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Superhydrophobic perfluoropolymer/polystyrene blend films induced by nonsolvent

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ABSTRACT

Statistical copolymers of perfluoroalkyl ethyl acrylate (Zonyl-TAN) and methyl methacrylate (MMA) were synthesized in a CO_2 polymerization system where a CO_2-expanded monomer mixture was formed at 13 MPa, and 80 °C by using AIBN as initiator. Flat and superhydrophobic surfaces were subsequently prepared on glass slides by applying a phase separation process where the synthesized p(TAN-co-MMA) copolymer and polystyrene (PS) were dissolved in THF solvent. Ethanol was added as the non-solvent to introduce superhydrophobicity during film formation. Water contact angle on the flat p(TAN-co-MMA) copolymer was 118° and increased up to 170° with the formation of surface roughness. The ratio of the ethanol non-solvent in the blend solution has an important effect on the magnitude of surface roughness during the phase separation process. Both pits and protrusions of 1–10 μm in size were formed on the surface when non-solvent was used. Surface roughness increased with the increase in the ethanol ratio and the PS content of the blend solution.

1. Introduction

Fluoroalkyl acrylate polymers were synthesized in conventional solvents [1], chlorofluorocarbons (CFC's) [2], and supercritical-CO_2 [3] by using solution polymerization, emulsion polymerization [4], and bulk polymerization methods [5]. Polymerizations in sc-CO_2 were generally carried out at high CO_2 pressures due to the low solubility of resultant polymers in the sc-CO_2 medium [6]. CO_2-expanded monomer medium where dense CO_2 was present in the reactor was proposed to reduce the applied CO_2 pressures substantially [7,8]. In a previously study, we synthesized random copolymers of perfluoroalkyl ethyl methacrylate (Zonyl-TM) and methy methacrylate (MMA) in the CO_2-expanded monomer phase under a low pressure of 10–13 MPa at 80 °C. We monitored the phase change during the reaction to by taking photographs and it was found that an increase in the CO_2/total monomer weight ratio and the decrease of Zonyl-TM content in the comonomer feed resulted in an increase in the molecular weight of the copolymers [8]. Wettability is one of the most important properties of a solid surface and both surface energy and surface roughness are the dominant factors to affect the water contact angle on the surfaces [9,10]. The presence of fluorine atoms having the lowest surface energy at a surface leads to an increase in water contact angle, approaching to a maximum value of approximately 120° for flat surfaces [11]. The introduction of surface roughness is necessary in order to synthesis a superhydrophobic surface having water contact angle larger than 150° and enables the rolling of the water drop with a very small tilt angle. Superhydrophobic surfaces were synthesized by using expensive methods such as plasma etching [12], chemical vapor deposition [13], and also with simple method such as phase separation [14–17], adding silica powders [18] and electrospining [19]. The incorporation of fluorine containing perfluoroalkyl ethyl (meth)acrylate polymers into the coating formulations is generally preferred to repel both water and oil, produce low adhesion, and obtain self-cleanable, biocompatible and antifouling coatings [20]. In usual practice, the expensive fluorinated polymers are copolymerized with non-fluorinated low-cost monomers [8,16] or blended with cheap polymers [21] to reduce the cost of final coating. On the other hand, it is possible to increase the surface roughness of a polymer by applying a phase separation method with adding non-solvents into the polymer solution [8,14–17]. Such methods were also applied to fluorine containing polymers before. For example, Xie et al. prepared a super-hydrophobic surface by casting fluorine-end-capped polyurethane (FPU) and PMMA mixture on a glass surface [14]. Wei et al. synthesized random copolymer of styrene and 2,2,3,4,4,4-hexafluorobutyl methacrylate by bulk polymerization and a super-hydrophobic copolymer film

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was prepared subsequently using the phase separation technique [15].

In general, blending two or more polymers is carried out to obtain new materials that combine the advantages of the individual components in a convenient and economical means [21]. Polymer blends were used for the fabrication of rough patterned polymer surfaces in the past [22–25]. Most of the methods to obtain micro-patterned surfaces require expensive and delicate equipment and/or specially designed polymer materials, which limits their applications in most areas [26]. Therefore, blending suitable low cost polymers with others is advantageous to obtain simple and cheap rough patterned polymer surfaces [27]. The success of a polymer blend depends mainly to the miscibility of the individual components and their chemical nature [27]. When a low surface free energy polymer is added to another polymer, it is expected that the first one will migrate to the air/coating interface during the film formation by a phase separation process and this process changes the surface morphology and free energy characteristic [9,10]. However, when the enthalpic and entropic effects overcome the surface free energy difference of main parts in a polymer blend, then the polymer with higher surface free energy may enrich at the blend film surface [28]. For the special case of polystyrene/polymethyl methacrylate (PS/PMMA) blends, their surface properties have been extensively investigated by several authors [23,28,29]. In most of these studies, it was found that PS having the lower surface free energy was enriched at the air-polymer interface in order to minimize the interfacial free energy [23,29]. However, Tanaka et al. showed that PMMA having the higher surface free energy could be enriched at the air-polymer interface due to the enthalpic and entropic effects in some instances [24,28]. Ma et al. obtained a super-hydrophobic coating by using a PS/PMMA blend film [30].

The surface free energy and polymer-solvent interactions play a more important role in the surface separation of polymers [23,25,31]. When a low surface free energy copolymer is added to PS, it is expected that the first one will migrate to the air/coating interface during the film formation by a phase separation process and will change the surface roughness and free energy characteristics of the polymer blend surface [23,25]. While fluoroacrylate/MMA copolymer (p(TAN-co-MMA)) has a low surface free energy (12.41 mJ/m^2) due to the presence of polar fluor groups, PS has a much higher surface free energy (42 mJ/m^2) than the p(TAN-co-MMA) copolymer. Therefore, polymeric surfaces with various morphologies and wettability could be prepared by blending these polymers with quite different surface free energy in this study. In addition to surface tension forces, solvent evaporation rates has an effect on film properties especially for the non-equilibrium conditions such as the preparation of blend films spin cast from a volatile solvent [25]. The system is not at equilibrium since the solvent evaporates relatively quickly and polymer chains can be immobilized in the films before attainment of a thermodynamically favorable state. The different solubility of polymers in the casting solvent can also cause de-mixing of the polymers as the solvent evaporates, leading to the component of higher solubility being enriched at the film surface [25]. In addition, the difference in molecular weight or chain length between the blended polymers could cause a morphologic change due to the enrichment of polymeric groups with low molecular weight on the surface and the conformational entropy of a chain at the film surface is much smaller than that in the bulk [28]. Thus, the polymeric chains existing at the film surface are compressed along the direction perpendicular to the film surface. In this respect, molecular weight effect is decisive so that the lower the M_w, the lower the entropy effect and the surface is enriched with the lower M_w macromolecule [28].

In this study, we synthesized random copolymers of MMA and perfluroethylalkyl acrylate (Zonyl-TAN) monomers in a CO_2-expanded monomer phase at 13 MPa and 80 °C. Later, we prepared flat p(TAN-co-MMA) copolymer and also superhydrophobic/hydrophobic rough fluorinated polymer blend surfaces by a phase separation process using a dip coating method. p(TAN-co-MMA) copolymer and PS homopolymer blends were prepared in THF with the blend ratios are kept constant at 20/80, 50/50, and 80/20. We investigated two types of blend surfaces; one of them is a hydrophobic surface having a water contact angle between $113^\circ \pm 1$ and $118^\circ \pm 2$ which was prepared using a dip coating method with THF as the solvent. The other blend surface was superhydrophobic having a water contact angle of between $142^\circ \pm 2$ and $170^\circ \pm 2$ which was prepared with the same dip coating method with THF as a solvent and ethanol as a non-solvent. There was no report of superhydrophobic PS/fluoroacrylate blend surfaces in the literature to the best of our knowledge. Superhydrophobic p(perfluoro-methacrylate-co-styrene) [17] and superhydrophobic blend surfaces including fluor without PS [15] were reported by a phase separation process in the literature. We also investigated the variation of components in the blend solution on the surface roughness of the coatings and we found that the difference of the solubility of polymers in blends is an important parameter for the control of the surface morphology, pit and protrusion diameter.

2. Experimental

2.1. Materials

Perfluoroethyl alkyl acrylate monomer mixture (Zonyl-TAN) was purchased from Dupont-Turkey and used directly. Zonyl-TAN is a commercial fluoroacrylate monomer which contains mixtures of homologous fluoroalkyl ethyl methacrylates having varying length side chains containing $(-CF_2-)_x$. Its chemical formula is given in Fig. S1 where x was reported to be between 8–10 and the fluorine content of the mixture is 63.5%. Zonyl-TAN shows a narrow homologue distribution and approximately 85% of the mixture is composed of $(CF_2)_8$ and $(CF_2)_{10}$ [32]. Methyl methacrylate (MMA) monomer, polystyrene homopolymer (PS, $M_w = 300.000$ g/mol, $M_n = 130.000$ g/mol, Sigma Aldrich), chloroform, tetrahydrofuran (THF), ethanol, and AIBN initiator were purchased from Aldrich. Ultrapure water, methylene iodide, formamide, ethylene glycol, hexadecane and α-bromonaphthalene were purchased from Merck. Technical grade methanol and toluene were supplied by Tekkim, Turkey. High-purity carbon dioxide gas (99.9%) was purchased from Linde Gases, A.S., Turkey. Glass slides (76 × 26 mm, ISOLAB, Turkey) were used as substrates and Milli-Q® water was used for the final cleaning of these glass slides.

2.2. Synthesis and characterization of p(TAN-ran-MMA) copolymers

Zonyl-TAN and MMA monomers were copolymerized in a CO_2-expanded monomer phase at 13 MPa, 80 °C with an AIBN concentration of 1% by weight with respect to the total monomers in a period of 16 h. The details of copolymerization reactions are similar to our previous studies where the heterogeneous random copolymerization of perfluoroalkyl ethyl methacrylate monomer (Zonyl-TM) with MMA in CO_2-expanded monomer medium was reported [8]. CO_2 mole fraction was calculated to be 0.83 mol in the reactor by using the compressibility factor (z) of CO_2. At the end of the reaction, white solid copolymer was collected from the reactor and the product was dissolved in toluene and precipitated in methanol to separate the unreacted residues (e.g monomers and oligomers), to purify the copolymer which will be used in