

Synthesis and characterization of a superhydrophobic surface from cyclic olefin copolymer

E. Doganci and H. Y. Erbil*

*Gebze Institute of Technology, Department of Chemical Engineering,
Cayirova, Gebze 41400, Kocaeli, Turkey*

Cyclic olefine copolymer (COC) which is an engineering plastic was tried to form a superhydrophobic surface by a phase separation process using solvent + non solvent mixtures. The cloud points of the COC + solvent + non-solvent mixtures were determined and evaluated by using Hansen 3-solubility parameter approach. It was determined that the amorphous COC polymer is not suitable to prepare a superhydrophobic surface when used alone. However, a superhydrophobic surface with a water contact angle of $158\pm 2^\circ$ was obtained when COC is mixed with crystalline polypropylene homopolymer. The water contact angle and surface morphology of the polymer coatings were examined.

1. INTRODUCTION

Wettability of a surface can be expressed by measuring the contact angle of a water droplet on the surface [1]. Surfaces with a water contact angle larger than 150° where the water drop rolls off the surface with a tilt (sliding) angle less than 5° are called “superhydrophobic” surfaces. Flat materials with low surface energy, for example a surface with hexagonally packed $-\text{CF}_3$ groups give water contact angles as high as 120° . These surfaces are easy to clean, however, they do not have self-cleaning properties because the water droplets cannot roll-off the surface at a small tilt angle and cannot remove the contaminants from the surface. Thus, there must be another property giving very large water contact angles and self-cleaning property. We need to look to nature for the correct answer because there are many surfaces in nature having superhydrophobic and self-cleaning ability such as the wings of butterflies, the legs of water strider and the leaves of the lotus plant (*Nelumbo nucifera*) [2], cabbage and Indian cress.

Electron microscopy of the surface of lotus leaves shows protrusions about 20–40 μm apart each covered with a smaller scale rough surface of epicuticular wax crystalloids [2]. The lotus plant gives a contact angle of 160° by using paraffinic wax crystals containing predominantly $-\text{CH}_2-$ groups. It is clear that the nature does not require the lower surface free energy of $-\text{CH}_3$ or $-\text{CF}_3$ groups to achieve these effects, so that the control on the morphology of a surface on micron and nanometer length scales is the key. Many recent studies have shown that this combination of micrometer and nanometer-scale roughness, along with a low surface energy material leads to apparent water contact angles larger than 150° , a low sliding angle and the self-cleaning effect [3-8].

Mimicking the nature opens up many possibilities for engineering surfaces where properties such as anti-sticking, anti-contamination and self-cleaning are desired such as anti-biofouling paints for ship hulls and leisure boats, anti-sticking of snow for antennas and windows, self-cleaning windshields for automobiles, stain-resistant textiles, anti-soiling architectural coatings, self-cleaning solar energy panels, photovoltaics, heat transfer surfaces in air conditioning equipment. Superhydrophobic surfaces are also used in biomedical applications ranging from blood vessel replacement to wound management and DNA analysis by microfluidics methods. While the industrial applications of superhydrophobic surfaces are enlarging besides water repellency, other properties such as transparency and color, anisotropy, reversibility, flexibility and breathability are also expected to be incorporated into the capabilities of these surfaces [1, 3-8].

Techniques to make superhydrophobic surfaces can be simply divided into two categories: making a rough surface from a low surface energy material and modifying a rough surface with a material of low surface energy. The transformation of a simple and cheap plastic (polypropylene) into a superhydrophobic surface is an example for the first method and was achieved for the first time in 2003 by applying a phase separation process using solvent + non solvent mixtures under controlled temperature conditions [9]. More than 250 different polymers had been tried afterwards by the same solvent phase separation method to obtain new superhydrophobic surfaces for various applications.

Cyclic olefine copolymer (COC) was not used as a superhydrophobic surface before. COC is obtained by using metallocene catalysts during polymerization of norbornene and ethylene and its various forms are used as engineering thermoplastics having properties such as high glass transition temperatures in combination with excellent transparency, low density, low birefringence, very low moisture absorption, outstanding moisture barrier effect, heat distortion resistance up to 170°C , high rigidity, strength and hardness, very good electrical insulation properties, low dielectric loss, very good melt processability /

flowability and good chemical resistance to acids and alkalis and polar organic solvents, excellent biocompatibility, very good blood compatibility [10-22]. However, COC has some weakness in chemical resistance so that it is attacked by non-polar organic solvents such as toluene and naphtha and polar solvents such as methylene chloride. Since the first report on the synthesis of COCs in 1991 [10], the synthesis of COCs has been the subject of a large amount of research: There are several types of commercial cyclic olefin copolymers based on different types of cyclic monomers and polymerization methods. Cyclic olefin copolymers are mainly produced by chain copolymerization of cyclic monomers such as 8,9,10-trinorborn-2-ene (norbornene) or (tetracyclododecene) with ethylene or propylene [10-15]. The scheme of the synthesis of COC from ethylene and norbornene in two steps is given in Figure 1.

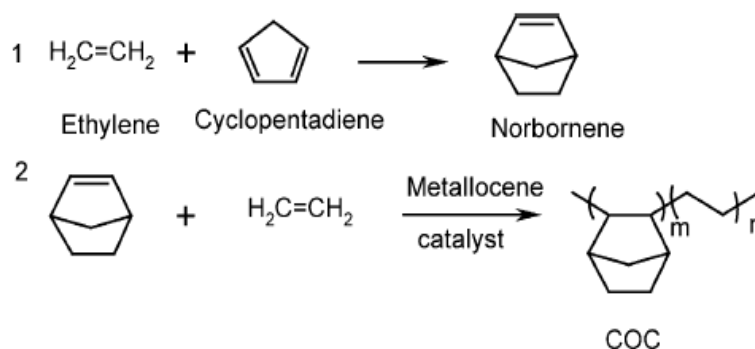


Fig. 1. Synthesis steps of the COC copolymer.

All cyclic olefin copolymers are completely amorphous. This morphology is due to the steric hindrance created by the incorporation of norbornene in the polymer chains. In fact, norbornene is much bulkier than ethylene and has rigid bridged-ring structure that prevents crystallization. COC copolymers were used as high-performance optical, medical, electrical, packaging and other applications owing to their rigid cyclic monomer units. COC is mainly used as pharmaceutical blister pack films due to their high moisture barrier effect; as packaging films in composite films for food packaging; as metallized films for capacitors; as prefillable syringes, microtitre plates, vials, ampoules; as pharmaceutical primary packaging and diagnostic articles; as lenses, prisms, rain sensors due to their high transparency and as toner binder in color printers. COC can be readily colored due to the polar norbornene group present in the chain. [16-22].

In the present work, COC was tried to form a superhydrophobic surface having superior mechanical and transparency properties. Solvent + non solvent pairs were used to dissolve the polymer at various temperatures to prepare dip coated films. In addition, polypropylene was also used to prepare a polymer blend with COC polymer to impart roughness on the final coating surface.

2. EXPERIMENTAL

Materials: COC copolymer (TOPAS 6013S of Ticona GmbH, Germany) with a density of 1.02 g/cm and glass transition temperature, $T_g = 140^\circ \text{C}$, $M_w = 65.400$ g/mol was used. The norbornene molar content is 52 % whereas the ethylene molar content is 48 % for this grade. The water absorption at 23°C is 0.01 %. The degree of light transmission is 91 % [17]. Polypropylene homopolymer (PETOPLN MH-418 of PETKIM, Turkey) was used to prepare polymer blends. Cyclohexane, xylene (mixture of o-, m-, p-), methyl ethyl ketone, n-butanol, isopropanol, acetone, ethyl acetate solvents are all analytical grade of Sigma-Aldrich and used as received. COC was dissolved in cyclohexane, carbontetrachloride and xylene between $24\text{--}51^\circ \text{C}$ and non solvents such as methyl ethyl ketone, n-butanol, isopropanol, acetone, ethyl acetate were dropwise added by using a burette in order to determine the cloud points of the polymer solution. Glass slides were cleaned in chromic acid solution and rinsed by distilled water and dried in oven at 105°C . COC polymer and also the polymer mixtures were dip coated onto these glass slides 10°C above the cloud points of the solutions by using a mechanical dipper having adjustable dipping speed. The coated slides were dried at room temperature and water contact angles were measured by KSV CAM-200 contact angle meter. Nikon SMZ 1500 optical microscopy was used to investigate the surface topography of the coatings.

3. RESULTS AND DISCUSSION

Hansen 3-parameter solubility approach was used to determine the solution properties. The values of these parameters for all the solvents [23] and also for the TOPAS 6013 polymer [24] are given in Table 1.

These parameters were also calculated for the solvent + non-solvent mixtures at the cloud point according to the molar additivity rule depending on mole fractions of the solution as given with the equation below:

$$\delta_i^{\text{mix}} = \delta_i^{\text{solvent}} X_{\text{solvent}} + \delta_i^{\text{non-solvent}} X_{\text{non-solvent}} \quad (1)$$

Tab. 1. Hansen 3-parameter solubility parameters of the solvents and non solvents used with COC polymer.

		$\delta_d (\text{J/cm}^3)^{1/2}$	$\delta_p (\text{J/cm}^3)^{1/2}$	$\delta_h (\text{J/cm}^3)^{1/2}$
Good Solvent	TOPAS 6013	18	3	2
	Cyclohexane	16,8	0	0,2
	Xylene	17,6	1	3,1
	Carbontetrachloride	17,8	0	0,6
Non-Solvent	Methyl ethyl ketone	16	9	5,1
	Isopropanol	15,8	6,1	16,4
	n-Butanol	16	5,7	15,8
	Acetone	15,5	10,4	7
	Ethyl Acetate	15,8	5,3	7,2

The values of mixed solvent parameters at the cloud point which were determined by non-solvent titration of the polymer solution are given in Table 2.

The average values of the solvent mixtures, $\delta_d = 17.1 (\text{J/cm}^3)^{1/2}$, $\delta_p = 1.9 (\text{J/cm}^3)^{1/2}$, and $\delta_h = 3.3 (\text{J/cm}^3)^{1/2}$ are close to TOPAS 6013 values given in Table 1, confirming that a solvent + non solvent mixture shows a cloud point very near to the 3- parameter solubility values of the dissolved polymer.

The advancing water contact angle values of all the COC films on the glass slides varies between $\theta_a = 101 - 104^\circ$ and the receding contact angles $\theta_r = 82 - 86^\circ$ and far from forming a superhydrophobic surface. The close examination of the optical microscopy images shows that the COC surfaces are very flat. This is due to the complete amorphous structure of the COC polymer. However, the addition of polypropylene in xylene solvent increased the contact angle up to $\theta_a = 156 - 160^\circ$ ($\theta_e = 150-152^\circ$) giving a superhydrophobic rough structure. The optical microscopy of this polymer blend film is given in Figure 2.

Tab. 2. Hansen 3-parameter solubility parameters of the mixed solvents at the cloud point composition of COC polymer solution calculated from Eq.1.

Sample No	Solvent	Non-Solvent	X_{solvent}	$X_{\text{non-solvent}}$	$\delta_d (\text{J/cm}^3)^{1/2}$	$\delta_p (\text{J/cm}^3)^{1/2}$	$\delta_h (\text{J/cm}^3)^{1/2}$
1	Cyclohexane	Methyl Ethyl Ketone	0.671	0.329	16.54	2.96	1.81
2	Xylene	Methyl Ethyl Ketone	0.849	0.151	17.36	2.21	3.40
3	CCl_4	Methyl Ethyl Ketone	0.759	0.241	17.37	2.17	1.68

Sample No	Solvent	Non-Solvent	X_{solvent}	$X_{\text{non-solvent}}$	δ_d (J/cm^3) ^{1/2}	δ_p (J/cm^3) ^{1/2}	δ_h (J/cm^3) ^{1/2}
4	Cyclohexane	Isopropanol	0.765	0.235	16.56	1.43	4.01
5	Xylene	Isopropanol	0.836	0.164	17.31	1.83	5.27
6	CCl_4	Isopropanol	0.777	0.223	17.35	1.36	4.12
7	Cyclohexane	n-Butanol	0.766	0.234	16.61	1.33	3.85
8	Xylene	n-Butanol	0.839	0.161	17.34	1.76	5.14
9	CCl_4	n-Butanol	0.787	0.213	17.42	1.22	3.84
10	Cyclohexane	Acetone	0.700	0.300	16.41	3.12	2.24
11	Xylene	Acetone	0.880	0.120	17.35	2.13	3.57
12	CCl_4	Acetone	0.781	0.219	17.30	2.28	2.00
13	Cyclohexane	Ethyl Acetate	0.668	0.332	16.47	1.76	2.53
14	Xylene	Ethyl Acetate	0.855	0.145	17.34	1.62	3.70
15	CCl_4	Ethyl Acetate	0.769	0.231	17.34	1.23	2.13

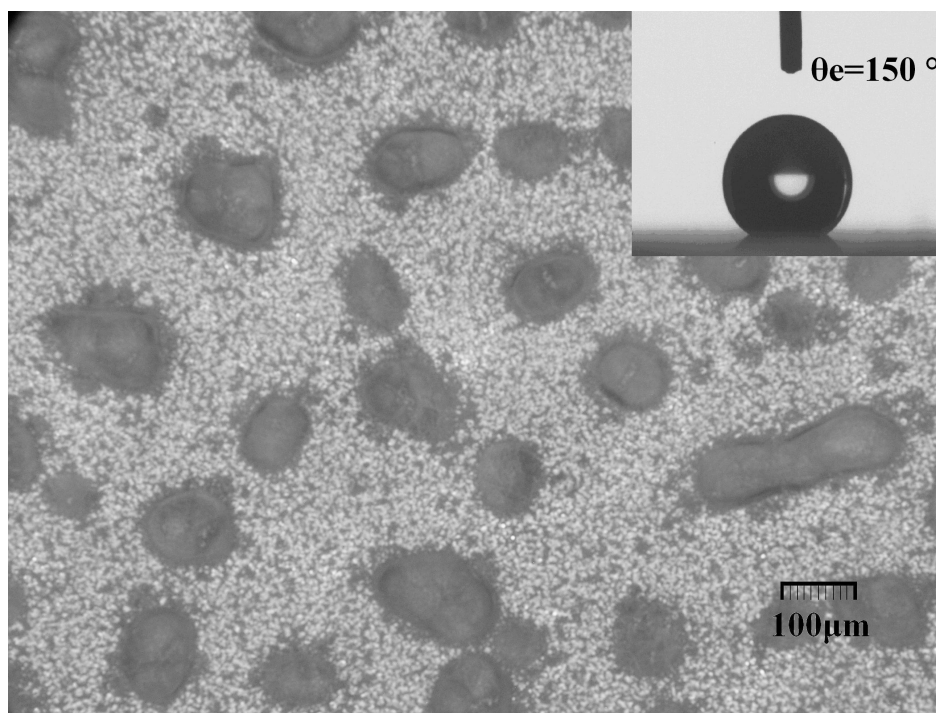


Fig. 2. Optical microscopy of the surface of COC + polypropylene polymer blend film obtained from xylene solvent (x100 magnification). Water contact angle profile image is also given in the insert.

4. CONCLUSION

Amorphous COC polymer is not suitable to prepare a superhydrophobic surface when used alone. The cloud points of the COC + solvent + non-solvent mixtures were determined and evaluated by using Hansen 3-solubility parameter approach and the results confirmed that the average values of the solvent mixtures, $\delta_d = 17.1 \text{ (J/cm}^3)^{1/2}$, $\delta_p = 1.9 \text{ (J/cm}^3)^{1/2}$, and $\delta_h = 3.3 \text{ (J/cm}^3)^{1/2}$ are close to TOPAS 6013's $\delta_d = 18 \text{ (J/cm}^3)^{1/2}$, $\delta_p = 3 \text{ (J/cm}^3)^{1/2}$, and $\delta_h = 2 \text{ (J/cm}^3)^{1/2}$ values. A superhydrophobic surface with a water contact angle of $156\text{-}160^\circ$ was obtained when COC is mixed with crystalline polypropylene homopolymer.

5. REFERENCES

- [1] H. Y. Erbil, *Surface Chemistry of Solid and Liquid Interfaces*, Blackwell Publishing, Oxford 2006.
- [2] W. Barthlott, C. Neinhuis, *Planta*, 202, 1 (1997).
- [3] T. L. Sun, L. Feng, X. F. Gao, L. Jiang, *Acc. Chem. Res.*, 38, 644, (2005).
- [4] D. Quere *Rep. Prog. Phys.*, 68, 2495(2005).
- [5] M. Ma, R. M. Hill, *Current Opinion in Colloid & Interface Science*, 11, 193 (2006).
- [6] X. Feng, L. Jiang, *Advan. Mater.*, 18, 3063, (2006).
- [7] J. Genzer, K. Efimenko, *Biofouling*, 1 (2006).
- [8] X. M. Li, D. Reinhoudt, C. C. Mercedes, *Chem. Soc. Rev.*, 36, 1350 (2007).
- [9] H. Y. Erbil, A. L. Demirel, Y. Avci and O. Mert, *Science*, 299, 1377 (2003).
- [10] W. Kaminsky, A. Bark, M. Arndt, *Macromol. Chem. Macromol. Symp.*, 47, 83 (1991).
- [11] W. Kaminsky, A. Noll, *Polym. Bull.*, 31, 175 (1993).
- [12] G. M. Benedikt, B. L. Goodall, N. S. Marchant, L. F. Rhodes *New J. Chem.*, 18, 105 (1994).
- [13] H. Chedron, M. J. Brekner, F. Osan, *Angew. Macromol. Chem.*, 223, 121 (1994).
- [14] W. Kaminsky, R. Engehausen, J. Kopf, *Angew. Chem.*, 107, 2469 (1995).
- [15] W. Kaminsky, M. Arndt, *Adv. Polym. Sci.*, 127, 144 (1997).
- [16] T. Rische, A. J. Waddon, L. C. Dickinson, W. J. MacKnight *Macromolecules*, 31, 1871 (1998).
- [17] Ticona GmbH Brochure, Frankfurt, Germany (2000),.
- [18] R. R. Lamonte, D. McNally, *Plastic Eng.*, 56, 51 (2000).
- [19] R. R. Lamonte, D. McNally, *Adv. Mater. Process.*, 159, 33 (2001).
- [20] M. C. Delpech, F. M. B. Coutinho, M. E. S. Habibe *Polym. Testing*, 21, 411 (2002).
- [21] M. J. Young, C. Wen-Sheng, C. C. M. Ma *Eur. Polym. J.*, 39, 165 (2003).
- [22] M. Limam, L. Tighzert, F. Fricoteaux, G. Bureau, *Polym. Testing*, 24, 395 (2005).
- [23] C. M. Hansen, *Hansen Solubility Parameters: A User's Handbook*, CRC Press, Boca Raton, 2000.
- [24] C. M. Hansen and L. Just *Ind. Eng. Chem. Res.*, 40, 21 (2001).

CURRICULUM VITAE



H. Yildirim Erbil is a professor at Gebze Institute of Technology, Department of Chemical Engineering, Turkey. His research interest covers surface free energy characterization of polymers; emulsion copolymerization; modeling evaporation of sessile drops on polymer surfaces; novel methods to measure receding contact angles; superhydrophobic surfaces at micro- and nanometer scale roughness; copolymers to be used in marine anti-biofouling; supercritical carbon dioxide polymerizations.

Selected publications:

1. Surface Chemistry of Solid and Liquid Interfaces, H. Y. Erbil, Blackwell Publishing, Oxford, UK, 2006.
2. Vinyl Acetate Emulsion Polymerization and Copolymerization with Acrylic Monomers, H. Y. Erbil, CRC Press Inc., Boca Raton, USA, 2000.
3. Interfacial Interactions of Liquids, and Surface Tension of Polymers, H. Y. Erbil, Chapters 2 and 9, in " Handbook of Surface and Colloid Chemistry ", Ed. K. S. Birdi, CRC Press Inc., Boca Raton, USA, 1997.
4. Determination of Peripheral Contact Angle of Sessile Drops on Solids from the Rate of Drop Evaporation, H. Y. Erbil, Journal of Physical Chemistry B, 102, (46), 9234 - 9238 (1998).
5. Transformation of a Simple Plastic into a Super-Hydrophobic Surface, H. Y. Erbil, A. L. Demirel, Y. Avci and O. Mert, Science, 299, 1377-1380 (2003).