurements

Even though electrical strength is one of the most important property for application in capacitors, other electrical properties, such as permittivity, loss factor, and surface electrical conductivity may play a signifi-

cant role with respect to the performances of electrical devices. Therefore, the effect of ceramer coatings has been investigated also for these properties. Table II reports the surface conductivity of all the investigated samples determined as described before at 3600 s after voltage set. Although the values of surface conductivity of all coated samples are even one order of magnitude higher than that of uncoated PET for the thickest ones, all PET-coated samples can still be classified as electrically insulating on their surface. Such an increase should be caused by the presence of ionic impurities in the coatings: moreover, the formation of a continuous silica phase of even small thickness on the very surface of the coating should also be ruled out, as the presence of water molecules on the same surface would lead to higher conductivity values than those obtained.

Figures 4 and 5 show the permittivity and the loss factor, respectively, as a function of frequency at room temperature for all samples belonging to the PEO-based ceramers. All coatings, and particularly those belonging to the 2 : 1 composition, tend to increase the permittivity of the PET samples (Fig. 4): this increase is restricted in the industrial range of frequency but becomes relevant at frequencies below 10 Hz. Even though the a.c. characterization of the coatings alone has not been performed in the present article, dielectrical characterizations carried out on coatings of similar composition^{17,27} provided ϵ' data around 3.5–4.0, at frequencies between 1 and 10 kHz, which is probably quite consistent with our results in the same frequency range. From the loss factor data (Fig. 5), we can observe that coatings tend to increase also dielectrical losses, particularly in the same range of frequencies (< 10 Hz) previously observed for permittivity: it is also interesting to note that for the 2 : 1 samples a maximum appears at frequencies about 5×10^{-2} Hz. Measurements carried out with different types of electrodes

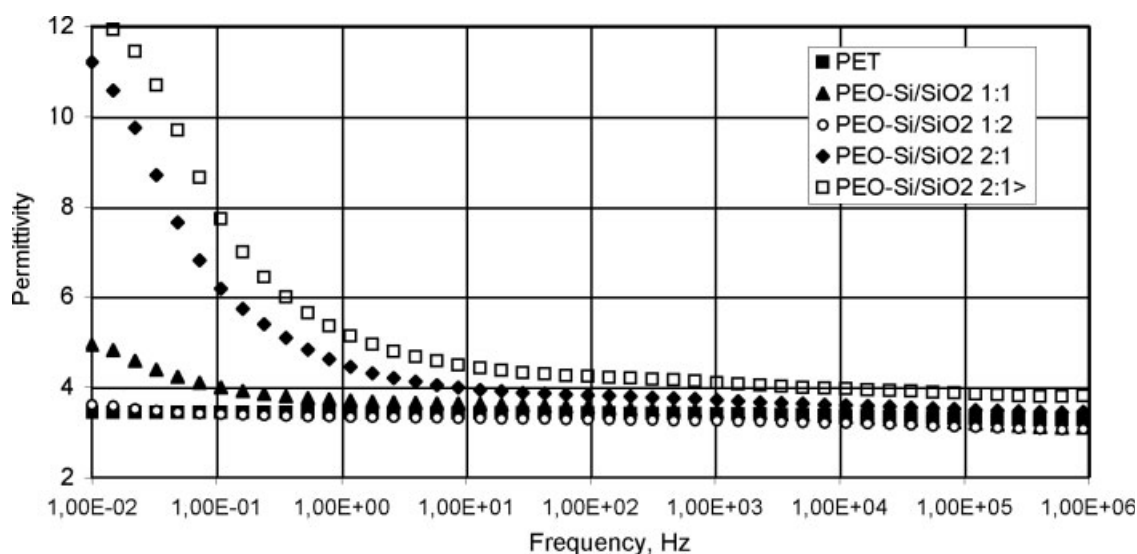


Figure 4 Permittivity versus frequency for PET films coated with PEO-Si/SiO₂ hybrids (at room temperature).

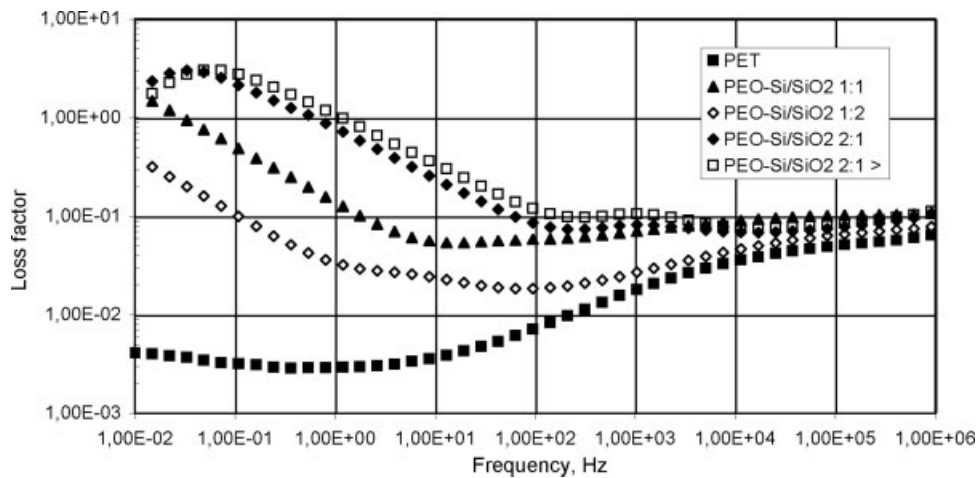


Figure 5 Loss factor versus frequency for PET films coated and uncoated with PEO-Si/SiO₂ hybrids (at room temperature).

ruled out the possibility of electrode polarization. Similar results had been previously obtained for different systems showing, however, similar nanosized siliceous domains.^{28,29} A further maximum is present at higher frequency ($> 10^2$ Hz) and in all the investigated samples which is probably to be related to a dipolar relaxation involving the mobility of PEO chains. At 100°C, the trend of permittivity with frequency is similar to that observed at 25°C, with the highest increase for the same 2:1 coated samples in the low-frequency range (Fig. 6). The loss factor data at 100°C are reported in Figure 7; both the curve profiles and the loss factor data are significantly different from those measured at 25°C. In particular, there is a significant increase of loss factor for uncoated PET at low frequencies, which leads to a reduction of the difference between coated and uncoated PET. Moreover, the low frequency maximum for the 2 : 1 composition is shifted of about one decade of frequency towards higher frequency disclosing the thermal dependence of the relaxation process. The low frequency relaxation has a similar behavior.

To explain the permittivity increase, we can postulate that in the bulk structure of the coatings, macromolecular segments (PEO or PCL), although constrained by the inorganic domains (and therefore unable to crystallize), have sufficiently high mobility which increases with temperature for all samples, as demonstrated by the permittivity values, and which is higher for samples with higher organic/inorganic ratios, as shown by the percent increase of permittivity. We have also speculated that a small amount of impurities (probably ions deriving from the sol-gel process) are present, as also suggested by the increase of surface conductivity previously underlined; the presence of supplementary charge carriers (which are absent in the PET films) can account for both these effects. Moreover, the nanostructuring of the coatings leading to phase separation suggests the effect of an interfacial polarization. In particular, the absorption maximum at the lower frequencies can be attributed to a Maxwell-Wagner-Sillars polarization effect, deriving from charge accumulation at different phase boundaries, which can also account

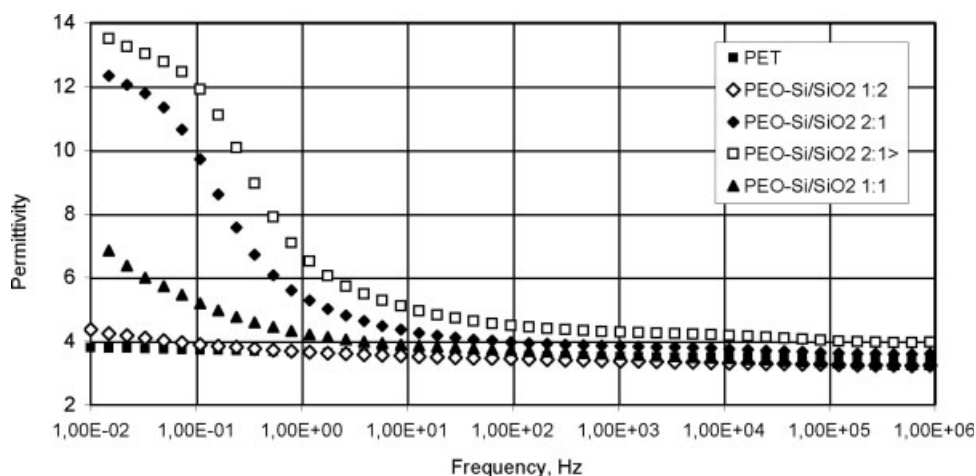


Figure 6 Permittivity versus frequency for PET films coated with PEO-Si/SiO₂ hybrids (at 100°C).

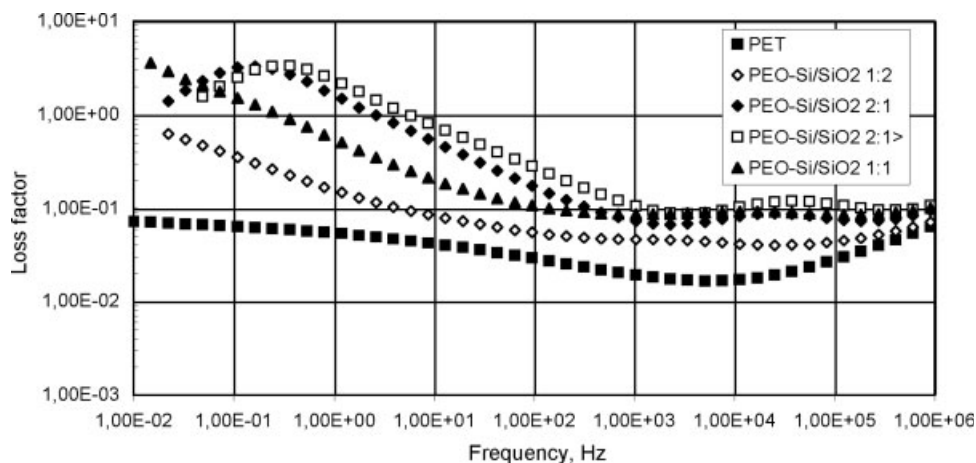


Figure 7 Loss factor versus frequency for PET films coated with PEO-Si/SiO₂ hybrids (at 100°C).

for the large increase in permittivity at low frequency. As the maximum is not present for coatings compositions 1 : 1 and 1 : 2, we have to suppose that there is a significant difference in the coatings morphology, and in this respect, loss factor measurement can be considered a potential technique for the investigation of the nanomorphology.^{28,29} Coatings based on PCL show a dielectrical behavior similar to that observed for PEO-based coatings and curves are not reported for sake of brevity.

These results indicate that the insulating properties of PET films can be improved by organic-inorganic hybrid coatings and suggest that a further improvement should be possible through a better control of the coating thickness and of the amount of ions present inside the same coatings. This approach can in principle be applied to other polymer substrates and it is our opinion that it can create a number of potential applications and improve the scientific knowledge.

CONCLUSIONS

PET films have been successfully coated by nanostructured organic-inorganic coatings using TEOS, as a precursor of silica networks, and organic oligomers, based either on PEO or PCL at different organic/inorganic weight ratios. The adhesion of the coatings to the substrate proves to be quite efficient at all the investigated compositions and it increases when the organic/inorganic ratio in the coating is increased. The main effects on the electrical properties can thus be summarized:

- hybrid coatings with thickness below 5 μm provide significant increase of the electrical strength, up to about 10–15% that of the unmodified PET and this result is almost independent from the organic/inorganic ratio and from the nature of the organic phase (PEO or PCL): higher thickness (> 5 μm), on the contrary, leads to the decreasing

of the electrical strength, probably on account of the formation of small defects;

- although the surface electrical conductivity of the coated surfaces is always higher than that of the uncoated PET films, due to the presence of ions in the coatings, all the surfaces of the investigated materials can still be classified as electrically insulating;
- permittivity and dielectrical losses tend to increase in coated samples: at frequencies higher than 10² Hz, the effect is rather limited and can be related to the relaxation of PEO and PCL chains in the coating. At low frequencies (< 10 Hz) and for the highest content of organic phase the increase is remarkable and can be explained again assuming that ions deriving from the sol-gel process are present in the coatings and that an interfacial polarization takes place in the coating itself on account of presence of nanophase separation

References

1. Kusabiraki, M.; Aozasa, M. *Thin Solid Films* 1996, 281, 533.
2. Job, A. E.; Alves, N.; Zanin, M.; Ueki, M.; Mattoso, L.; Teruja, M.; Giacometti, J. A. *J Phys D: Appl Phys* 2003, 36, 1414.
3. Kim, H. K.; Kim, Y. B.; Cho, J. D.; Hong, J. W. *Prog Org Coat* 2003, 48, 34.
4. Sanchez, C.; Julian, B.; Belleville, P.; Popall, M. *J Mater Chem* 2005, 15, 3559.
5. Sanchez, C.; Soler-Illia, J.; Ribot, F.; Lalot, T.; Mayer, C. R.; Cabuil, V. *Chem Mater* 2001, 13, 3061.
6. Uhlmann, D. R.; Teowee, G. *J Sol-Gel Sci Technol* 1998, 13, 153.
7. Frings, S.; Meinema, H. A.; Nostrum, C. F.; Linde, R. *Prog Org Coat* 1998, 3, 126.
8. Brinker, C. J.; Scherer, G. W. *Sol-Gel Science*; Academic Press: Boston, 1990.
9. Mackenzie, J. D.; Bescher, E. P. *J Sol-Gel Sci Technol* 2000, 19, 23.
10. Seepur, S.; Kunze, N.; Werner, B.; Schmidt, H. *Thin Solid Films* 1999, 351, 216.
11. Yunfa, C.; Lianming, J.; Yusheng, X. *J Sol-Gel Sci Technol* 1998, 13, 735.
12. Mackenzie, J. D.; Bescher, E. P. *J Sol-Gel Sci Technol* 2003, 27, 7.

13. Messori, M.; Toselli, M.; Pilati, F.; Fabbri, E.; Fabbri, P.; Busoli, S.; Pasquali, L.; Nannarone, S. *Polymer* 2003, 44, 4463.
14. Messori, M.; Toselli, M.; Pilati, F.; Fabbri, E.; Fabbri, P.; Busoli, S. *Surf Coat Int B Coat Trans* 2003, 86, 181.
15. Azuta, K.; Tadanaga, K.; Minami, T. *J Ceram Soc Jpn* 1999, 107, 293.
16. Messori, M.; Toselli, M.; Pilati, F.; Fabbri, E.; Fabbri, P.; Busoli, S.; Pasquali, L.; Nannarone, S. *Polymer* 2004, 45, 805.
17. Houbertz, R.; Domann, G.; Schmitt, A.; Martin, H.; Park, J. U.; Frohlich, L.; Popall, M.; Buestrich, R.; Streppel, U.; Dannberg, P.; Wachter, C.; Brauer, A. *Thin Solid Films* 2003, 442, 194.
18. Houbertz, R.; Domann, G.; Schultz, J.; Orłowski, B.; Frohlinch, L.; Kim, W. S. *Appl Phys Lett* 2004, 84, 1105.
19. Wojcik, A. B.; Ting, A.; Klein, L.C. *Mater Sci Eng C Biomimetic Mater Sens Syst* 1998, 6, 115.
20. Klein, L. C.; Beaudry, C. L.; Wojcik, A. B.; Mandanas, M. *Ceram Trans* 1998, 81, 273.
21. Jiang, S.; Yu, D.; Ji, X.; An, L.; Jiang, B. *Polymer* 2041, 2000, 41.
22. Tian, D.; Dubois, P.; Jerome, R. *Polymer* 1996, 37, 3983.
23. Tian, D.; Dubois, P.; Jerome, R. *J Polym Sci Part A: Polym Chem* 1997, 9, 2295.
24. Tian, D.; Blancher, S.; Dubois, P.; Jerome, R. *Polymer* 1998, 39, 855.
25. Kohjiya, S.; Ochiai, K.; Yamashita, S.; Yamashita, S. *Polymer Gels: Fundamentals and Biomedical Applications*; Plenum: New York, 1991.
26. Tian, D.; Blacher, S.; Dubois, P.; Jerome, R. *Polymer* 1999, 40, 951.
27. Robertsson, M.; Hagel, O.; Gustafsson, G.; Dabek, A.; Popall, M.; Cergel, L.; Wennekers, P.; Kiely, P.; Lebbby, M.; Lindahl, T. In *Proceedings of the 48th Electronic Components and Technology Conference*; 1998; pp 1413–1421.
28. Mauritz, K. A.; Stefanithis, I. D. *Macromolecules* 1990, 23 1380.
29. Mauritz, K. A. *Macromolecules* 1989, 22, 4483.