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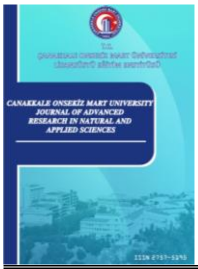

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Fabrication of Self-Cleaning Perfluoroacrylate Blend Films by Spray Coating Method

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Research Article

Abstract − The superhydrophobic surfaces are contained two essential principles. First, low surface energy polymers, such as fluoropolymers pushing the liquid onto the surface are necessary. The surface roughness is the second necessity to obtain superhydrophobicity, providing air packets between the roughness and reducing surface interaction with the liquid. This study fabricated the superhydrophobic blend coating using a spray coating method. The flat surface of PFMA homopolymer synthesized in $scCO_2$ medium was fabricated free meniscus coating method due to the lack of solubility in the conventional solvent. To overcome the solubility problems of the PFMA, the p(Perfluoromethacrylate-ran-Styrene) copolymer was fabricated in a $scCO_2$ medium. Blend solutions are prepared to reduce costs and provide high hydrophobicity by using p(Perfluoromethacrylate-ran-Styrene) copolymer and PS homopolymers. The surface roughness of the blend films was altered using silica nanoparticles coated on a glass slide by a spray coating. The surface morphology was characterized by SEM analyses indicating that double-scale surface morphology was obtained by increasing the SNp of the composite solution. The water contact angle indicated that the superhydrophobic rough surface was obtained with TMS_{70} and PS blend formation having 33.0 % PS and 12.5% silica nanoparticles.

Keywords − *Blend, fluoropolymer, self-cleaning, spray coating, superhydrophobic*

1. Introduction

The control of wettability is curial in many industrial applications such as self-cleaning surfaces (Topcu, Erdogan, & Cengiz, 2018), antifogging (Wang, Yao, Ren, & He, 2019), oil-water separation (Li et al., 2018), anti-icing (Ozbay, Yuceel, & Erbil, 2015). The superhydrophobic surface is expressed as the water contact angle (WCA) higher than 150° and tilt angle or contact angle hysteresis (CAH) values lower than 10° (Erbil, Demirel, Avci, & Mert, 2003). The artificial superhydrophobic surface was fabricated using alkyl ketene dimer wax for the first time in 1996 (Erbil et al., 2003). After that, the superhydrophobic surfaces were fabricated using different techniques such as phase separation (Gengec, Cengiz, & Erbil, 2016), electrospinning (Han & Steckl, 2009), sol-gel (Latthe, Imai, Ganesan, & Rao, 2010), chemical vapor deposition (Meng & Park, 2012), etching (Lee et al., 2011), and spray coating method (Bayer, Brown, Steele, & Loth, 2009). These studies reported that the fabrication of the superhydrophobic surfaces needs to provide two critical conditions: a necessity of low surface energy polymers such as fluoropolymer and surface roughness. However, not only the high expense of the flora polymers or monomers but also the environmental causes pushed researchers to non-fluorinated surface fabrication by obtaining a double-scale surface in the nano- and micron scales roughness (Lee et al., 2011; Topcu et al., 2018; Wang et al., 2019). The double-scale surface is caused a higher surface

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roughness. The air pocket is penetrated in this roughness, so the adhesion between water and surface decreases due to the reduction of the solid water contact line. In addition, some researchers reduced the cost by fabricating a copolymer between fluorinated monomers with non-fluorinated low-cost monomers (Gengec et al., 2016) or blending with cheap polymers (Gengec et al., 2016; Huang, Goh, Lai, Huan, & Wee, 2004). A blend formation ensures an essential benefit to combining the advantages of the individual polymers besides the economic (Huang et al., 2004). For example, fluorinated polymer is provided liquid repellency, while polystyrene has dimensional stability. However, a blend formation depends on the miscibility of the individual polymers (Kraus, 1978). The solubility parameter is important in providing a blend formation. Because it is undesirable the agglomeration of the polymer chains in the bad solvent. Phase separation occurred when one of the polymer chains started to agglomerate (Kraus, 1978). Generally, phase separation caused the heterogenous rough surfaces. This event can sometimes occur under control by adding the bad solvent into the polymer solution (Gengec et al., 2016). The controlled surface roughness by adding the nonsolvent in the polymer solution is provided to coat with the phase separation instant. However, this can also cause undesirable problems such as lower mechanical film durability or lower light transmittance due to the increasing roughness. When the well-dispersed blend solution was provided, it is obtained not only good-arranged surface roughness but also higher mechanical behavior of the film surface due to the combination of individual polymer behavior.

This study fabricated the perfluroethylalkyl methacrylate (PFMA) homopolymer in $scCO_2$ medium at 200 bar, 65 ^oC. The cloud point data were collected in a $scCO_2$ medium depending on temperature and pressure at constant polymer content of 1.55 wt. When the pressure decreased, the polymer chains agglomerated, and a cloudy form was obtained. The TMS_{70} statistical copolymer was synthesized in a CO_2-expanded styrene phase at 150 bar and 65^{o}C using styrene and PFMA monomers. The WCA of the TMS_{70} is reported as 115^o, which is lower than the p(PFMA) homopolymer, about 5^o. The smooth WCA is critical to obtaining a superhydrophobic surface with increasing roughness. The blend formation was formed using PS homopolymer with TMS_{70} copolymers. The smooth surface was prepared with PFMA and TMS_{70} polymers. The PFMA surfaces were coated with free meniscus coating (FMC) due to being soluble in only $scCO_2$, while TMS_{70} surfaces were spray coated. The rough superhydrophobic blend surface was formed using TMS_{70} and PS with silica nanoparticles (SNp). An increasing the SNp content of the blend solution caused rising WCA due to the higher surface roughness. The smooth PFMA and TMS_{70} film contact angles were found as 120^o and 115^o, respectively. The rough blend surface reached 166^o of WCA depending on spray time and distance.

2. Materials and Methods

2.1 Materials

Perfluoroethyl alkyl methacrylate (Zonyl-TM) was purchased from Dupont-Turkey. The CO_2 (99.9%) was obtained from Edremit Gases, A.S., Türkiye. Styrene (99.8%), toluene (99.8%), tetrahydrofuran (THF) (99.8%), polystyrene (PS), and Azobisisobutyronitrile (AIBN) were purchased from Aldrich. In addition, Wacker Silicones-Türkiye supplied pyrogenic silica (HDK-H18) with 99.8 % SiO_2 and a surface area of 170-230 m^2/g.

2.2. Polymer Synthesis and Characterization

2.2.1. Polyperfluoroalmethacrylate homopolymer (PFMA) synthesis:

The p(PFMA) homopolymer was synthesized in a $scCO_2$ medium similar to the literature (Ozbay, Cengiz, & Erbil, 2019) at 24 hours, 200 bar, and 65°C in a high-pressure 100 mL reactor (Bena Lab). The cloud point determination of PFMA homopolymer was determined in the reactor equipped with two sapphire windows.

2.2.2. The styrene-ran-perfluoro methacrylate (TMS_{70}) random copolymer synthesis:

TMS_{70} having 70 wt % styrene and 30 wt % PFMA was fabricated in a CO_2-expanded styrene phase medium according to the literature, in which the polymerization details were given in previous studies (Cengiz & Erbil, 2014; Gengec et al., 2016). The free radical random copolymerization reaction was carried out at 150 bar and 65°C in the high-pressure 100 mL reactor (Bena Lab). The styrene, PFMA, and AIBN were weighed and added to the high-pressure reactor. The CO_2 introduced the monomer mixture, the monomer phase expanded, and a new phase occurred. The reaction started as homogenous but lasted heterogeneous due to the agglomeration of the higher molecular weight polymer chains. The polymerization finished heterogeneous and called precipitation polymerization. The molecular weight of the copolymers of TMS_{70} was characterized by using GPC.

2.3. Fabrication of the flat and rough films

The thin films of p(PFMA) were fabricated by using a free meniscus coating system (Novick, DeSimone, & Carbonell, 2004) (Ozbay et al., 2019). The TMS_{70} and TMS_{70}-PS blend surfaces were prepared by spray coating dissolving in toluene (50 mg/mL). Pen spray apparatus was used to coat glass slides 20 and 30 cm in length under a 5 bar N_2 atmosphere (Figure 1).

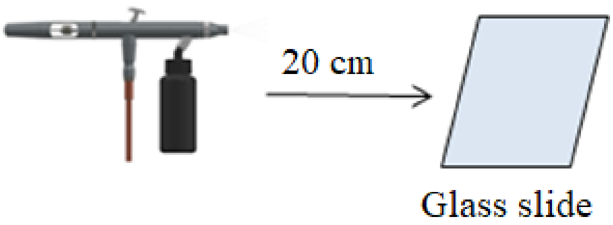

Figure 1. The schematic illustration of Pen spray coating systems

The blend solution of PS and TMS_{70} copolymer was prepared by mixing these polymer solutions and stirred mechanically for 2 h at room temperature. Firstly, the TMS_{70} copolymer solution was prepared as 50 mg/mL in toluene. Next, PS homopolymers were prepared in toluene at 50 mg/mL. Both of the polymer solutions were mixed and stirred. The opaque and the rough blend films were prepared by spray coating. A rough blend solution was prepared by adding silica nanoparticles of 2.5 to 12.5 % wt., which was kept in an oven at 105 ^{o}C for 2 hours due to moisture removal before use. The WCA of the flat and rough films was measured using the Attention Theta contact angle. All CA values were measured 3 times, having $\pm 1^{o}$ of standard deviation.

3. Results and Discussion

3.1 Polymer synthesis and characterization

The p(PFMA) homopolymer is soluble in $scCO_2$ due to its CO_2-philic character. The solubility of p(PFMA) homopolymer depends on pressure and temperature. The cloud point data were collected depending on pressure and temperature variation at a constant polymer amount, as shown in figure 2. This study kept the P(PFMA) polymer amount constant at 1.55 wt. due to comparing the literature data(Mawson, Johnston, Combes, & DeSimone, 1995; Ozbay et al., 2019). The rate of cloud point pressures of P(PFMA) with temperature change was defined as $\left(\frac{\partial P}{\partial T}\right)_X$ determined to be 2.15±0.23 bar/°C (Figure 2). In the literature, the similar polymer $\left(\frac{\partial P}{\partial T}\right)_X$ results was reported at 3.0±0.1 bar/°C (Mawson et al., 1995) and 2.4±0.2 bar/°C (Ozbay et al., 2019). The slight differences in the slopes are due to the minor molecular weight of p(PFMA) homopolymers.

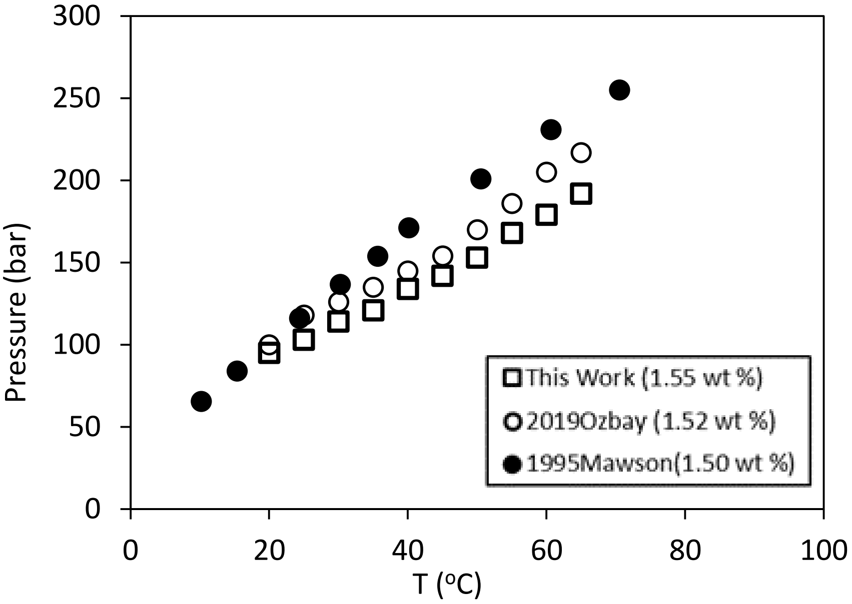

Figure 2. P(PFA) homopolymer Cloud point pressures with temperature in comparison with the Mawson and Ozbay data

The random copolymer of the TMS_{70} was synthesized in $scCO_2$ medium at 80 °C, 250 bar for 8 hours (Cengiz & Erbil, 2014). The polymerization started the homogeneous radical polymerization in CO_2 expanded styrene phase (Cengiz & Erbil, 2014). The monomer phase expands rapidly when CO_2 gas is introduced to the monomer mixtures. Thus, a new phase was obtained called the CO_2-expanded phase (Cengiz & Erbil, 2014). This phase is a stronger solvent than the liquid CO_2 or $scCO_2$ in the presence of the CO_2 -phobic monomers such as styrene or methyl methacrylate. However, the p(PFMA) homopolymer was synthesized homogenous medium in the $scCO_2$ phase due to the CO_2-philic monomer of PFMA. In TMS_{70} copolymerization, the homogenous reaction medium depended on the monomer amount acting like a co-solvent (Cengiz & Erbil, 2014). Thus, the co-monomer amount in the CO-expanded phase increased in the homogenous reaction time (Cengiz & Erbil, 2014). The GPC result of the TMS_{70} was measured, and the molecular weights were found as 15000 (Mn) and 45000 (Mw). The PDI values are determined as Mw/Mn=3. The Intrinsic viscosity values were also measured in chloroform solution as 0.245 dl/g comparisons with literature values (Cengiz & Erbil, 2014).

3.2 Wettability properties of Flat and rough films

The flat P(PFMA) thin films were prepared by the free meniscus coating (FMC) method in $scCO_2$, depending on P(PFMA) concentration. (Table 1).

Tablo 1.
The WCA of P(PFMA) thin films depending on the PFMA amount

Code	M_{PFA} (g)	P (bar)- Reaction Reactor	P (bar)-Coating Reactor	WCA (°)
PFMA-1	0.2	125	60	115
PFMA-2	0.5	125	60	114
PFMA-3	0.7	125	60	116
PFMA-4	1.0	125	60	118
PFMA-5	1.5	125	60	117
PFMA-6	2.0	125	60	120

The P(PFAM) homopolymer was coated in a glass slide in FMC due to the lower solubility of the homopolymer in a conventional solvent such as THF, toluene, or chloroform. As a result, the WCA of the PFMA thin films increased from 115° to 120° depending on the PFMA concentration in the $ScCO_2$ solution (Table 1). The WCA of PFMA-6 was found as 120°, which is the maximum value for a smooth surface (Nishino, Meguro, Nakamae, Matsushita, & Ueda, 1999). The WCA values of PS homopolar surface prepared for 0.5 g/mL in toluene concentration were found between 60^o to 85^o depending on spray time and length by the spray coating method (Table 2).

Table 2.
The water CA values of spray-coated PS homopolymer dissolved in toluene solution

Code	Spray time (s)	Spray length (cm)	CA (^{o})
T_S1	5	20	75
T_S2	10	20	78
T_S3	15	20	80
T_S4	5	30	80
T_S5	10	30	60
T_S6	15	30	86

This table showed a linear correlation between CA values and spray times at 20 cm of spray distance. Thus, the 20 cm distance was chosen for the spray-coated experiment. The WCA of TMS$_{70}$ smooth copolymer surfaces containing % 30 wt PFMA is measured as $115^{o,}$ which was a sufficient WCA value to obtain a superhydrophobic surface by increasing surface roughness. The blend surface was prepared to reduce the structure's fluorine content due to its lower mechanical properties and cost. Thus, the blend solution was prepared by increasing the PS content, and the solutions were coated by the spray coating method for 20 cm of distance and 20 s of spray time. The changing of WCA values depending on PS content on the blend solution is given in figure 3.

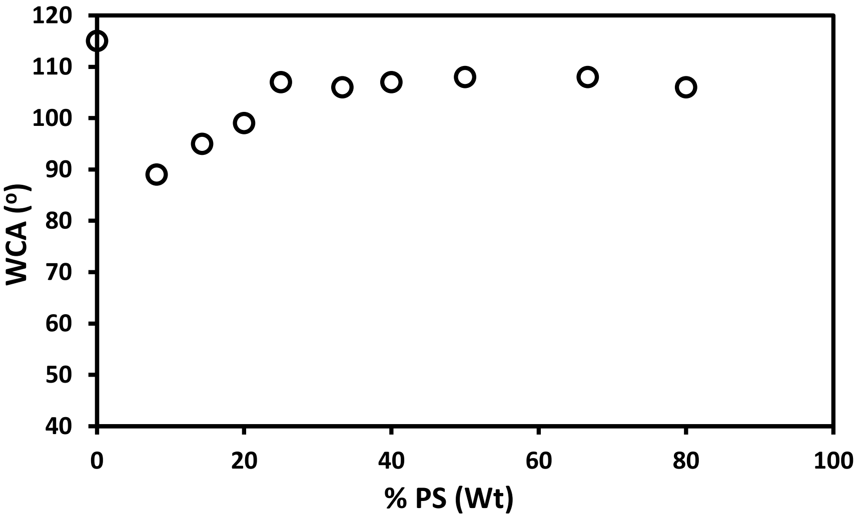

Figure 3. The WCA values of the blend solution depend on the PS content

An increase in the PS content of the blend solution firstly decreases the water contact angle from 115^o to 90^o compared to the TMS$_{70}$ copolymer surfaces due to the decreasing flor content. Then, however, the WA values increased from 90^o to 110^o linearly up to % 40 wt. of PS. However, after this content, the contact angle values stayed steady despite the increasing PS content (figure 3). Therefore, the mechanical performance of the blend films decreases with increasing the PS content after % 50 wt. For example, the water drop penetrated the film's coating at the TMS$_{70}$-PS$_{70}$ surface, having 70 wt PS content. Thus, the maximum PS content of the blend formation was arranged as 50 wt %. In addition, the blend solution's contact angle values indicate that the optimum spray coating experimental condition is 20 cm of spray distance, 10 s of spray time, and % 22 to 50 of PS content in the blend solution.

The superhydrophobic surfaces occurred by increasing the surface roughness using SNp. The rough blend surfaces were prepared using TMS$_{70}$, PS, and silica nanoparticles using optimized spray coating experimental conditions, as given in Table 3. The "NP" code in the TMS$_{70}$-PS blend is implied by adding silica nanoparticles.

The maximum SNp percentages are arranged up to 12.5 wt %. Higher SNP content in the composite solution results in lower light transmittance. Therefore, the subscript of the codes is related to the amount added. For example, the spray coating code of "TMS_{70}-$PS_{22}NP_{2.5}$" is indicated the blending of TMS_{70} and PS (22 %) and NP (2.5 %).

Table 3.
The CA values of the rough blend films (Spray coating conditions: 20 cm distance and 10 s of spray coating times)

Code	PS (wt, %)	Silika (wt. %)	WCA (°) (±1°)
TMS_{70}-$PS_{22}NP_{2,5}$	22.5	2.5	110
TMS_{70}-$PS_{22}NP_{5,0}$	22.5	5.0	110
TMS_{70}-$PS_{22}NP_{7,5}$	22.5	7.5	115
TMS_{70}-$PS_{22}NP_{10}$	22.5	10.0	117
TMS_{70}-$PS_{22}NP_{12,5}$	22.5	12.5	148
TMS_{70}-$PS_{33}NP_{2,5}$	33.0	2.5	103
TMS_{70}-$PS_{33}NP_{5,0}$	33.0	5.0	109
TMS_{70}-$PS_{33}NP_{7,5}$	33.0	7.5	115
TMS_{70}-$PS_{33}NP_{10}$	33.0	10.0	125
TMS_{70}-$PS_{33}NP_{12,5}$	33.0	12.5	154
TMS_{70}-$PS_{50}NP_{2,5}$	50.0	2.5	106
TMS_{70}-$PS_{50}NP_{5,0}$	50.0	5.0	107
TMS_{70}-$PS_{50}NP_{7,5}$	50.0	7.5	110
TMS_{70}-$PS_{50}NP_{10}$	50.0	10.0	112
TMS_{70}-$PS_{50}NP_{12,5}$	50.0	12.5	161

The WCA of the TMS_{70}-$PS_{22}NP$ series indicated that increasing the SNp content of the blend solution resulted in an increase in the WCA from 110 to 148° (figure 4). While the PS content of the blend surface was 33 (wt, %), the superhydrophobic surface was obtained at the 12.5 % wt. of the silica nanoparticles due to the phase separation by adding PS (Gengec et al., 2016) (figure 5). The higher WCA angle of 161° was obtained when the PS content of the blend solution was 50 % wt. (figure 4).

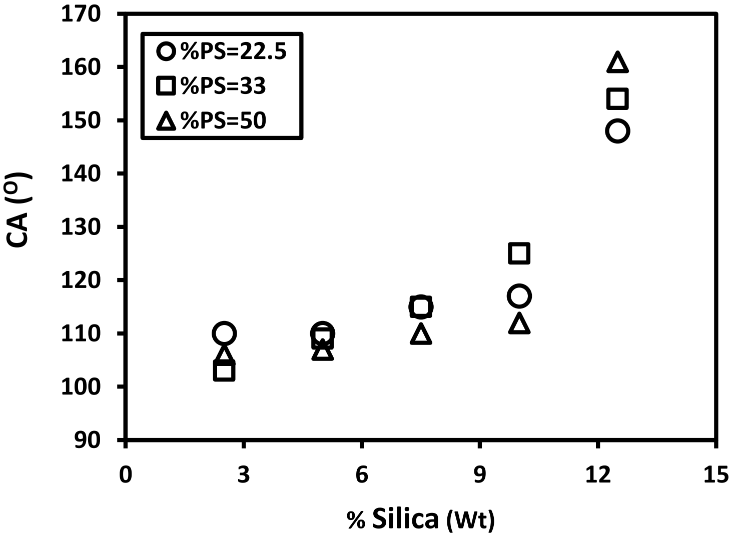

Figure 4. Change of CA (°) results in the change in silica wt % of blend surface

An increase in the PS content at the same nanoparticle content (12.5) increased the CA values of the rough surface. The SEM images also supported the WCA values (Figures 5 and 6). Especially higher magnification SEM images (20000X) indicated that a homogenous coating was obtained with higher PS content of the blend solution (Figure 6) due to the surface covering.

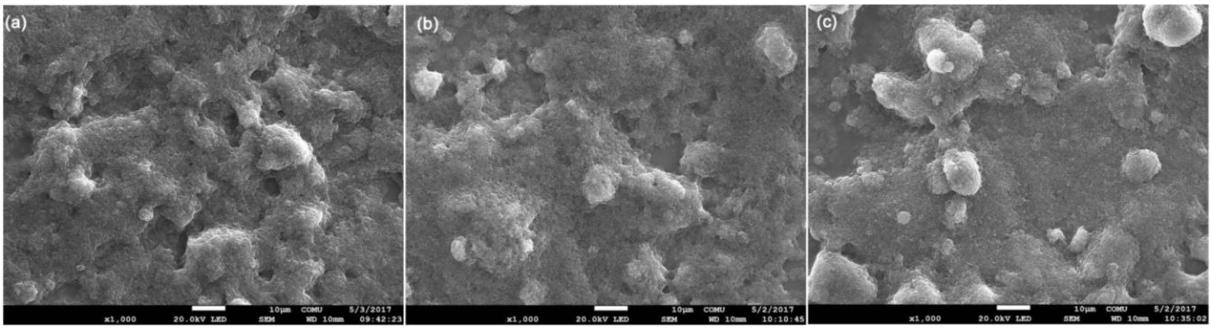

Figure 5. The SEM (1000X) images of spray coating of TMS_{70}-$PS_xNP_{12,5}$ blend coating with increasing the PS content a) TMS_{70}-$PS_{22}NP_{12,5}$ b) TMS_{70}-$PS_{33}NP_{12,5}$ c) TMS_{70}-$PS_{50}NP_{12,5}$ (20 cm distance for 10 s spray coating time)

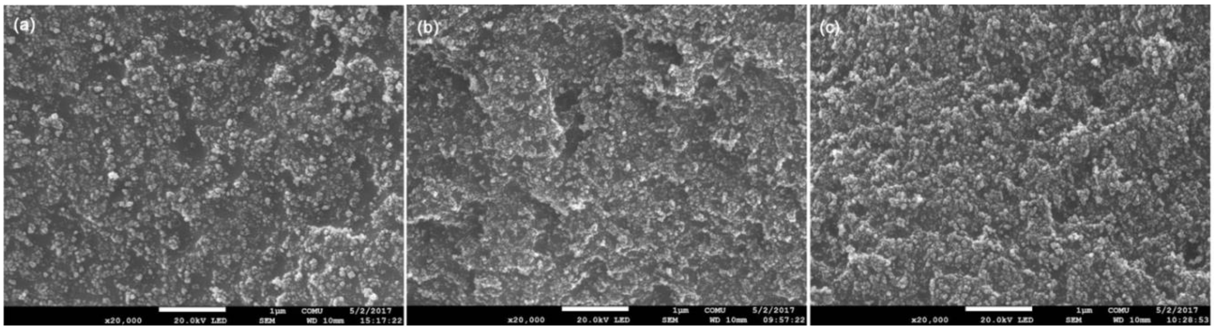

Figure 6. The SEM (20000X) images of spray coating of TMS_{70}-$PS_xNP_{12,5}$ blend coating with increasing the PS content a) TMS_{70}-$PS_{22}NP_{12,5}$ b) TMS_{70}-$PS_{33}NP_{12,5}$ c) TMS_{70}-$PS_{50}NP_{12,5}$ (20 cm distance for 10 s spray coating time)

The spray coating time effect was also investigated at the constant blend composition of TMS_{70}-$PS_{33,}$ as given in figure 7. The superhydrophobic surface of about 170° of contact angle is obtained when increasing the silica content at 15 seconds of spray time. On this surface, the water drop moved rapidly, and the CA value was measured hardly due to the water drop's rapid movement. This phenomenon is due to the lower adhesion attraction between liquid and solid surfaces. However, no correlation is observed between spray time and contact angle. Generally, the CA value is increased depending on surface roughness due to the introduction of the air pockets onto the surfaces, and it is expected that the surface roughness increases depending on spray time due to the accumulation on the surface. Therefore, the best CA values were obtained at 15 s spray time. However, 10 s of spray time is almost close the 15 s.

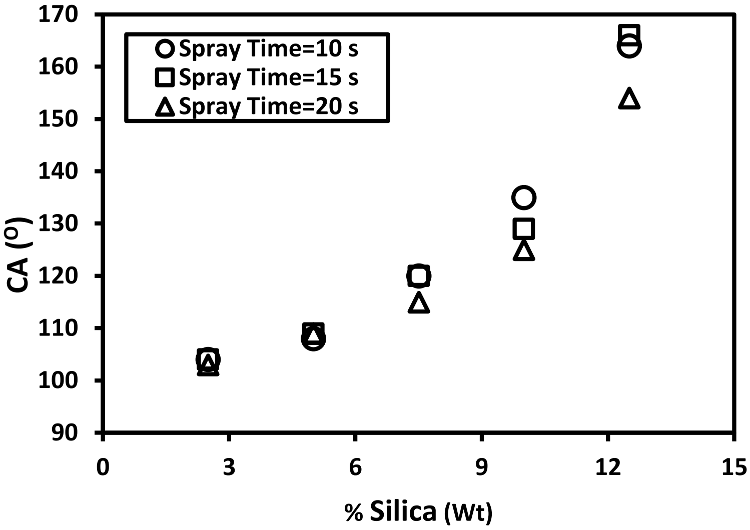

Figure 7 Change of CA (°) results with the change in silica wt % and spray time of blend surface

The spray coating experiment results showed that the flat and rough TMS70-PS blend surface was fabricated by the spray coating method at 20 cm of distance, 10 s of the spray time. In addition, the superhydrophobic surface was obtained at 12.5 % wt silica content. Therefore, the best spray coating formulation is found as TMS_{70}-$PS_{50}NP_{12,5}$.

4. Conclusion

In this study, the $scCO_2$ medium polymerizations of PFMA homopolymers and TMS_{70} statistical copolymers were fabricated by free-radical polymerization technic as AIBN is an initiator. The cloud points data were collected at 1.55 wt. of PFMA homopolymer in $scCO_2$ medium. This experiment indicated that the p(PFMA) homopolymer molecular weight is partly close to the literature on similar polymers. The TMS_{70} copolymer was also fabricated in the CO_2-expanded styrene phase. The TMS_{70} polymerization started as a homogenous phase and lasted heterogeneous due to the agglomeration of the polymer chains. The copolymerization terminated as a precipitation polymerization. The flat copolymer of the TMS_{70} is coated by spray coating, and the WCA is found as 115°. The WCA of the TMS_{70}-PS blend surfaces increased depending on PS content, reaching a plateau of around 40% of PS. The rough blend surface was prepared by adding silica nanoparticles to the TMS_{70}-PS blend solution. Increasing the silica nanoparticles increased the WCA of the rough blend surface. As a result of the spray experiments, the superhydrophobic surfaces were obtained by coating glass slides TMS_{70}-$PS_{50}NP_{12.5}$ blend composition at a 20 cm distance for 10 s of spray time. As a result of the WCA result of the everyday pollutant such as water, milk, tea, coffee, and juice showed the rough blend surface was fabricated successfully. However, the mechanical performance of the surface should have been improved.

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Author Contributions

Özge Ünzal: Experimental, Investigation, Software,

Sema Nur Belen: Methodology, Writing – original draft.

Uğur Cengiz: Conceptualization, Writing – review & editing, Supervision.

Conflicts of Interest

The authors declare no conflict of interest.

References

Bayer, I. S., Brown, A., Steele, A., & Loth, E. (2009). Transforming Anaerobic Adhesives into Highly Durable and Abrasion Resistant Superhydrophobic Organoclay Nanocomposite Films: A New Hybrid Spray Adhesive for Tough Superhydrophobicity. *Applied Physics Express, 2*(12). doi:10.1143/APEX.2.125003

Cengiz, U., & Erbil, H. Y. (2014). Perfluoromethacrylate-styrene statistical copolymers synthesized in CO2-expanded monomers. *Colloid and Polymer Science, 292*(9), 2207-2215. doi:10.1007/s00396-014-3250-8

Erbil, H. Y., Demirel, A. L., Avci, Y., & Mert, O. (2003). Transformation of a simple plastic into a superhydrophobic surface. *Science, 299*(5611), 1377-1380. doi:DOI 10.1126/science.1078365

Gengec, N. A., Cengiz, U., & Erbil, H. Y. (2016). Superhydrophobic perfluoropolymer/polystyrene blend films induced by nonsolvent. *Applied Surface Science, 383,* 33-41. doi:10.1016/j.apsusc.2016.04.160

Han, D. W., & Steckl, A. J. (2009). Superhydrophobic and Oleophobic Fibers by Coaxial Electrospinning. *Langmuir, 25*(16), 9454-9462.

Huang, H. L., Goh, S. H., Lai, D. M. Y., Huan, C. H. A., & Wee, A. T. S. (2004). Surface Properties of Miscible Poly(1,1,1,3,3,3-hexafluoroisopropyl methacrylate)/Phenoxy Blends. *Journal of Applied Polymer Science, 91*, 1798-1805.

Kraus, G. (1978). Block Copolymers in Blends with Other Polymers In D. R. Paul & S. Newman (Eds.), *Polymer Blends* (Vol. 2, pp. 243-261): Academic Press.

Latthe, S. S., Imai, H., Ganesan, V., & Rao, A. V. (2010). Porous superhydrophobic silica films by sol-gel process. *Microporous and Mesoporous Materials, 130*(1-3), 115-121. doi:10.1016/j.micromeso.2009.10.020

Lee, E. J., Jung, C. H., Hwang, I. T., Choi, J. H., Cho, S. O., & Nhos, Y. C. (2011). Surface Morphology Control of Polymer Films by Electron Irradiation and Its Application to Superhydrophobic Surfaces. *Acs Applied Materials & Interfaces, 3*(8), 2988-2993. doi:10.1021/am200464a

Li, B. G., Lian, Z. X., Yu, H. D., Xu, J. K., Shi, G. F., Yu, Z. J., & Wang, Z. B. (2018). Underwater superoleophobic stainless steel mesh fabricated by laser cladding a copper foil for oil-water separation. *Materials Research Express, 5*(7). doi:ARTN 075014

10.1088/2053-1591/aac200

Mawson, S., Johnston, K. P., Combes, J. R., & DeSimone, J. M. (1995). Formation of Poly(1,1,2,2-Tetrahydroperfluorodecyl Acrylate) Submicron Fibers and Particles from Supercritical Carbon Dioxide Solutions. *Macromolecules, 28*, 3182–3191.

Meng, L. Y., & Park, S. J. (2012). Effect of growth of graphite nanofibers on superhydrophobic and electrochemical properties of carbon fibers. *Materials Chemistry and Physics, 132*(2-3), 324-329. doi:10.1016/j.matchemphys.2011.11.024

Nishino, T., Meguro, M., Nakamae, K., Matsushita, M., & Ueda, Y. (1999). The Lowest Surface Free Energy Based on -CF3 Alignment. *Langmuir, 15*, 4121-4123.

Novick, B. J., DeSimone, J. M., & Carbonell, R. G. (2004). Deposition of Thin Polymeric Films from Liquid Carbon Dioxide Using a High-Pressure Free-Meniscus Coating Process *Industrial and Engineering Chemical Research, 43*, 515–524.

Ozbay, S., Cengiz, U., & Erbil, H. Y. (2019). Solvent-Free Synthesis of a Superamphiphobic Surface by Green Chemistry. *Acs Applied Polymer Materials, 1*(8), 2033-2043. doi:10.1021/acsapm.9b00322

Ozbay, S., Yuceel, C., & Erbil, H. Y. (2015). Improved Icephobic Properties on Surfaces with a Hydrophilic Lubricating Liquid. *Acs Applied Materials & Interfaces, 7*(39), 22067-22077. doi:10.1021/acsami.5b07265

Topcu, A. S. K., Erdogan, E., & Cengiz, U. (2018). Preparation of stable, transparent superhydrophobic film via one step one pot sol-gel method. *Colloid and Polymer Science, 296*(9), 1523-1532. doi:10.1007/s00396-018-4377-9

Wang, Y., Yao, L., Ren, T. T., & He, J. H. (2019). Robust yet self-healing antifogging/antibacterial dual-functional composite films by a simple one-pot strategy. *Journal of Colloid and Interface Science, 540*, 107-114. doi:10.1016/j.jcis.2019.01.008