



Invited paper

A multi-functional polymer coating that is heat-resistant, hydrophobic and transparent



Tianyuan Zhao^a, Dongmei Zhang^a, Chunmei Ding^a, Jinglun Zhou^b,
Jinsong Zhu^{b,*}, Lei Jiang^{a,c,**}

^a Key Laboratory of Bio-Inspired Smart Interfacial Science and Technology of Ministry of Education, School of Chemistry and Environment, Beihang University, Beijing 100191, China

^b National Center for Nanoscience and Nanotechnology, Beijing 100190, China

^c Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

ARTICLE INFO

Article history:

Received 11 March 2014

Received in revised form 6 April 2014

Accepted 13 April 2014

Keywords:

Wettability

Heat-resistance

Superhydrophobic

Micro-/nano-structure

ABSTRACT

A multi-functional polymer film with high hydrophobicity and transparency was formed by simple casting of a polycarbonate solution onto a substrate having micro-scale roughness. The high hydrophobicity was heat-resistant, which can be retained up to 390 °C. The polymer film may have potentially wide-ranging applications in industry and high technology.

© 2014 Published by Elsevier B.V. on behalf of Chinese Society of Particuology and Institute of Process Engineering, Chinese Academy of Sciences.

Introduction

Functional materials with multiple useful properties are becoming increasingly desirable for applications under various environmental conditions (Min, Jiang, & Jiang, 2008; Schottner, 2001; Zhang, Li, Sun, & Shen, 2008). Superhydrophobicity is one of the most important properties of some solid materials that have micro-/nano-morphological roughness, and has anti-wetting and self-cleaning applications (Dong, Liu, & Li, 2012; Sun, Feng, Gao, & Jiang, 2005; Yang, Jin, Liu, & Jiang, 2013). Thermal stability is another important feature for materials utilized in the aerospace industry (Deng et al., 2013; Honda, Yamamoto, & Tezuka, 2013; Njuguna & Pielichowski, 2003). However, the combination of both these valuable properties is rarely found in light and moldable polymers, which are desirable in mechanical engineering. Metals and ceramics that have high heat-resistance are heavy and not moldable (Cha et al., 2013; Fei, Chen, & Lin, 2014; Lin, Chen, Fei, Liu, & Zhang, 2013). Aromatic polyimides are

heat-resistant polymers that also exhibit many useful properties such as chemical resistance, low flammability, and excellent mechanical properties. However, they have poor anti-wetting properties due to the presence of hydrophilic imide groups (Le & Chung, 2014; Tsuda, 2013). Fluoro-organic polymers have emerged as new heat-resistant materials that also have low surface energies. Amphiphobic polymer coatings with heat resistance up to 300 °C have been reported, but these fluorine-containing materials cannot be used because of toxicity to humans and the environment (Seitz, Vineberg, Zuniga, & Ojima, 2013; Wang et al., 2014). Therefore, ecologically and biologically safe coatings having both excellent water repellency and thermal resistance are urgently needed for numerous applications in the aerospace and food industries (Schmidt, 1994). Here, a polycarbonate coating, formed by a simple dip-coating method, is shown to exhibit simultaneous hydrophobicity and high temperature durability. In addition, it is very transparent to visible light, and is environmentally friendly. Thus, this new material may have extensive applications ranging from industry to daily life.

Experimental

The synthesis of the polycarbonate has been reported previously (Nishiguchi & Tokuda, 1995). Briefly, 24.9 g of deionized water

* Corresponding author. Fax: +86 10 82621396.

** Corresponding author at: Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. Fax: +86 10 82621396.

E-mail addresses: jizhu@nanocr.cn (J. Zhu), jianglei@iccas.ac.cn (L. Jiang).

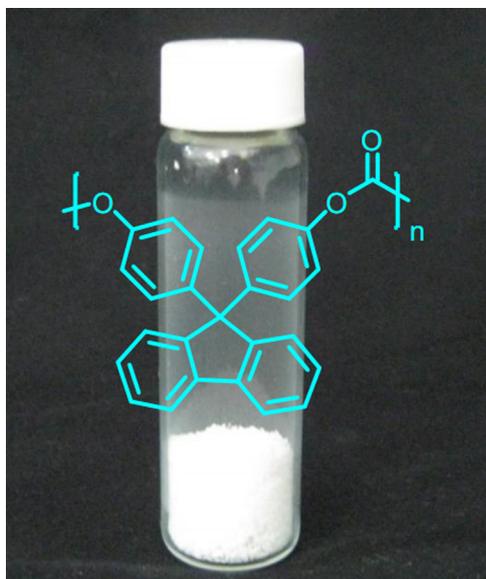


Fig. 1. Molecular structure and sample of the polycarbonate.

and 1.64 g of aqueous sodium hydroxide solution (48.5 w/w%) were placed into a reflux condenser, and nitrogen gas was bubbled through the solution for 30 min to de-oxygenate it. Then 0.005 g of hydrosulfite was added, and 2.71 g of 2,2-bis(4-hydroxyphenyl)hexafluoropropane (99.98% purity) and 0.314 g of 9,9-bis(4-hydroxyphenyl)fluorene (99.8% purity) were dissolved in the solution. Then 26.7 g of methylene chloride was added, and 1.04 g of phosgene was bubbled into the solution at 14–16 °C, followed by about 60 min of stirring. To this was added 0.56 g of aqueous sodium hydroxide solution (48.5 w/w%) and 0.067 g of *p*-tert-butylphenol, and the solution was stirred for emulsification. Finally, 0.002 g of triethylamine was added, followed by stirring at 30 °C for 2 h. The polymer product has a molecular weight of approximately 300,000. Fig. 1 shows the sample of this polycarbonate prepared together with its molecular structure.

To prepare polycarbonate coatings, the polymer was dissolved (1 mg/mL) in 1,2-dichloroethane and was strongly stirred for 1 h to ensure complete dissolution. The polymer solution was then spread onto silicon substrates and dried in a clean-room atmosphere.

The silicon substrates were initially cleaned in an ultrasonic bath for 5 min in ethanol and acetone, sequentially, and then treated with hot sulfuric acid (Ma, Liu, Xu, & Cui, 2005). The clean, pure silicon substrates were dried under nitrogen.

Water contact angles (CAs) were measured with an OCA20 apparatus (DataPhysics, Germany) at saturated humidity. Thermogravimetric analysis (TGA) result was performed with a Pyris 1 TGA (Perkin-Elmer).

Results and discussion

TGA of the synthesized polymer was performed a heating rate of 10 °C/min (Fig. 2), and indicated that the polycarbonate had a very high thermal stability up to 400 °C. At temperatures greater than 400 °C, the polymer started to steadily decompose and displayed a 10% weight loss at 463.2 °C. As a polymer having a melting point higher than 300 °C, this polycarbonate should therefore be defined as heat-resistant. Furthermore, it should be considered as a breakthrough in the field of heat-resistant polymers, which has been dominated by aromatic polyamides for decades.

The polycarbonate film was obtained by casting the polymer solution onto a clean silicon substrate (both rough and flat). The

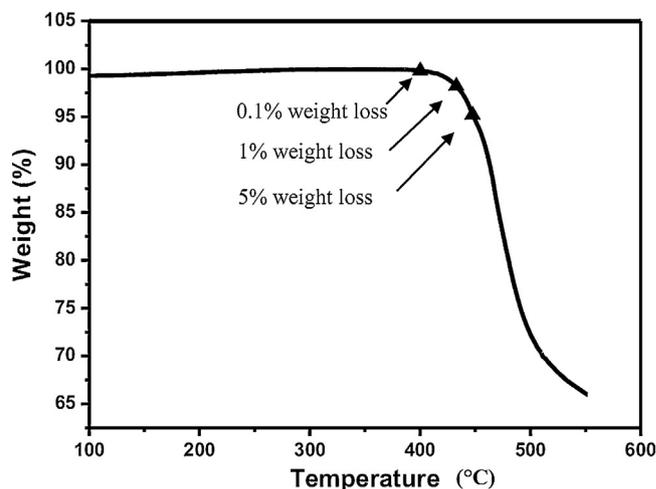


Fig. 2. Thermogravimetric analysis of the polycarbonate, exhibiting excellent stability up to 400 °C.

wettability of the film was examined by measuring water contact angles (CAs) with 2- μ L water droplets at five different positions on the surface. The average value on flat substrates was $(86.9 \pm 1.1)^\circ$, which is hydrophobic; in comparison, clean silicon substrates were hydrophilic with CAs less than 20°. Thus the polycarbonate modified the substrate by making it hydrophobic. The thermal stability of the hydrophobicity was investigated by annealing the polymer film at a series of temperatures in the range 20–450 °C (Fig. 3). The annealing was performed in air in a muffle furnace, with a heating rate of 10 °C/min, and the temperature was maintained for 6 h before cooling to room temperature. The CA remained stable at 87.6° from 20 °C to almost 400 °C. After annealing at 400 °C, the CA of the film decreased to 57.3°; thus the polymer began to significantly lose its hydrophobicity. Relative to the TGA data for the bulk polymer discussed above, the polycarbonate film was also thermally stable up to about 400 °C, before it began to decompose slightly. Thus the thermal stability and the hydrophobicity both decrease around the same temperatures. Although the polymer only lost 5% of its weight at 400 °C, the hydrophobicity completely disappeared. Therefore, tiny changes in the chemical composition can lead to dramatic differences in wettability.

It has been shown theoretically and experimentally that surface roughness can enhance hydrophobicity (Feng et al., 2004; Nakajima, Fujishima, Hashimoto, & Watanabe, 1999). The relationship of the contact angle for a coated film on a rough substrate (θ_r) with that for the same film on a flat substrate (θ) can be expressed as (Bormashenko, 2011; Koishi, Yasuoka, Fujikawa, Ebisuzaki, & Zeng, 2009; Marmur, 2004):

$$\cos \theta_r = f_1 \cos \theta - f_2, \quad (1)$$

where f_1 and f_2 are the fractions of rough substrate and air in contact with water respectively (*i.e.*, $f_1 + f_2 = 1$). Thus, for a hydrophobic coated film, increasing f_2 increases θ_r to a more hydrophobic state; in contrast, for a hydrophilic coated film, increasing f_2 decreases θ_r to a more hydrophilic state. The CA of the polycarbonate film on a flat substrate is about 80° for pure water, indicating a hydrophobic film (the new hydrophilic/hydrophobic boundary is about 65°) (Bhushan, Wang, & Maali, 2009; Zhao, Moore, & Beebe, 2001), while the polymer film on a substrate with micro scale roughness had a superhydrophobic CA of $(156.4 \pm 3.1)^\circ$.

The transmittance of the polymer film was examined by casting it onto a quartz substrate. As shown in Fig. 4, the polymer film exhibited high transmission (>90%) of light over the visible range 400–800 nm. Meanwhile, the same film had a hydrophobic CA of

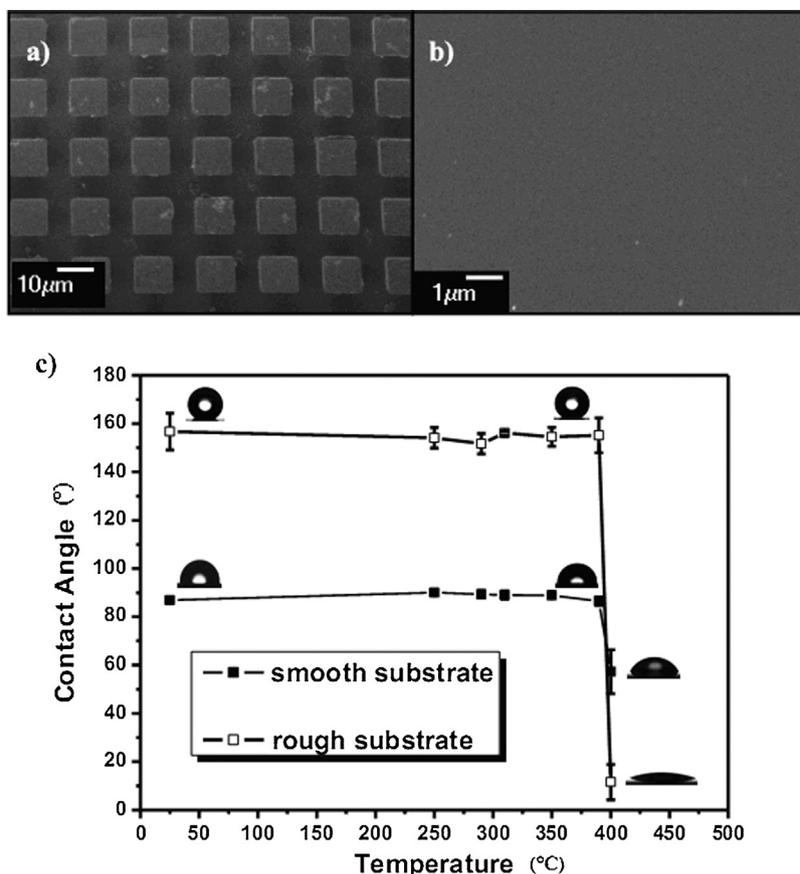


Fig. 3. Polycarbonate films on (a) a rough Si substrate, and on (b) a smooth Si substrate. (c) Contact angles of polycarbonate films on smooth and rough substrates as a function of annealing temperatures in the range of 20–400 °C.

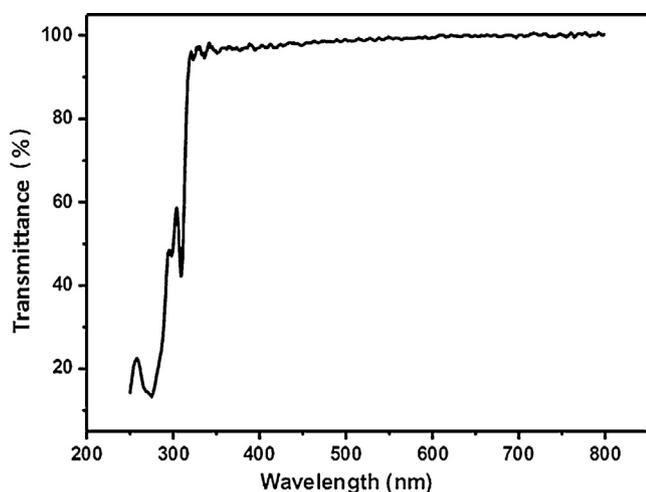


Fig. 4. UV-vis transmission spectrum of the polycarbonate film.

~90.4°, almost the same as that for a film coated on the flat silicon substrate.

Conclusions

With a simple spin-coating process, an environmentally safe polycarbonate film with high hydrophobicity, thermal stability, and visible light transmittance was prepared. Such a

multifunctional coating could be widely applied in aerospace and food industries.

Acknowledgements

The authors thank the National Natural Science Foundation of China (grant no. 21101010) and the Innovation Foundation of BUAA for PhD Graduates (296181) for continuing financial support.

References

- Bhushan, B., Wang, Y., & Maali, A. (2009). Boundary slip study on hydrophilic, hydrophobic, and superhydrophobic surfaces with dynamic atomic force microscopy. *Langmuir*, 25(14), 8117–8121.
- Bormashenko, E. (2011). Comment on water droplet motion control on superhydrophobic surfaces: Exploiting the Wenzel-to-Cassie transition. *Langmuir*, 27(20), 12769–12770.
- Cha, S.-C., Her, E. K., Ko, T.-J., Kim, S. J., Roh, H., Lee, K.-R., et al. (2013). Thermal stability of superhydrophobic, nanostructured surfaces. *Journal of Colloid and Interface Science*, 391, 152–157.
- Deng, G., Bo, S., Zhou, T., Zhang, R., Liu, J., Liu, X., et al. (2013). Hydrogen-bonded network: An effective approach to improve the thermal stability of organic/polymer electro-optic materials. *Science China Chemistry*, 56(2), 169–173.
- Dong, M., Liu, Q., & Li, A. (2012). Displacement mechanisms of enhanced heavy oil recovery by alkaline flooding in a micromodel. *Particology*, 10(3), 298–305.
- Fei, T., Chen, H., & Lin, J. (2014). Transparent superhydrophobic films possessing high thermal stability and improved moisture resistance from the deposition of MTMS-based aerogels. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 443, 255–264.
- Feng, L., Zhang, Z., Mai, Z., Ma, Y., Liu, B., Jiang, L., et al. (2004). A super-hydrophobic and super-oleophilic coating mesh film for the separation of oil and water. *Angewandte Chemie International Edition*, 43(15), 2012–2014.
- Honda, S., Yamamoto, T., & Tezuka, Y. (2013). Tuneable enhancement of the salt and thermal stability of polymeric micelles by cyclized amphiphiles. *Nature Communications*, 4, 1574. <http://dx.doi.org/10.1038/ncomms2585>

- Koishi, T., Yasuoka, K., Fujikawa, S., Ebisuzaki, T., & Zeng, X. C. (2009). Coexistence and transition between Cassie and Wenzel state on pillared hydrophobic surface. *Proceedings of the National Academy of Sciences*, *106*(21), 8435–8440.
- Le, N. L., & Chung, T.-S. (2014). High-performance sulfonated polyimide/polyimide/polyhedral oligosilsesquioxane hybrid membranes for ethanol dehydration applications. *Journal of Membrane Science*, *454*, 62–73.
- Lin, J., Chen, H., Fei, T., Liu, C., & Zhang, J. (2013). Highly transparent and thermally stable superhydrophobic coatings from the deposition of silica aerogels. *Applied Surface Science*, *273*, 776–786.
- Ma, J., Liu, B., Xu, Q., & Cui, F. (2005). AFM study of hippocampal cells cultured on silicon wafers with nano-scale surface topograph. *Colloids and Surfaces B: Biointerfaces*, *44*(2), 152–157.
- Marmur, A. (2004). The lotus effect: Superhydrophobicity and metastability. *Langmuir*, *20*(9), 3517–3519.
- Min, W.-L., Jiang, B., & Jiang, P. (2008). Bioinspired self-cleaning antireflection coatings. *Advanced Materials*, *20*(20), 3914–3918.
- Nakajima, A., Fujishima, A., Hashimoto, K., & Watanabe, T. (1999). Preparation of transparent superhydrophobic boehmite and silica films by sublimation of aluminum acetylacetonate. *Advanced Materials*, *11*(16), 1365–1368.
- Nishiguchi, M., & Tokuda, T. (1995). Aromatic polycarbonate copolymer, a process for producing the same, and a plastic optical waveguide using the same. U.S. Patent No. 5475786 A.
- Njuguna, J., & Pielichowski, K. (2003). Polymer nanocomposites for aerospace applications: Properties. *Advanced Engineering Materials*, *5*(11), 769–778.
- Schmidt, H. (1994). Multifunctional inorganic–organic composite sol–gel coatings for glass surfaces. *Journal of Non-Crystalline Solids*, *178*, 302–312.
- Schottner, G. (2001). Hybrid sol–gel-derived polymers: Applications of multifunctional materials. *Chemistry of Materials*, *13*(10), 3422–3435.
- Seitz, J., Vineberg, J. G., Zuniga, E. S., & Ojima, I. (2013). Fluorine-containing taxoid anticancer agents and their tumor-targeted drug delivery. *Journal of Fluorine Chemistry*, *152*, 157–165.
- Sun, T., Feng, L., Gao, X., & Jiang, L. (2005). Bioinspired surfaces with special wettability. *Accounts of Chemical Research*, *38*(8), 644–652.
- Tsuda, Y. (2013). Surface wettability controllable polyimides bearing long-chain alkyl groups by UV light irradiation. *Journal of Photopolymer Science and Technology*, *26*(3), 345–350.
- Wang, J., Sánchez-Rosello, M., Acaña, J. L., del Pozo, C., Sorochinsky, A. E., Fustero, S., et al. (2014). Fluorine in pharmaceutical industry: Fluorine-containing drugs introduced to the market in the last decade (2001–2011). *Chemical Reviews*, *114*(4), 2432–2506.
- Yang, S., Jin, X., Liu, K., & Jiang, L. (2013). Nanoparticles assembly-induced special wettability for bio-inspired materials. *Particuology*, *11*(4), 361–370.
- Zhang, L., Li, Y., Sun, J., & Shen, J. (2008). Mechanically stable antireflection and antifogging coatings fabricated by the layer-by-layer deposition process and postcalcination. *Langmuir*, *24*(19), 10851–10857.
- Zhao, B., Moore, J. S., & Beebe, D. J. (2001). Surface-directed liquid flow inside microchannels. *Science*, *291*(5506), 1023–1026.