J Mater Sci (2011) 46:2600–2605
DOI 10.1007/s10853-010-5112-1

Fabrication and characterization of superhydrophobic high opacity paper with titanium dioxide nanoparticles

Lianghui Huang · Kefu Chen · Chunxiang Lin · Rendang Yang · Rosario A. Gerhardt

Received: 6 October 2010 / Accepted: 23 November 2010 / Published online: 14 December 2010

Abstract A new type of paper with superhydrophobic surface was prepared by addition of modified nano-TiO_2 to cellulose pulp. Nano-TiO_2 powder was first dispersed with a high-speed homogenizer, followed by surface modification with the coupling agent, 3-(trimethoxysilyl) propyl methacrylate (MPS). The superhydrophobic and opaque paper was obtained by adding the modified nano-TiO_2 to plant fiber to change its characteristics from hydrophilic to hydrophobic. The effects of the initial content of the coupling agent MPS used, on the weight percentage of MPS attached on the surface of nano-TiO_2 were studied. The obtained paper was characterized by contact angle measurements and SEM. The results showed that the water contact angles for the modified paper ranged from 126.5 to 154.2°, and the sliding angle was <3°. Moreover, many well-dispersed nano-TiO_2 protuberances were observed on the surface of the paper, which further confirmed that the obtained paper was superhydrophobic on account of its nanostructure. Comparative optical studies performed on the paper handsheets revealed a much higher opacity for the sample with the MPS-modified-TiO_2 nanoparticles.

Introduction

Paper materials have been widely used in many fields due to the nontoxic, biodegradable, renewable, and also good mechanical properties of natural fibers. However, the high water and moisture absorption properties of cellulose fibers result in some deficiencies of paper materials when compared to plastics, metals, and other materials [1, 2]. Various methods have been used to fabricate high water resistant surfaces, such as plasma treatment [3, 4], desktop printing technology [5], and supercritical CO_2 [6], but these technologies would lower the efficiency if used in the paper industry. Existing high water resistant paper materials are normally prepared by coating [7, 8] them with wax [9], and other hydrophobic polymers [10]. A thick coating layer (>20 μm) is normally necessary to obtain the best results, while the cost is higher and results in poor paper recyclability [11].

Nano-TiO_2 can improve significantly the brightness and opacity of paper materials because of its high index of refraction compared to cellulose fibers or other fillers [12]. However, due to the extremely large surface-area/particle-size ratio, nanosized-TiO_2 pigments, when mechanically mixed with fibers, are poorly retained in the fiber materials [13]. In this article, we report on the preparation of a new type of paper with superhydrophobic and photocatalytic properties. MPS-modified-nano-TiO_2 particles were added to the pulp before the process of beating to inhibit agglomeration of TiO_2 on the surface of the fibers, and the obtained paper was characterized by contact angle measurements and SEM.

Experimental methods

Chemicals and materials

The coupling agent, 3-(trimethoxysilyl) propyl methacrylate (MPS) (98% purity, 1.040 g/mL) was purchased from

L. Huang · K. Chen · C. Lin · R. Yang
State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, China

L. Huang · R. A. Gerhardt (✉)
School of Materials Science and Engineering,
Georgia Institute of Technology, Atlanta, GA 30332, USA
e-mail: rosario.gerhardt@mse.gatech.edu

Nanjing Yudeheng Fin Chemical Co., Ltd. Titanium (IV) dioxide nanopowder (TiO_2) (99.9% of purity, with a median particle size from 10 to 20 nm, and specific surface area of 90 m^2/g) was received from Hangzhou Wan Jing New Material Co. Ltd. The fibers used in this work were in the form of board paper supplied by Sichuan Jinan Pulp mill. All chemicals and solvents were analytical grade and used as received and without further purification.

Characterization methods

FT-IR spectra were recorded on a Spectrum GX Infrared spectrophotometer (USA Perkin-Elmer Company) using KBr pellets. Scanning electron microscopy (SEM) images were obtained using a scanning electron microscope (Holland Philips Co.) at 25 kV. A Zetasizer Nano-ZS (USA Malvern) was used to determine the size of the TiO_2 particles and to measure their zeta potential in an aqueous medium. Contact angles (CA) were measured with a JC2000A static drop contact angle and interface tension measurement instrument (Shanghai Zhongchen Digital Technique Equipment Limited Company).

Surface modification of nano-TiO_2 with MPS coupling agent

Silane grafting reaction onto the surface of TiO_2 nanoparticles was carried out in ethanol as described by Rong et al. [14]. Titanium dioxide nanoparticles (5 g) were dispersed in 108 mL of ethanol, 2.83 g of water, and 1.52 g of ammonia (25 wt%) solution and various amounts of MPS were added. The mixture was strongly stirred at room temperature for 1 h. Then the solvent was distilled at ambient temperature under reduced pressure. The presence of the coupling agent MPS on the surface of oxide particles was confirmed by FT-IR spectroscopy, and the weight amount of MPS attached on the surface of TiO_2 was determined by elemental analysis. The dispersion was purified to render it free from MPS by using water or ammonia by centrifugation in absolute ethanol. The re-dispersion and centrifugation were repeated until no MPS could be detected by FT-IR in the ethanol solution after centrifugation. The product was freeze-dried for 24 h.

Zeta potential–pH curves were obtained to investigate the surface characteristics of the original TiO_2 and TiO_2 modified with MPS. Samples were prepared by mixing TiO_2 powder (0.02 g) and distilled water (200 mL), and the mixtures were ultrasonicated for 1 min. The pH value of the solution was adjusted to 2–12 by the addition of 0.1 mol/L NaOH solution and 0.1 mol/L HCl solutions.

Preparation of paper handsheets with MPS-modified-TiO_2 nanoparticles

Pulp mixtures containing MPS-modified-TiO_2 nanoparticles were prepared by adding the MPS-modified-TiO_2 nanoparticles to blank fiber in variable weight proportions, ranging from 3 to 17%. The pulp mixtures (containing MPS-modified-TiO_2 nanoparticles) were mechanically dispersed and mixed in distilled water in a laboratory disintegrator (30,000 rpm) and then diluted with water to about 0.3% solids content. Handsheets (60 g/m^2) were prepared by vacuum filtration in a laboratory sheet machine and dried in a hot press according to ISO standard 5269/1 and allowed to stabilize in a temperature and humidity controlled room (23 °C, 50% RH), before mechanical and optical testing. Tensile strength and opacity were determined in handsheets by ISO standards 1924/2 and 2471, respectively. Reference pulp mixtures were prepared by mixing blank fibers with unmodified TiO_2 at different contents. The morphological structures of the papers were examined by SEM.

The sessile drop method was used for water contact angle measurements at ambient temperature. Water droplets (about 5 μL) were dropped carefully onto the paper surface. The average WCA value was determined by measuring the same sample at five different positions. The advancing and receding contact angle were measured as follows: a 5 μL water droplet was placed on the sample using a syringe, and the advancing contact angle was recorded by increasing water volume to 8 μL with a speed of 0.3 μL/s, then the receding contact angle was recorded by decreasing the water volume at the same speed as that used for adding water. The sliding angle was measured by tilting the sample stage until the water droplet began to move in the downhill direction.

Results and discussion

Surface modification of nano-TiO_2 particles with MPS

It is known that nano-sized TiO_2 particles have a significant number of hydroxyl groups on their surface [15]. Silane coupling agents such as MPS that contain three inorganic reactive groups on silicon will bond well to the hydroxyl groups on most inorganic substrates such as TiO_2. This is the basis for modifying TiO_2 particles with MPS coupling agent. Bauer et al. [16] have previously described experimental conditions used to anchor MPS onto the surface of oxide particles. The reaction which occurs is depicted in Fig. 1. Methoxy groups of the MPS are hydrolyzed in the presence of base to give silanol groups. The reactive trisilanol groups formed can be absorbed

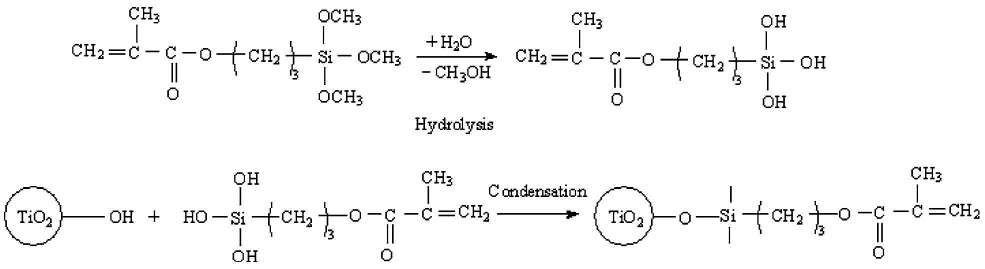

Fig. 1 Surface modification of nano-TiO_2 by the coupling molecule 3-(trimethoxysilyl) propyl methacrylate

rapidly through condensation with the hydroxyl groups present on the TiO_2 surface to form Ti–O–Si bond linkages. This reaction results in the chemically bonded MPS to the nano-TiO_2 particle surface.

The presence of the coupling agent MPS on the surface of TiO_2 particles was confirmed by FT-IR spectroscopy. Figure 2 shows the FT-IR spectra of pure MPS, unmodified TiO_2 and MPS-modified TiO_2. As shown in Fig. 2a, a strong absorption peak at 555 cm^{-1} attributed to Ti–O–Ti linkages in the unmodified TiO_2 nanoparticles is observed. The broad absorption peak at 3440 cm^{-1} [17] is due to the stretching vibrations of the –OH groups, while the peak at 1632 cm^{-1} [18] corresponds to C=O on the surface of the TiO_2 nanoparticles (Fig. 2a). For the MPS-modified TiO_2 (Fig. 2c), the peak at around 938 cm^{-1} [19] comes from the stretch vibration band of Ti–O–Si_{14}, which indicates that the condensation reaction between silanol groups and surface hydroxyl groups has occurred. The peak at around 1450 cm^{-1} [20] is attributed to the methylene C–H bending vibration of MPS (Fig. 2b), and the two well-resolved peaks which appear at around 1324 and 1300 cm^{-1}, as well as the peak at around 1169 cm^{-1} [21], are assigned to the –C–O– skeletal vibrations originating from the methacryloxy group of MPS (Fig. 2b). Moreover, the strong adsorption peak at 1717 cm^{-1} [22] is assigned to the stretching vibration of the C=O groups of the MPS (Fig. 2b).The peak of C=C at 1635 cm^{-1} [23] could not be detected separately, probably due to the overlapping with the strong peak of adsorbed water on the TiO_2 nanoparticles in the same frequency region. In addition, the broad band at around 1114 cm^{-1} [24], corresponding to the Si–O–Si bond, indicates the condensation reaction between silanol groups. From these spectra, it can be deduced that the MPS coupling agent has been grafted onto the surface of the TiO_2 nanoparticles through the formation of covalent bonds. The main IR vibration peaks for MPS-modified-TiO_2 compared to the unmodified TiO_2 are listed in Table 1.

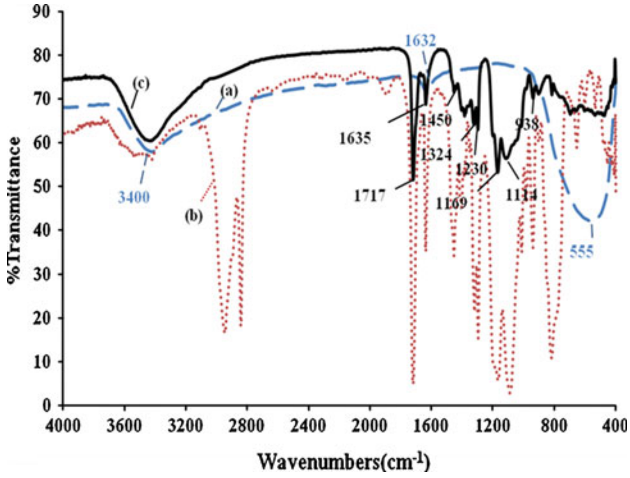

Fig. 2 FT-IR spectra of (*a*) unmodified TiO_2 nanoparticles, (*b*) MPS, and (*c*) MPS-modified TiO_2

The weight percentage of MPS ($wt\%_{(MPS)}$) grafted onto the surface of TiO_2 was determined by elemental analysis, and the wt% (MPS) and grafting efficiency (%) were calculated according to the following equations:

$$wt\%_{(MPS)} = \left(M_{MPS} \times wt\%(C)_{elemental\ analysis}\right)/(N_C \times M_C) \tag{1}$$

$$\text{Grafting efficiency }(\%) = m_{MPS\ grafted}/m_{MPS\ introduced} \times 100, \tag{2}$$

where M_{MPS} is the molecular weight of MPS, wt% (C) is the weight percentage of carbon, N_C is the number of carbon atoms in MPS, M_C is the atomic mass of carbon, $m_{MPS\ grafted}$ and $m_{MPS\ introduced}$ are the amounts of MPS used for grafting.

Figure 3 shows the results obtained from elemental analysis. The weight percentage of MPS attached onto the surface of TiO_2 seems to increase by increasing the initial content of MPS. A maximum weight percentage of 3.85% is obtained when the initial content of MPS was 80%, while

Table 1 FT-IR vibration peaks of regular and MPS-modified TiO_2

Peak (cm^{-1})	Band group	Peak (cm^{-1})	Band group
555	Ti–O–Ti	1324	–C–CO–O
938	Ti–O–Si14	1450	C–H
1114	Si–O–Si	1632	C=O
1717	C=O	1635	C=C
1169	–C–O–	3440	–OH
1300	–C–CO–O–		

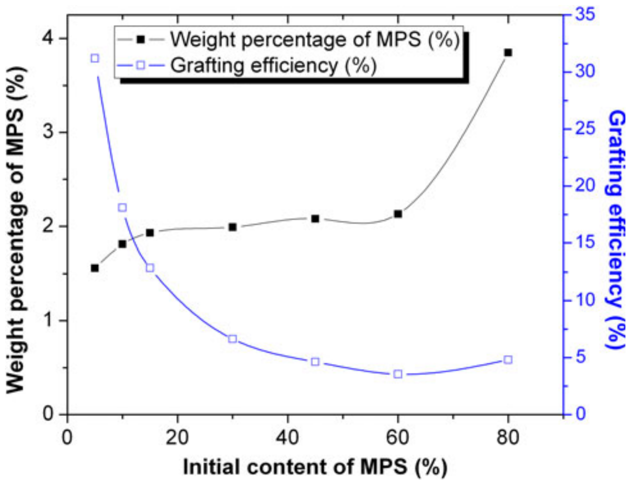

Fig. 3 Weight percentages of MPS (wt%, MPS) determined from elemental analysis of modified-TiO_2 nanoparticles

the values of the grafting efficiency are found to decrease with increasing MPS/TiO_2 ratio in the mixture.

Figure 4 shows the zeta potential–pH curve of original TiO_2 and samples modified with MPS. The isoelectric point (IEP) of the unmodified TiO_2 was about 6.3. After surface modification, the IEP of modified TiO_2 shifted to higher pH values. This indicates that the surface character of TiO_2 changed drastically after surface modification. The TiO_2 nanoparticles also disperse more evenly in water after surface modification.

Preparation of paper handsheets with MPS-modified-TiO_2 nanoparticles

Handsheets with different contents of MPS-modified-TiO_2 nanoparticles (containing a 1.93 wt% MPS) were prepared. Contact angle measurements were conducted to examine the surface wettability of the handsheets. Pure paper sheets can be completely wetted with water as indicated by the water contact angle WCA = 0°, which is common and well known for regular paper sheets. In addition, the paper treated with unmodified TiO_2 particles also presents good water absorption because of the hydrophilic property of TiO_2. In contrast, the samples treated with modified-TiO_2 nanoparticles were made highly hydrophobic, with a water static WCA larger than 120°. By the pretreatment with a higher content of modified-TiO_2 particles, the hydrophobicity is further enhanced, as shown in Fig. 5. The water static WCA range from 126.5° to 154.2° for a 5 µL droplet, and the obtained samples are completely water repellent. From Fig. 5, it can be observed that a maximum hydrophobicity is reached when the content of TiO_2 is 13%. When the content of TiO_2 nanoparticles was increased above 13%, the nano-TiO_2 agglomerated and the WCA decreased somewhat. Figure 6 shows the water contact angle of the handsheets with MPS-modified-TiO_2 nanoparticles containing 13 wt% MPS-modified TiO_2.

The measurement of advancing and receding CA was also attempted. The advancing and receding CA carried out for this same sample were found to be 153.5±0.8° and 157.7±1.3°, respectively. A water droplet was hardly able to stick to the modified surface, which moved around rapidly when it was slightly disturbed, and dripped off the substrate rapidly when the substrate was tilted <3°.

SEM pictures of handsheets shown in Fig. 7 illustrate that the uncoated paper sheet has a relatively smooth, continuous structure (Fig. 7a). After addition with modified TiO_2 in pulp (Fig. 7b), the particles cover the fiber surfaces uniformly, while in the case of the handsheets with a similar unmodified TiO_2 content (Fig. 7c) the pigment is mainly retained by the fibers as agglomerates on the fiber surfaces. As shown in Fig. 7b, the surface of the paper sheet exhibited a compact coating with a number of

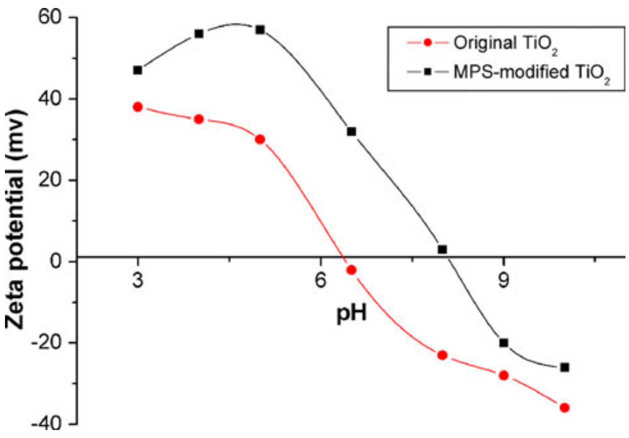

Fig. 4 Zeta potential of original and MPS-modified TiO_2

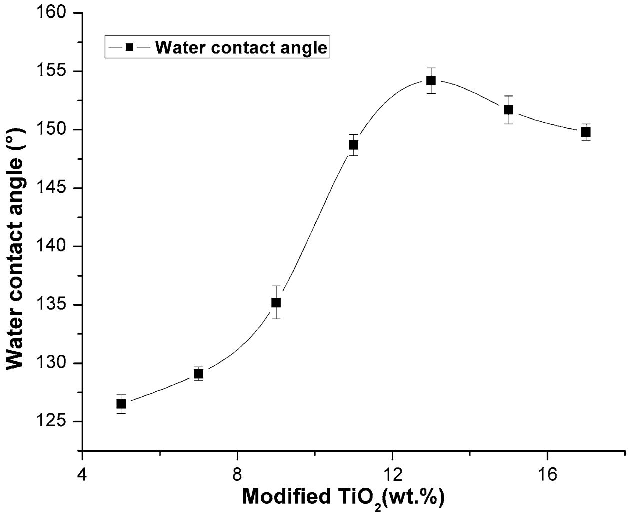

Fig. 5 Water contact angle on TiO_2-modified paper sheets

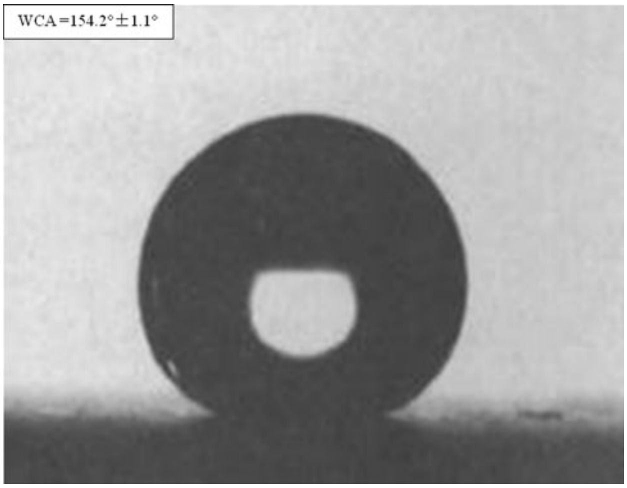

Fig. 6 Water contact angle photo of superhydrophobic paper

modified-TiO_2 particles, which made the surface rough, thus generating a dual-size surface structure on the fabrics.

The expected decrease in tensile strength with increasing TiO_2 content [12, 13] is more pronounced in the case of handsheets prepared with modified TiO_2 addition in pulp than with the mixture with unmodified TiO_2 (Fig. 8). This observation may be explained by larger fiber surface coverage with TiO_2 in the latter, thus hindering the interfibrillar hydrogen bonding in the sheet.

The opacity of the handsheets, increased from 78.2% in the case of blank fibers to 86.7% in handsheets prepared with modified TiO_2 addition in pulp (Fig. 9). When the unmodified TiO_2 was mechanically mixed with the fibers, this marked effect on the opacity of the corresponding handsheets was not apparent. The higher opacity observed for the chemically grafted samples may be due to the more uniform distribution of TiO_2 particles on the fiber surfaces, allowing a larger TiO_2 surface area available for light scattering and increased hydrophobicity (Fig. 10).

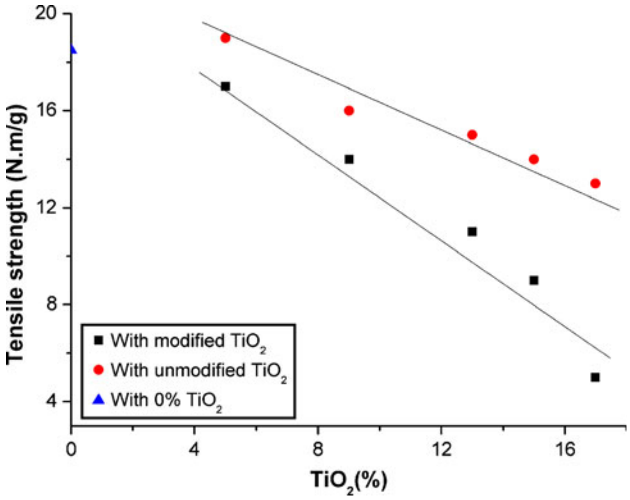

Fig. 8 Tensile strength of handsheets made with unmodified and modified TiO_2 as a function of TiO_2 % content

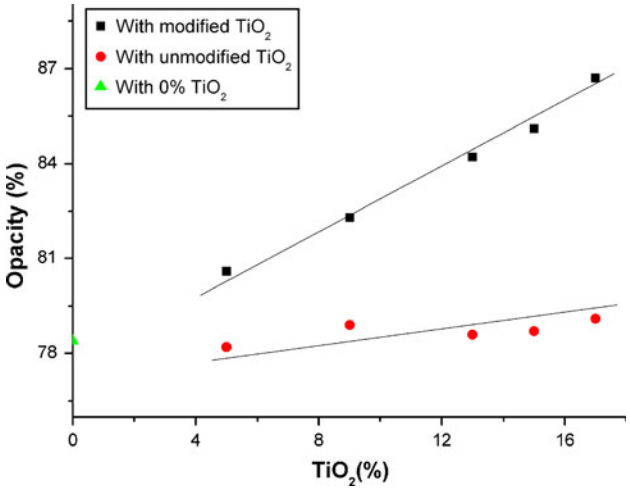

Fig. 9 Percentage of opacity of handsheets made with unmodified and modified TiO_2 as function of wt% TiO_2 added

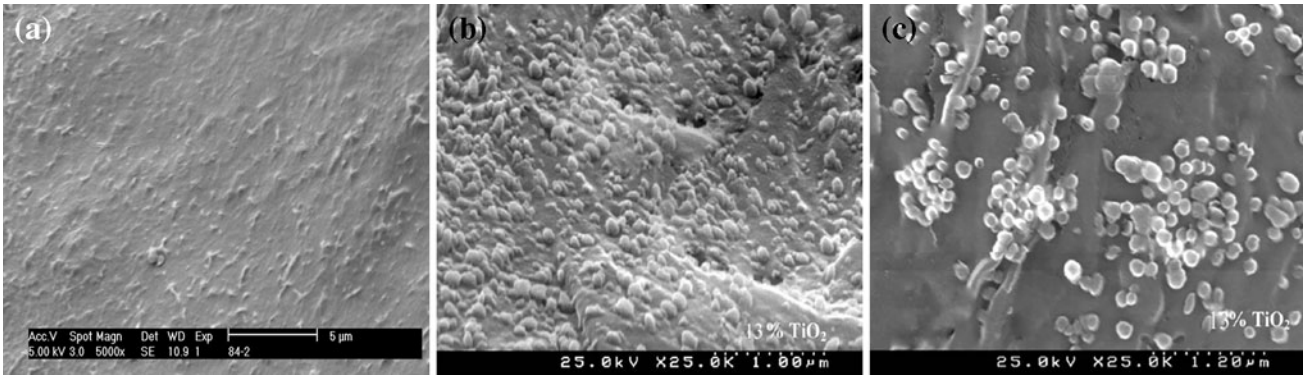

Fig. 7 SEM images of handsheets without (**a**) and with 13 wt% content of modified TiO_2 (**b**) compared with handsheets made with 13 wt% of unmodified TiO_2 (**c**)

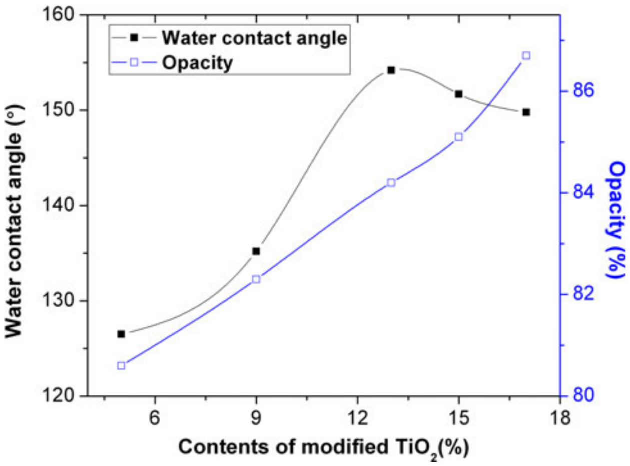

Fig. 10 The water contact angle and opacity of the paper surface change as a function of MPS-modified TiO_2 content

Conclusions

Paper handsheets with superhydrophobic and opacity properties were prepared by the addition of MPS-modified-TiO_2 nanoparticles to pulp before final paper fabrication. Nano-TiO_2 particles were first modified with MPS to impart them with hydrophobic properties and then added them to the pulp in the beating process before final paper fabrication. The obtained handsheets showed a slight decrease in tensile strength, while they had great hydrophobic properties and much higher opacity. These enhancements to the paper handsheet properties are ascribed to the uniform distribution of MPS-modified-TiO_2 nanoparticles on the fiber surfaces.

References

1. Sjostrom E (1993) Wood chemistry—fundamentals and applications. Academic Press, London
2. Klemm D, Heublein B, Fink HP, Bohn A (2005) Angew Chem Int Ed Engl 44:3358
3. Balu B, Kim JS, Breedveld V, Hess DW (2009) J Adhes Sci Technol 20:361
4. Balu B, Breedveld V, Hess DW (2008) Langmuir 24:4785
5. Balu B, Berry AD, Hess DW, Breedveld V (2009) Lab Chip 9:3066
6. Can Q, Werner O, Lars W, Charlotta T (2009) J Supercrit Fluid 49:117
7. Zou JH, Chen H, Anindarupa C, Yu Y, Huo Q, Lei Z (2008) Adv Mater 20:3337
8. Hu ZS, Zen XY, Gong J, Deng Y (2009) Colloid Surf A 351:65
9. Oskar W, Can Q, Charlotta T, Bert P, Lars W (2010) Cellulose 17:187
10. Bruzewicz DA, Meital R, George MW (2008) Anal Chem 80:3387
11. Yang H (2008) J Colloid Interf Sci 325:588
12. Roberts JC (1996) Paper chemistry, 2nd edn. Backi Academic and Professional, Glasgow
13. Neimo L (ed) (1999) Papermaking science technology: papermaking chemistry. Fapet Oy, Helsinki
14. Rong Y, Chen HZ, Wu G, Wang M (2005) Mater Chem Phys 91:370
15. Bedri E, Hunsicker RA, Simmons GW, Sudol ED, Dimonie VL, El-Aasser MS (2001) Langmuir 17:2269
16. Bauer F, Glasel HJ, Decker U, Ernst H, Freyer A, Hartmann E, Sauerland V, Mehnert R (2003) Prog Org Coat 47:147
17. Erhan S (2009) J Biomech 3:19
18. Tsafack MJ, Levalois-Grutzmacher J (2006) Surf Coat Technol 200:3503
19. Nitta SV, Pisupatti V, Jain A, Wayner PC Jr, Gill WN, Plawsky JL (1999) J Vac Sci Technol B 17(1):205
20. Antonow D, Graebin CS, Eifler-Lima VL (2004) J Braz Chem Soc 5:782
21. Matos MC, Ilharco LM, Almeida RM (1992) J Non-Cryst Solids 147:232
22. Guerra RM, Duran P, Ortiz (2008) J Oral Rehabil 23:632
23. Rueggeberg F, Hashinger DT, Fairhurst CW (1990) Dent Mater 6:241
24. Primeau N, Vautey C, Langlet M (1997) Thin Solid Films 310:47