



HAL
open science

Thermal ageing effects on polypropylene properties

A. Hedir, F. Slimani, M. Moudoud, O. Lamrous, Sombel Diaham

► **To cite this version:**

A. Hedir, F. Slimani, M. Moudoud, O. Lamrous, Sombel Diaham. Thermal ageing effects on polypropylene properties. 2019 IEEE Conference on Electrical Insulation and Dielectric Phenomena (CEIDP), Oct 2019, Richland, United States. pp.130-133, 10.1109/CEIDP47102.2019.9009700 . hal-04754763

HAL Id: hal-04754763

<https://hal.science/hal-04754763v1>

Submitted on 26 Oct 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Thermal ageing effects on polypropylene properties

A. Hedir^{1,2}, F. Slimani^{1,2}, M. Moudoud^{1,2}, O. Lamrous^{1,3} and S. Diaham^{4,5}

¹Université Mouloud Mammeri de Tizi-Ouzou BP 17 RP, Algérie

²Laboratoire des Technologies Avancées en Génie Electrique (LATAGE)

³Laboratoire de Physique et Chimie Quantique (LPCQ)

⁴Université de Toulouse; UPS, INPT; LAPLACE; 118 route de Narbonne - Bât. 3R3;
F-31062 Toulouse cedex 9, France

⁵CNRS; LAPLACE; F-31062 Toulouse, France.

Abstract- This work reports on the effects of the thermal ageing on the dielectric and physico-chemical properties of polypropylene (PP). The dielectric properties such as AC electrical conductivity (σ_{ac}), dielectric constant (ϵ') and dielectric losses (ϵ'') are measured at temperatures between 0 °C and 80 °C in the frequency range of 1 Hz – 10⁷ Hz. Whereas, the changes in the PP's structure were highlighted by Fourier Transformer Infrared Spectroscopy (FT-IR), Scanning Electron Microscope (SEM) and the estimated Hydrophobicity from measuring the contact angle.

The experimental results revealed that thermal ageing leads to a degradation of the dielectric properties. Indeed, σ_{ac} , ϵ' and ϵ'' increased by ageing. These variations may be explained by the changes in the polymers structure

I. INTRODUCTION

Organic polymer has been used widely as insulating materials in high voltage systems because of their high breakdown strength under electrical stress. Moreover, they have other advantages such as low cost, high resistance to chemical degradation and easy recycling. Such characteristics are especially relevant for the industry of electrical power electronic systems [1-6]. These polymers are exposed to much environmental stress during their service life. These stresses will initiate changes in the materials properties, which may potentially start the deterioration of the equipment and act directly on its reliability and lifetime. Temperature is one of the major reasons for long-term degradation of polymers used as insulation in electrical equipment. Consequently, some of their properties may alter and produce limitations on the effective service life of the equipment. Understanding the thermal ageing behavior is crucial to the formulation, design and application of polymeric materials. In fact, the overall effects of thermal ageing on the chemical properties are the oxidation reactions, cross-linking, chain scission, variation in crystallinity ...etc [7, 8].

This study concerns polypropylene (PP) material which offers a good balance of thermal, chemical and physical properties [9] whose chemical formula is given in Figure 1. Because of

his excellent mechanical, thermal and electrical properties the material is used in a wide spectrum of applications notably as

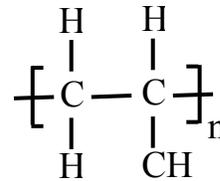


Fig.1. PP chemical formula

a dielectric in power capacitors, cable wraps and layer and phase separators for rotating electrical equipment and transformers. It is also used with paper laminates as the insulation of transmission-class power cables [10, 11, 12, 13].

This paper provides experimental results of AC electrical conductivity (σ_{ac}), dielectric constant (ϵ') and dielectric losses (ϵ'') of virgin and aged PP. The ϵ' and ϵ'' curves against frequency for different temperatures exhibit a peaks corresponding to alpha relaxation.

For better understanding the thermal ageing effects on the different parameters (AC electrical conductivity (σ_{ac}), dielectric constant (ϵ') and dielectric losses (ϵ'')) different complementary analysis techniques as Fourier Transformer Infrared Spectroscopy (FT-IR), Scanning Electron Microscope (SEM) and estimated Hydrophobicity by measuring the contact angle are used .

II. EXPERIMENTAL

The samples are cut from the same commercial plate of 1 mm thick to be sure that the properties of the material are similar. The thermal aging was carried out in a thermo-ventilated oven at a temperature of 90 °C during 30 days.

Dielectric Relaxation Spectroscopy (DRS) was used to probe the molecular dynamics of PP samples. The measurements were conducted from 1 to 10⁷ Hz at a temperature range of 0 to 80 °C, and performed on the metalized samples using a Novocontrol Alpha-A analyzer under N₂ atmosphere. The morphology and the physical properties for aged and virgin PP were characterized by a scanning electron microscope (SEM) (Philips XL 30) at 20 kV and FT-IR spectra (Perkin Elmer)

range of 4000 cm^{-1} to 400 cm^{-1} with a resolution of 4 cm^{-1} . The hydrophobicity was studied by measuring the contact angle formed between a water drop and PS surface from the photography taken with digital camera and analyzed with AUTOCAD view software.

III. RESULTS AND DISCUSSION

A. Dielectric behavior of virgin PP

The dielectric constant (ϵ'), the dielectric losses (ϵ'') and the volume conductivity (σ_{ac}) of virgin PP versus frequency for temperatures from 0 to 80° are shown in Figures 2, 3 and 4. The dielectric constant decreased with increasing frequency as shown in fig.2. We can find that α relaxation appears at the frequency lower than 1kHz. The dielectric losses increase at first, then decrease with increasing frequency as shown in fig. 3. The dielectric losses exhibits a peak in the frequency range 100 to 1000 Hz. This peak corresponding to α relaxation is due to relaxation in crystalline portion of the PP material [14]. The variation of AC conductivity of virgin PP as a function of frequency at different temperatures is depicted in figure 4. It is clearly observed that σ_{ac} increases rapidly with frequency and slightly with temperature.

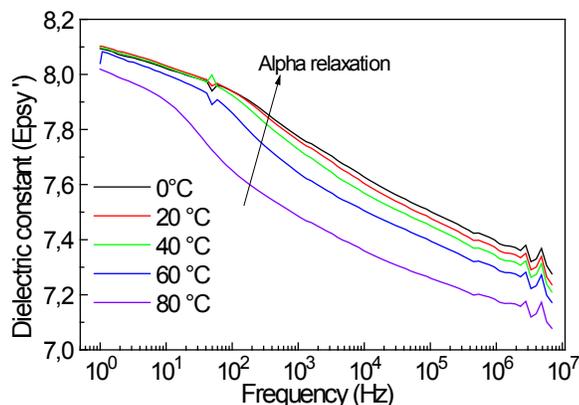


Fig.2. Dielectric constant versus frequency for different temperatures for virgin PP

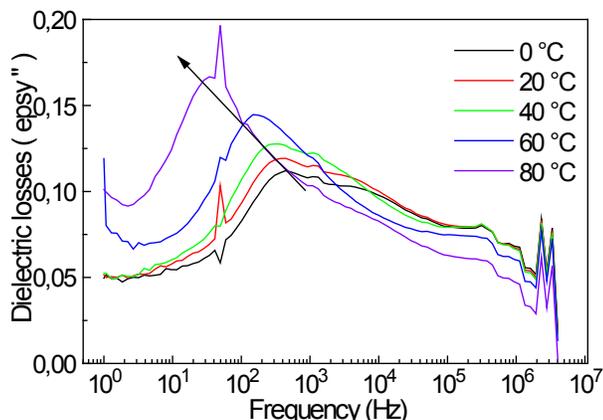


Fig.3. Dielectric losses versus frequency for different temperatures for virgin PP

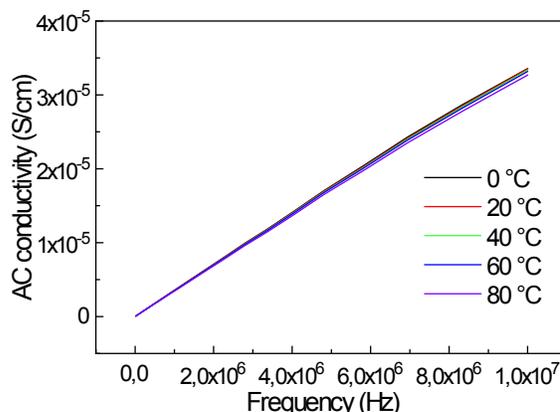


Fig.4. AC conductivity versus frequency for different temperatures for virgin PP

B. Thermal ageing effects on the dielectric behavior of PP

The dielectric constant (ϵ'), the dielectric losses (ϵ'') and the AC conductivity of virgin and aged PP versus frequency are shown in Figures 5, 6 and 7. The results shown that the dielectric losses (ϵ'') increases about 7 % after ageing. The dielectric losses (ϵ'') decreases between 1 to 100 Hz after ageing. Then it increases when the frequency is higher than 100 Hz. In addition, the α relaxation pic shifts to higher frequency after ageing. On the other hand, σ_{ac} increases slightly after electrical ageing as shown in figure 7. These increases are due to occurred modification of physical and chemical properties of the PP polymer. Indeed, the formation of dipole and impurities are all factors that could explain this increase in conductivity. From the observation results, after ageing, it appears damage marks on the polymer surface whose existence will be explained via complementary analysis technics.

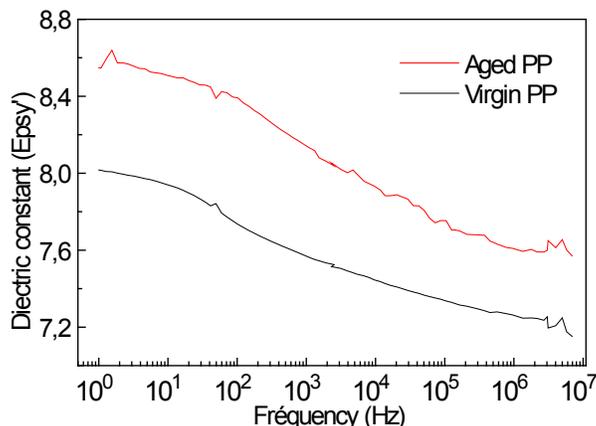


Fig.5. Dielectric constant versus frequency for different temperatures for aged and virgin PP

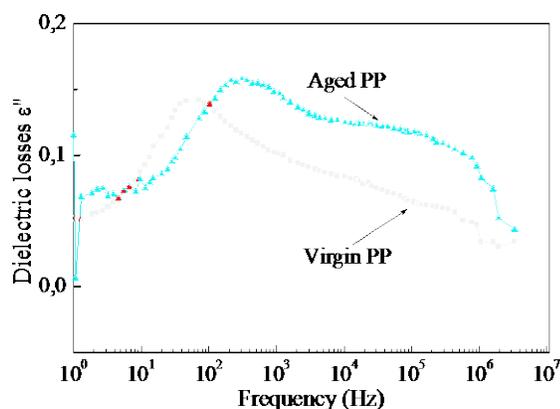


Fig.6. Dielectric losses versus frequency for different temperatures for aged and virgin PP

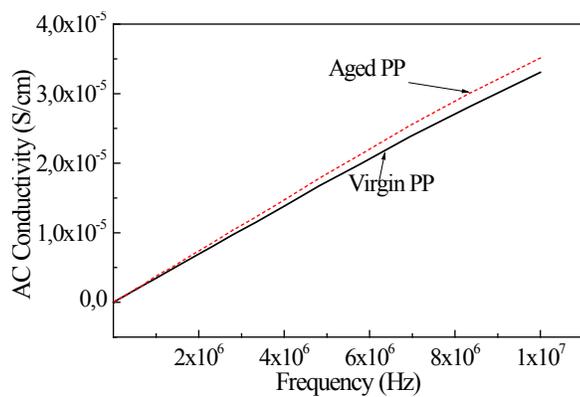


Fig.7. AC conductivity versus frequency for different temperatures for aged and virgin PP

C. FTIR analysis

Figure 8 displays representatives spectrums from virgin and aged PP. The results showed that the peaks are located in a wide range of spectra scale and are in agreement with the results presented in the literature [12, 15,16,17, 18]. The peaks at 3394 and 3194 cm^{-1} were ascribed to OH group. C-H bend of methyl group (CH_2 and CH_3) were observed at 2918, 2839, 1452, 1375 cm^{-1} and $\text{CH}_2 - \text{CH}(\text{C}-\text{H}_3)$ were observed at 1166, 972 and 840 cm^{-1} . The peaks at 1724, 1710, 1690 and 1658 cm^{-1} were assigned to carbonyl group ($\text{C}=\text{O}$), while the peak at 1630 cm^{-1} is assigned to aromatic $\text{C} = \text{C}$ stretching. The comparison between the two spectrums indicates that similar functional groups are present in the aged and virgin PP material. However, the aged specimen spectrum shows that for almost every peak, the band intensities increase. These increases aid conduction and indicate that the thermal ageing affect on electrical properties sample. Indeed, these increases indicate scission in main chain that leads to greater mobility of shorter degraded chains present in the amorphous phase [19].

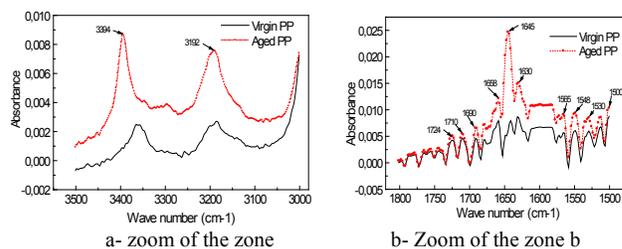
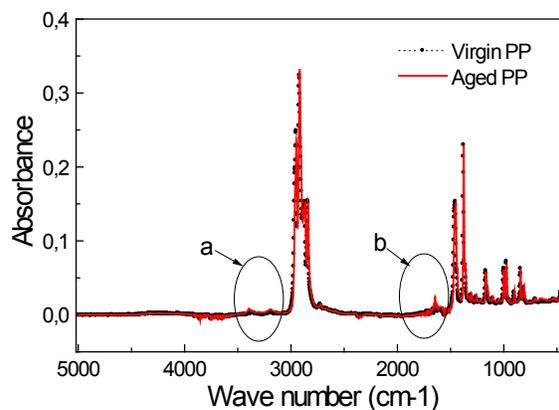


Fig.8. ATR-FTIR spectrums of virgin and aged PP

D. SEM analysis

Figure 9 shows the SEM micrographs of virgin and aged PP. The virgin sample has a smooth and homogeneous surface, figure 9a. There is no noticeable aberration. However, the micrographs of sample thermally aged exhibit craters damages of the surfaces, figures 9b. It was also noted that the surface morphology (shape, size and the arrangement of the particles on surface of the sample) appeared to change after ageing.

The changes in the surface structure (damages, craters, surface roughness...) of PP after thermal ageing are a result of chain scission and oxidize in the amorphous phase [9, 20, 21]. Generally, these processes are irreversible. The craters and damages of PP surface constitute a potential origin for the modification of the trap characteristics. This modification of traps energy as well as their density and distribution play an important role in the modifications of the dielectric properties [22].

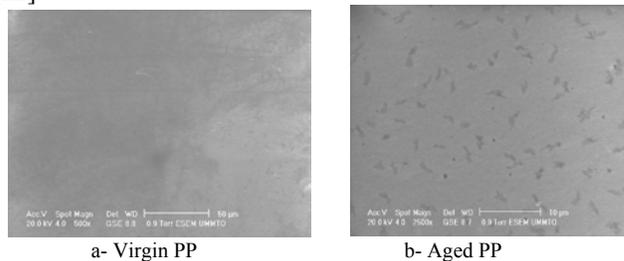
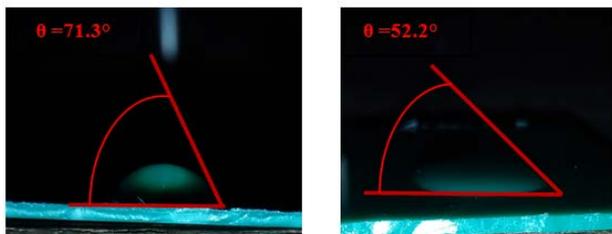


Fig.9. SEM micrographs of virgin and aged PP

E. Contact angle measurement and estimated hydrophobicity

The hydrophobicity of PP surface was studied by means contact angle measurements. According to this, figure 10

shows a representative water contact angle of virgin and aged PP which decreases after ageing from 71.3° to 52.2° . This indicates that the thermal ageing of PP polymer increases its hydrophobicity, presumably due to the formation of oxidized chemical species through chemical photo-oxidation reactions, such as carbonyl (C=O), carboxyl (COOH) or hydroxyl (OH) groups [23] and increasing of surface roughness according to the FTIR and SEM analysis.



a- Virgin ($\theta = 71.3^\circ$) b- Aged PP ($\theta = 52.2^\circ$)
Fig. 10. Contact angles of virgin (a) and aged (b) samples.

IV. Conclusions

This paper presents a study of thermal aging experiment on the commercial insulating PP polymer material. The dielectric and physico-chemical properties of this material were measured and analyzed. Some conclusions can be drawn as following:

- The results shown that the dielectric losses (ϵ'') increases about 7 % after ageing under 90°C during 30 days;
- The dielectric losses (ϵ'') decreases between 1 to 100 Hz after ageing. Then it increases when the frequency is higher than 100 Hz. In addition, the α relaxation pic shifts to higher frequency after ageing;
- AC conductivity (σ_{ac}) increases slightly after thermal ageing;
- The phenomenon of PP degradation by thermal aging was interpreted in terms of chemical and structure modifications. These modifications were highlighted by FTIR, SEM technics and estimated hydrophobicity.

ACKNOWLEDGMENT

The authors thank the Algerian Ministry of Higher Education and Scientific Research for supporting this work through the project PRFU A01L07UN150180005.

REFERENCES

- [1] S. Z. A. Dabbak, H. A. Illias, B. C. Ang, N. A. A. Latiff and M. Z. H. Makmud "Electrical Properties of Polyethylene/Polypropylene Compounds for High-Voltage Insulation" *Energies* 2018, 11, 1448
- [2] J. C. Salamone " Polymeric Materials Encyclopedia" *Twelve Volume Set CRC Press*, 1996.
- [3] Hasan Sabeeh Jabur "Electrical and optical properties modification of polystyrene by Vanadium (V) ion-pair organometallic complex" *Advances in Applied Science Research*, 2015, 6(8):1-6.
- [4] M.M. Hossain "Effect of humidity and thermal aging on the absorption characteristics in polymer film" *Bul. Mater. Sci.* Vol.15, N° 2, April 1992, pp 153-159.
- [5] B. Hadri, P.R. Mamy, J. Martinez, M. Mostefa "Electrical conduction in semicrystalline polyethylene terephthalate in high electric field" *Solid State Communications* 139 (2006) 35-39.
- [6] E. Baer and L. Zhu "50th Anniversary Perspective: Dielectric Phenomena in Polymers and Multilayered Dielectric Films" *Macromolecules*, 2017, 50 (6), pp 2239–2256;
- [7] A. Law, L. Simon, P. Lee-Sullivan "Effects of Thermal Aging on Isotactic Polypropylene Crystallinity " *Polymer Engineering and Science-2008*, pp 627-633 ;
- [8] A. Hedir , M. Moudoud . M.A. Handala , F. Bellabas " Caractérisation diélectrique du polyéthylène réticulé chimiquement soumis à la contrainte thermique" *10^{ème} Conf. de la Société Française d'Électrostatique (SFE)*, Poitiers 2016 ;
- [9] R. S. G. Romano, W. L. Oliani, D. F. Parra, A. B. Lugao "Effects of Environmental Aging in Polypropylene Obtained by Injection Molding" *AIP Conference Proceedings* 1914, 140001 (2017);
- [10] P. Mach, M. Horák, C. Stancu "Thermal Ageing of Polypropylene Film Capacitors" *38th Int. Spring Seminar on Electronics Technology (ISSE)* Hungary 2015 pp 272-276 ;
- [11] M. Horák, P. Mach "Study of Thermal Ageing of Polypropylene Film Capacitors" 2015 IEEE 21st *International Symposium for Design and Technology in Electronic Packaging (SIITME)*, pp 57-60 ;
- [12] L. Barbeş, C. Rădulescu, C. Stîhi "ATR-FTIR Spectrometry Characterisation of Polymeric Materials" *Romanian Reports in Physics*, Vol. 66, No. 3, P. 765–777, 2014 ;
- [13] A. Bulinski, S.S. Bamji, M. Abou-Dakka and Y. Chen "Dielectric Properties of Polypropylene Loaded with Synthetic Organoclay" 2009 *Annual Report Conference on Electrical Insulation and Dielectric Phenomena* pp 666-671;
- [14] N. Chand, N. Khare "Investigation on dielectric properties of polypropylene/ waste low density polyethylene blends" *Indian Journal of Pure & Applied Physics* Vol. 38. July 2000. pp. 526-529 ;
- [15] W.Xin-Sheng, Tu De-Min and Liu Zi-Yu "Electrical Ageing Of Polypropylene Film" *Proceedings of the 3rd International Conference on Properties and Applications of Dielectric Materials* July 8-12, 1991 Tokyo, Japan pp 719-722 ;
- [16] Yu. S. Akishev, M.E. Grushin, A.I. Drachev, V.B. Karalnik, A.V. Petryakov and N.I. Trushkin "On Hydrophilicity Ageing of PP and PET Films Induced by Ultraviolet Radiation and Hydrogen Atoms" *The Open Plasma Physics Journal*, 2013, 6, (Suppl 1: M4) 19-29 ;
- [17] John Petrovich " FTIR and DSC of polymer films used for packaging: LLDPE, PP and PVDC" *Casteau: SHAPE American High School*, 2015, p 1-13. available at. <http://homepages.rpi.edu/~ryuc/outreach_1/2015_004_John_P.pdf>
- [18] Q.iang Wu, Baojun Qu "Synergistic effects of silicotungstic acid on intumescent flame-retardant polypropylene " *Polymer Degradation and Stability* 74 (2001) 255–261
- [19] H. Kaczmarek, D. Oldak, P. Malanowski, H. Chaberska "Effect of short wavelength UV-irradiation on ageing of polypropylene/cellulose compositions" *Polymer Degradation and Stability* 88 (2005) 189–198
- [20] W. L. Oliani, D. F. Parra, L. F. C. P. Lima and A. B. Lugão " Effects Of Thermal Ageing On Hms-Pp Crystallinity" *Int. Nuclear Atlantic Conf. - INAC 2009 Rio de Janeiro,RJ, Brazil* ;
- [21] A. T. ERTÜK, T. ŞAHİN "Degradation Effect of Different Environments on Characteristics of Calcium Carbonate Reinforced Polyethylene" *GU J Sci* 30(4): 489-500 (2017) ;
- [22] M. Moudoud; M. Megherbi; M. Mekious and O. Lamrous "Thermal aging effect on charging and discharging currents in polymers under DC stress" *IEEE Int. Symp. On Elect. Insul.*, Vancouver 9-12 June 2008 ;
- [23] E. Díaz-Acosta, C. Rodríguez-González, L. Valencia-Gómez, S. A. Martel-Estrada, M. Hernández-González, H. Reyes-Blas, I. Armendáriz " Polystyrene and Low Density Polyethylene Oregano's Essential Oil Functionalization for Possible Antimicrobial Active Packaging Applications " *J. of Appl. Packaging Research*, Vol. 10, Issue 3, 2018, pp 70-82.