

PAPER • OPEN ACCESS

Thermal Treatment Temperature and Time Dependence of Contact Angle of Water on Fluorinated Polystyrene as Hydrophobic Film Coating

To cite this article: M S Tolentino *et al* 2017 *IOP Conf. Ser.: Mater. Sci. Eng.* **205** 012024

View the [article online](#) for updates and enhancements.

You may also like

- [Novel Single-Ion Conducting Gel Polymer Electrolyte with Honeycomb-Like Morphology Prepared Using Brush Copolymer for Lithium-Ion Battery Application](#)
Maral Ghahramani, Mehran Javanbakht, Seifollah Jamalpour et al.
- [Study on radiation chemistry of fluorinated polymers for EUV resist](#)
Naoya Nomura, Kazumasa Okamoto, Hiroki Yamamoto et al.
- [Study on UV-aging performance of fluorinated polymer coating and application on painted muds](#)
Hongpu Huang, Hong Guo and Yefeng Feng

ECS
The
Electrochemical
Society
Advancing solid state &
electrochemical science & technology

DISCOVER
how sustainability
intersects with
electrochemistry & solid
state science research

Thermal Treatment Temperature and Time Dependence of Contact Angle of Water on Fluorinated Polystyrene as Hydrophobic Film Coating

M S Tolentino¹, J F Carpena¹, R M Javier¹ and R R Aquino¹

¹School of Chemical Engineering and Chemistry, Mapua Institute of Technology, Manila, Philippines, 1002
rraquino@mapua.edu.ph

Abstract. The study focuses on the synthesis of fluorinated polystyrene (F-PS) as a hydrophobic film coating and on the investigation of the consequent effects of thermal treatment time and treatment temperature on its contact angle. The fluorinated polystyrene is synthesized via Friedel-Crafts acylation of the benzoic rings by electrophilic substitution of trifluoroacetic anhydride in the presence of AlCl_3 in an environment of dichloromethane as the aprotic solvent with a reaction temperature of 36°C . The reaction yielded fluorinated polystyrene characterized by a solid brown substance. FT-IR analysis of the substance had shown band peaks at 1150 cm^{-1} , a wavenumber indicating the presence of fluorine in the synthesized material, which lowers its surface energy. SEM images of the F-PS show nucleation sites giving rise to hierarchical structures on the surface of the material due to the action of fluorination. The contact angle of fluorinated polystyrene, upon application of thermal treatment, increased to as much as 29.26% when compared to the unmodified polystyrene manifesting a preferentially more hydrophobic behavior. It was also found that the contact angle increases linearly with treatment temperature while statistical analysis shows that thermal treatment time has no significant effect on the hydrophobicity of the F-PS.

1. Introduction

Due to the numerous impending industrial applications of hydrophobic and oleophobic characteristics of different surfaces, researchers became interested with the factors affecting the hydrophobicity of such surfaces [1-4].

The main purpose of this study is to fabricate a hydrophobic film coating from fluorinated polystyrene (F-PS) to improve its hydrophobic behavior upon the application of heat treatment. Specifically, this undertaking seeks to achieve the following: (1) to fluorinate polystyrene in order to increase its hydrophobicity (2) to characterize the surface morphology of the fluorinated polystyrene film through the use of scanning electron microscopy (SEM); (3) to characterize the surface chemical composition of the fluorinated polystyrene film using Fourier Transform Infrared Spectroscopy (FT-IR); and (4) to determine the static contact angle of the fluorinated polystyrene film at varying temperature conditions and thermal treatment times.

2. Methodology

Fluorination of polystyrene (PS) was carried out through a synthetic route involving different reactions on the PS aromatic ring. This step was based on the mechanism proposed by Donchak and Harhay [5].



Several modifications on parameters and solvents used in the said reaction mechanism were employed in the present study.

Through electrophilic substitution under the Friedel-Crafts condition, the benzoic rings of polystyrene were acylated by trifluoroacetic anhydride (TFA) in an environment of dichloromethane (DCM) as the aprotic anhydrous solvent with aluminum chloride (AlCl_3) as the Lewis acid catalyst. The sequence of reactions started with the loading of 3.33 g of PS pellets in a round bottom flask, which were then dissolved under heat (36°C) with 100 ml DCM. The flask was immersed in a water bath to avoid direct heating. After complete dissolution, it was allowed to be cooled to 20°C followed by the addition of TFA (13.32 g) with 2:1 molar ratio to PS. AlCl_3 catalysts (8.43 g) were then added in small quantities. Maintaining the same temperature, the system was mixed for one hour to ensure efficient contact of the polystyrene rings with the catalyst. It was then subjected under heat (36°C) where it was mixed for two hours. The resulting suspension had a characteristic brown color after the mixing period. It was cooled to room temperature and then 15 ml dimethylformamide (DMFA) was added to dissolve the suspension. The suspension was then filtered using a vacuum pump and the resulting residue was repeatedly washed with 10 ml DCM. The resulting filtrate was added to excess amounts of ether (preferably 250 ml) and was refrigerated to recrystallize the fluorinated polystyrene (F-PS) characterized by a brown solid substance. After recrystallization in ether, the solid was filtered from the ether, air-dried under ambient conditions, and oven-dried at 80°C for 5 minutes to vaporize all adhering solution yielding 0.75 g of brown solid F-PS. The preceding reactions are shown by the equation:

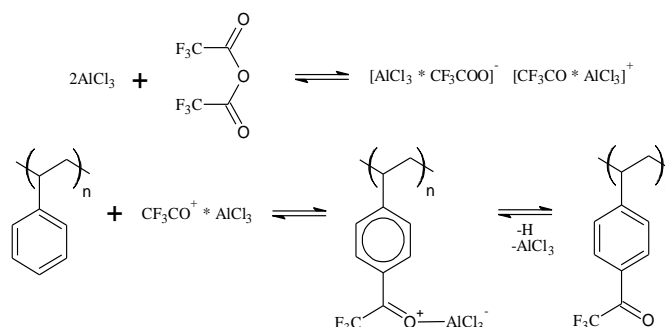


Figure 1. The Friedel-Krafts acylation for the fluorination of polystyrene.

To determine if the fluorination of polystyrene is successful, the sample was subjected to Fourier Transform Infrared Spectroscopy. To analyze the surface morphology, Scanning Electron Microscopy was employed. A contact angle goniometer was used to measure the angle between the surface and a tangent line of the droplet connected to the interface.

3. Results and Discussion

3.1. Fourier Transform Infrared Spectroscopy

Small amounts of the final product were tested using FT-IR spectroscopy. The Attenuated Total Reflectance (ATR) sampling technique was used in this step for the solid sample. Figure 2 shows a portion of the FT-IR results of the fluorinated polystyrene (F-PS). Band peaks at $1150/\text{cm}$ and $940/\text{cm}$ wavenumber indicates the presence of fluorine in the synthesized material.

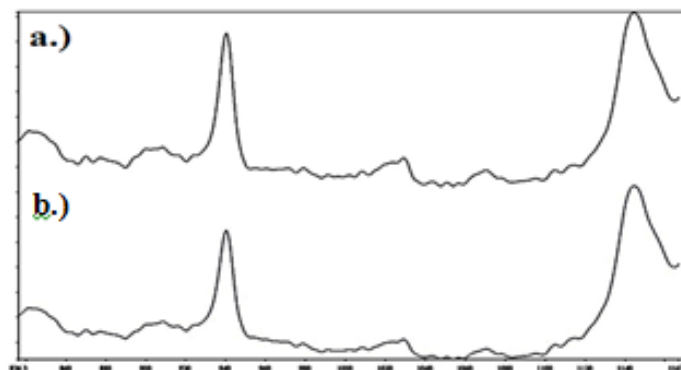


Figure 2. FT-IR spectra for (a) the synthesized F-PS and (b) the unmodified PS.

3.2. Scanning Electron Microscopy

The surface morphology of the fluorinated polystyrene (F-PS) was analyzed through SEM, and was compared to the surface morphology of the polystyrene (PS). Images of the surface of fluorinated and unmodified polystyrene were taken using an SNE 3200M model scanning electron microscope at a magnification power of 100x, 1000x and 3000x. It can be seen that rough structures are present on the surface of the F-PS, while a smooth surface morphology can be seen for the PS. Comparing the images of F-PS with that of PS, it can be deduced that the presence of fluorine makes the F-PS surface structure rough.

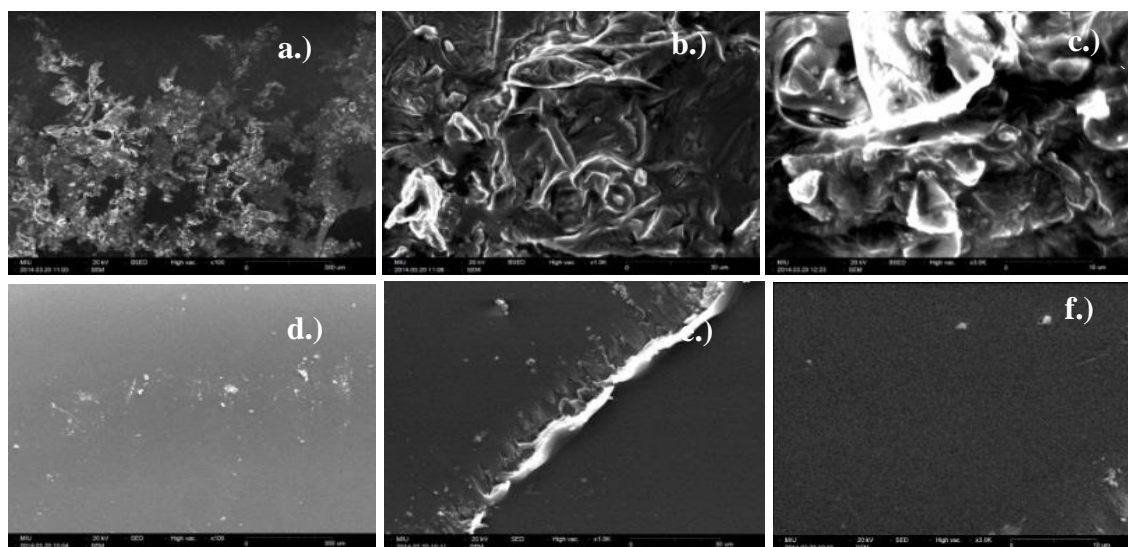


Figure 3. SEM images of F-PS (a,b,c) and PS (d,e,f) at 100x, 1000x, and 3000x magnifications respectively.

3.3. Effect of Thermal Treatment Time and Temperature on the Hydrophobicity of the Fluorinated Polystyrene Surface Coating

In order to quantify the effects of thermal treatment time and temperature in the hydrophobicity of the fluorinated polystyrene surface coating, its static contact angle were measured right after the treatment procedure. For comparative purposes, unmodified commercial-grade polystyrene material from Chemrez[®] was also subjected to the same treatment and its subsequent contact angle was measured as well.

Figure 4 shows that the contact angle of the fluorinated polystyrene (F-PS) increases with the temperature at all treatment times.

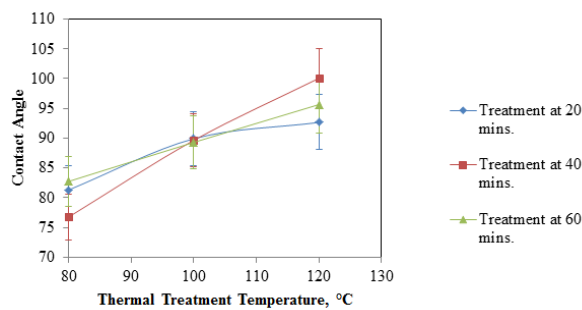


Figure 4. Treatment temperature dependence of contact angle of water on fluorinated PS.

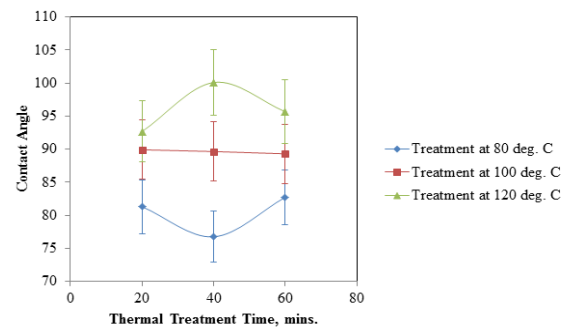


Figure 5. Treatment time dependence of contact angle of water on fluorinated PS

When the relationship of contact angle and treatment time is analyzed (Figure 5), it is apparent that there is no significant increase in contact angle when the treatment temperature is held constant. Nevertheless, the contact angles of the surface treated at 100 °C and 120 °C shows more hydrophobic character.

3.4. Effect of Thermal Treatment Time and Temperature on the Hydrophobicity of the Unmodified Polystyrene Surface Coating

The contact angle measurements at different treatment temperature for each treatment time of the unmodified polystyrene (PS) material are shown on Figure 6. As the temperature is increased from 80 °C to 120 °C, the contact angle also increases within the range of 70 ° to 80 °. Moreover, with regards to the relationship of contact angle and treatment time for PS, the same observations, with those of F-PS, transpired. Based on Figure 7, no significant increase in contact angle was observed at constant treatment temperature.

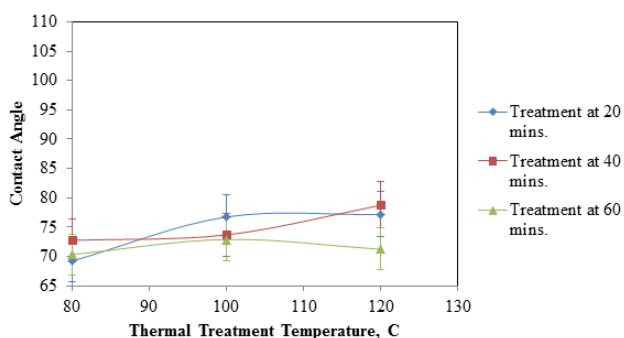


Figure 6. Treatment temperature dependence of contact angle of water on PS.

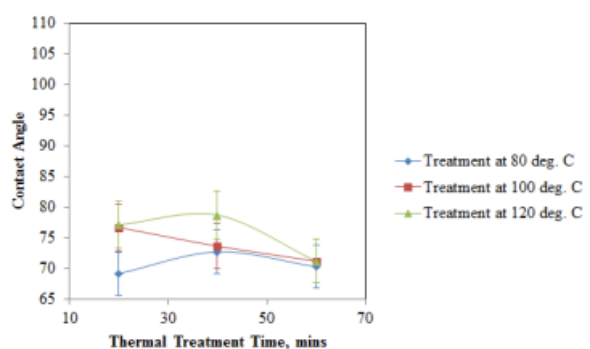


Figure 7. Treatment time dependence of contact angle of water on PS.

Upon comparison of the average contact angles of the fluorinated polystyrene and unmodified polystyrene, it is apparent that the F-PS has a more hydrophobic character. Furthermore, the contact angles are more significantly increased as the temperature is increased as well. For the 20-minute treatment time, the contact angle of the starting material (PS) is increased to as much as 18.24% at 120 °C treatment after fluorination.

On the other hand, the contact angle is increased further to 23.86% for the fluorinated polystyrene, when treated at 40 minutes at 120 °C. Likewise, at 60 minutes treatment time at 120 °C, the contact

angle of the F-PS and PS has a difference of 29.26%, representing an increase in hydrophobicity of the material upon fluorination (Figure 8).

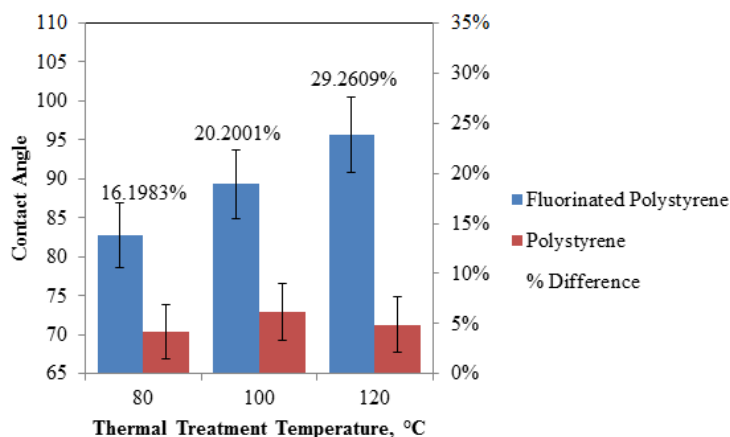


Figure 8. Comparison of contact angle of water on PS vs. Fluorinated PS at 60 minutes treatment.

4. Conclusion

Based on the results and analysis of this study, it is concluded that the results of Fourier Transform Infrared Spectrometer show that fluorine atoms are present in the synthesized material as indicated by the band peak at 1150 cm^{-1} wavenumber of the spectra. The images obtained through the scanning electron microscope show the apparent differences in the surface of the unmodified polystyrene and F-PS. From the said images, it can be inferred that the surface of the fluorinated polystyrene shows a rougher surface due to the nucleation sites upon fluorination. On the other hand, the surface of the unmodified PS shows a smooth texture revealing its high wetting behavior.

Thermal treatment temperature is concluded to be a strong factor for the increase in contact angle of the fluorinated polystyrene film coating. It can then be said that no matter what the treatment time is, there is no significant effect in the resulting contact angle of the F-PS since all of the contact angle readings obtained lie relatively within the 5% threshold of each other when measured at different thermal treatment times. Inducing the fluorinated polystyrene coating to a high temperature environment also increases the corresponding contact angle of water on its surface. Based on the findings of this research, the hydrophobicity of the surface (in terms of its contact angle) can be increased to as much as 29.26% when treated at $120\text{ }^{\circ}\text{C}$. The contact angle also shows a direct variation with temperature.

References

- [1] Godeau G, Amigoni S, Darmanin T and Guittard F 2016 Post-functionalization of plasma treated polycarbonate substrates: An efficient way to hydrophobic, oleophobic plastics *Applied Surface Science* **387** 28-35
- [2] Joki-Korpela F, Karvinen J, Paivanranta B, Partanen A, Suvanto M, Kuittinen M and Pakkanen T 2014 Hydrophobic and oleophobic anti-reflective polyacrylate coatings *Microelectronic Engineering* **114** 38-46
- [3] Li H, Yu S, Han X, Liu E and Zhao Y 2015 Fabrication of superhydrophobic and oleophobic surface on zinc substrate by a simple method *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **469** 271-278
- [4] Parale V, Mahadik D, Phadtare V, Pisal A, Park H and Wategaonkar S 2016 Dip coated superhydrophobic and anticorrosive silica coatings *International Journal of Materials Science and Engineering*, **4** 60-68
- [5] Donchak V and Harhay K 2008 Synthesis of Fluorinated Polystyrene *Chemistry and Chemical Technology* 11-14