Effect of Fiber Surface Morphology on the Hydrophilicity Modification of Cold Plasma-Treated Polypropylene Nonwoven Fabrics

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ABSTRACT: Cold oxygen plasma was employed to give hydrophilicity modification to polypropylene (PP) nonwoven fabric (NWF). It was found that, after plasma treatment, PP NWF made from fibers with smooth surfaces can only keep its hydrophilicity for a short time and then shows a quick hydrophobic recovery at room temperature. However, this hydrophilic property can last for a long time in the case of the PP NWF made from fibers with rough surfaces. To prove the contribution of the rough surface to the long-term hydrophilicity, this PP NWF was treated in an organic solvent to smooth the fiber surface. The hydrophilic feature of this PP NWF no longer lasts for a long time after the same plasma treatment. This observation strongly supports our opinion that the fiber surface morphology of PP NWF is a critical factor for long-term hydrophilicity improvement after plasma treatment, which gives a positive solution to overcoming the aging effect of hydrophilicity modification often found in this technique. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 2480–2486, 2010

Key words: plasma treatment; polypropylene nonwoven fabric; hydrophilicity modification; hydrophobic recovery; fiber surface morphology

INTRODUCTION

The interactions between inorganic gas plasma and a polymer surface can induce implantation reactions on the surface, which is an important and widely used surface modification process for polymer materials.[1–5] For instance, oxygen plasma treatment can implant oxygen atoms onto a polymer surface in the form of —C=O, —COOH, —OH, —C—O—C, etc.[6] These oxygen-containing functional groups can increase the surface energy of an inert polymer surface, which in turn effectively improves their surface hydrophilicity. However, an increase in surface energy leads to a thermodynamically unstable state of the modified surfaces, which have a strong tendency to recover their original state by lowering the surface energy. For a polymer material with a high glass transition temperature (T_g), such as polystyrene (T_g is around 100°C), the movements of its chain segments are frozen at room temperature so that its surface modification effect can retain for a long time.[7] However, for a polymer material with a low T_g, such as polypropylene (T_g is around −20°C), the movements of its chain segments are much easier at room temperature, which allows the segments with polar groups on the surface to move towards the bulk of the material.[8] By this way, the surface energy can effectively decrease and the improved hydrophilicity reduces at the same time. This is one of the widely accepted mechanisms for aging effect (or hydrophobic recovery) of plasma-treated surface over time.

The aging effect of plasma-treated polymer surface is a thermodynamically driven phenomenon.[9] It is an inherent feature of a material and mainly determined by its chemical composition. However, physical structures, such as woven structure and surface roughness, also play important roles in the materials' macroscopic behavior. Some articles have reported the influence of surface roughness on the hydrophilicity modification of polymer materials by plasma treatment.[9,10] But they were mainly substrates with flat surface. In this article, we report an interesting observation about how the fiber surface morphology of polypropylene nonwoven fabric (PP NWF) affects the lifetime of improved hydrophilicity after oxygen plasma treatment. Two PP NWFs with different fiber surface morphology and a flat surface PP film were chosen to be treated by oxygen plasma to illustrate this phenomenon.

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EXPERIMENTAL

Materials

Two melt-blown PP NWFs (PP1: 83 g/m^2, 0.37 mm in thickness, provided by Beijing Yanshan Petrochemical Company, China; PP2: 37 g/m^2, 0.24 mm in thickness, provided by Europlasma, Belgium) and one PP film (0.93 g/cm^3, 0.03 mm in thickness, provided by Beijing Yanshan Petrochemical Company, China) were treated as received. Oxygen ($\geq$99.99%) and decilin (98%) were used as plasma gas and solvent, respectively.

Plasma treatment

Plasma treatments were carried out inside a chamber plasma machine (CD 1200, Europlasma, Belgium) at a working pressure of around 15 Pa. The oxygen plasma was generated at a radio frequency of 40KHz. During all the treatments, the gas flow rate was fixed at 400 cm^3/min, treatment power changed from 200W to 600W and treatment time varied from 1 minute to 8 min. A series of plasma treatments were given to PP films to obtain an optimum condition for PP NWF hydrophilicity modification. After plasma treatment, all the samples were exposed to the air and stored at room temperature.

Contact angle measurement

Contact angle (CA) of plasma-treated PP film was measured at room temperature with triple distilled water for hydrophilicity evaluation by using a contact angle meter (JC98A, Shanghai Zhongchen Economic Developing Co., China). Each water contact angle (WCA) result reported in this article was the average of six different measurements.

Wettability evaluation of PP NWF

The spreading and penetration of the water droplet on the PP NWF was observed to evaluate its wettability or the effect of hydrophilicity modification. During the experiment, the status of five red water droplets (5 μL) on the PP NWF surface was recorded within 10 s by a digital camera (Cyber-shot, CCD 2.1/5, Sony, Japan).

Surface element analysis

The surface chemical composition was analyzed by Mg Kα X-ray photoelectron spectroscopy (XPS) (PHI 5100 ESCA, Perkin–Elmer) with energy source of 1253.6 eV and X-ray source power at 240W. The analysis chamber pressure was maintained at 5×10^{-6} Pa.

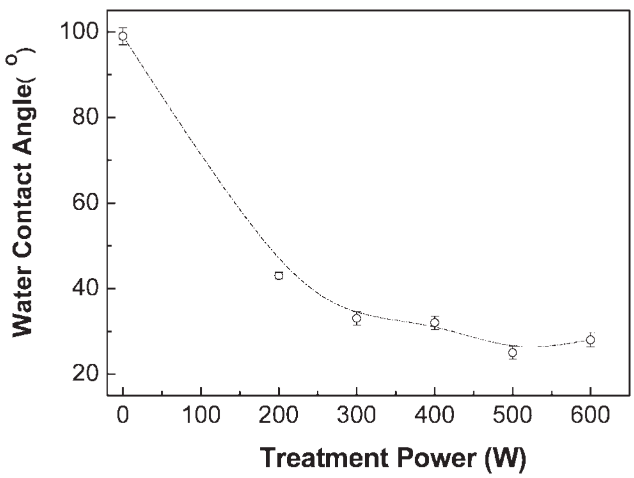


Figure 1 Effect of treatment power on the WCA of PP film (treated for 4 min).

Surface morphology observation of PP NWF

The woven structure and fiber surface morphology of two PP NWFs were observed under scanning electron microscopy (SEM) (JSM-6360, JEOL, Japan) under different amplifications. Before observation, the sample was coated with gold in a sputter coating system (Polaron Equipment, British) for 2 min at 1.4KV and 20mA.

RESULTS AND DISCUSSION

Hydrophilicity modification of PP film

A PP NWF consists of a great amount of fibers disorderly gathered together, which also forms spacing between fibers. The uneven surface of PP NWF makes it impossible to measure the contact angle accurately. Therefore, a PP film with a flat surface was treated first to obtain an optimum treatment condition.

First of all, the PP film was treated by varying treatment powers at a fixed treatment time. As shown in Figure 1, the WCA of PP film decreased rapidly from 99° to 43° when treated at 200W for 4 min. Further increase in treatment power could not give a great decrease in contact angle anymore. A contact angle of 28° was achieved while treated at a power of 600W.

Secondly, the PP film was treated for a different period of time at 600W as seen in Figure 2. Similar to the effect of treatment power, WCA decreased rapidly at first and then leveled off by increasing the treatment time from 1 to 6 min. A contact angle of 13° was found after a treatment for 8 minutes.

From the above studies, an optimum treatment condition for hydrophilicity modification of PP film was obtained. In other words, a treatment power of

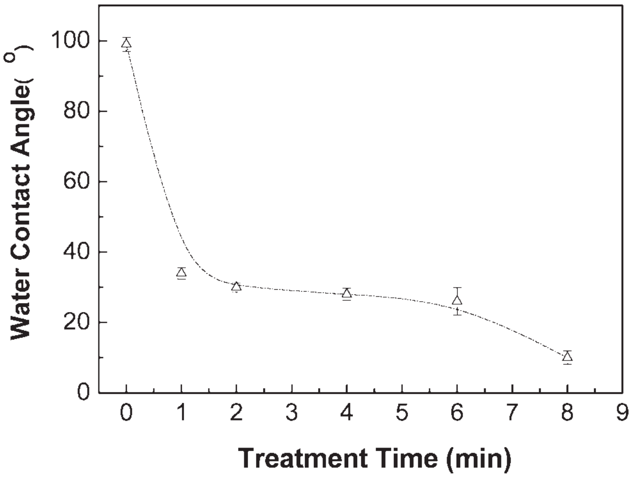


Figure 2 Effect of treatment time on the WCA of PP film (treated at 600W).

600W and treatment time of 8 min at a gas flow rate of 400 cm^3/min were selected as optimum plasma treatment parameters for PP NWF treatment.

Hydrophilicity modification of PP NWF

Under the optimum condition obtained in the previous section, two PP NWFs, PP1 and PP2, were treated by oxygen plasma, respectively. A series of pictures showing the wettability of untreated PP1 and PP2 as well as treated PP1 and PP2 over time were collected in Table I for comparison. The WCAs of PP film with the same plasma treatment and storage history were also listed in the table.

It was clear that, without plasma treatment, water formed droplets and cannot penetrate into PP NWF at all since they were originally hydrophobic. Within 5 min after plasma treatment, both PP1 and PP2 can absorb water droplets completely at once. This can be explained by the low WCA (13°) obtained by the PP film with the same plasma treatment. In other words, these two PP NWFs become very hydrophilic after plasma treatment. However, this improved hydrophilicity of PP1 can not last for a long period of time at room temperature. Twelve days after treatment, water could not penetrate into PP1 any more but formed droplets again on the PP1 surface.

TABLE I
Wettability Comparison During Storage of Two PP NWFs with the Same Plasma Treatment

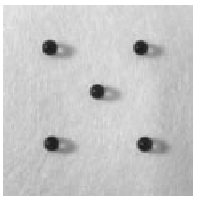
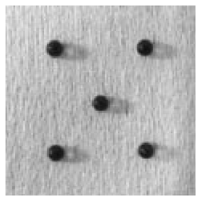
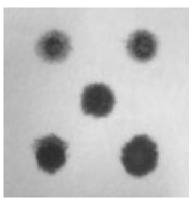
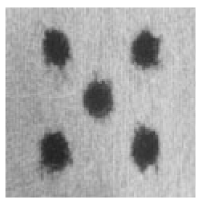
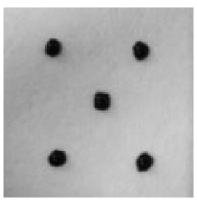
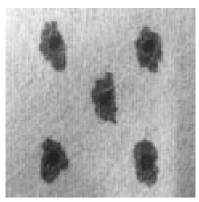
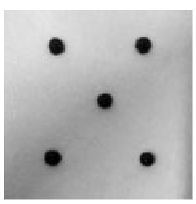
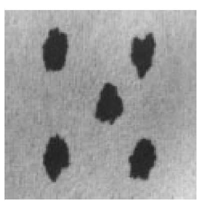
	PP1	PP2	PP film (WCA)
Untreated			(99 ± 1)°
Within 5 min after treatment			(13 ± 2)°
12 days after treatment			(57 ± 1)°
30 days after treatment			(71 ± 1) °

TABLE II
Surface Element Ratio of C1s, N1s and O1s on PP Film, PP1 and PP2 Nonwoven Fabric Before and After Plasma Treatment

	Untreated			2 days after treatment			22 days after treatment		
	C1s	N1s	O1s	C1s	N1s	O1s	C1s	N1s	O1s
PP film	99.47	0.28	0.25	70.14	0.34	29.52	72.85	0.12	27.03
PP1	98.88	0.20	0.91	73.15	0	26.85	65.46	1.59	32.94
PP2	95.71	0	4.29	74.2	1.10	24.70	74.52	1.66	23.82

While the situation was completely different for PP2. It was found that PP2 retained its hydrophilic feature even 30 days after treatment. Actually, the WCA of the corresponding PP film had already increased to around 71°, which is much close to the general WCA bottom limit (90°) of a hydrophobic material.

Surface chemical composition on the PP film and PP NWFs were analyzed by XPS. Limited to the experimental condition, XPS analysis cannot impart to the samples right after plasma treatment. Data collected 2 days and 22 days after plasma treatment were listed in Table II. First of all, it was found that the change in surface chemical composition was independent on the sample's physical structure. In other words, there is no difference between film and nonwoven samples. Secondly, in comparison to untreated PP samples, a pronounce increase in ratio of oxygen atom but trivial change in ratio of nitrogen atom was detected in all plasma-treated samples. There is a general idea that newly formed oxygen-containing groups on the sample surface contribute to the improved hydrophilicity.[11] The improved hydrophilicity observed in this work and XPS analyzes are consistent with this idea. Actually, a higher O/C ratio on the sample surface contributing the low WCA of PP film right after plasma treatment was expected. Since hydrophobic recovery was very fast at the early stage and then leveled off, the O/C ratio at the early stage cannot be obtained if the analysis performed several days later. While, the remained oxygen atoms on the treated samples after 2 days and even 22 days could help explain why the WCA of treated PP film cannot fully recover to its original value over time and, meanwhile, contribute to the residual hydrophilicity.

Based on the above-mentioned observation, a further discussion about how the microscopic surface morphology of composed fiber plays an important role in the lifetime of the improved hydrophilicity of PP NWFs was given after SEM analysis. SEM pictures in Figure 3 give us a clue about the reason why these two plasma-treated PP NWFs behaved so differently in wettability over time. From Figure 3(a,b) (×500), it shows that the average diameter of composed fiber and spacing between fibers in these two PP NWFs are very close to each other. In other words, they have a very similar physical structure at this scale level. If we look at a single fiber at a much higher amplification (×6500), the difference between these two PP NWFs is much clearer. The fiber in PP1 has a smooth surface as seen in Figure 3(c). However, the fiber surface of PP2 has many fine concaves and convexes at a scale less than 10 μm as shown in Figure 3(d). It was our opinion that the different fiber surface morphology of these two PP NWFs at a microscopic level could be the critical factor causing such a big difference in the lifetime of their improved hydrophilicity.

It is known that surface roughness of a material could affect its wettability, which was theoretically explained by Wenzel's formula about 60 years ago,[12]

$$\mathrm{Cos}\theta_r = r\,Cos\theta$$

where r refers to roughness ratio, i.e. the ratio of actual solid–liquid contact area to apparent solid–liquid contact area ($r \geq 1$). θ_r and θ are actual contact angle of rough surface and apparent contact angle of corresponding flat surface, respectively. From the formula, it is clear that if a material with flat surface is inherently hydrophobic (contact angle is greater than 90°), a rough surface will make the material more hydrophobic as seen in Figure 4(a); if a material with flat surface is inherently hydrophilic (contact angle is less than 90°), a rough surface will make the material more hydrophilic (seen Figure 4b). Here, 90° is the generally accepted WCA limit to classify the hydrophilic and hydrophobic materials.

Actually, in our experience, a flat surface sample behaves more like a hydrophobic material if its WCA is around 60°. Some researchers had claimed that a new WCA limit between hydrophilic and hydrophobic materials should be around 65°.[13] Our observation matched the above-mentioned study to some extent. In our case, PP film and PP NWF can be regarded as a material with flat and rough surface, respectively. From SEM pictures in Figure 3(a,b), we know that PP1 and PP2 generally have a similar physical structure at a scale level of 20–100 μm, which determined that they have the similar surface roughness at this scale level. Before plasma treatment, the surface roughness of the two PP

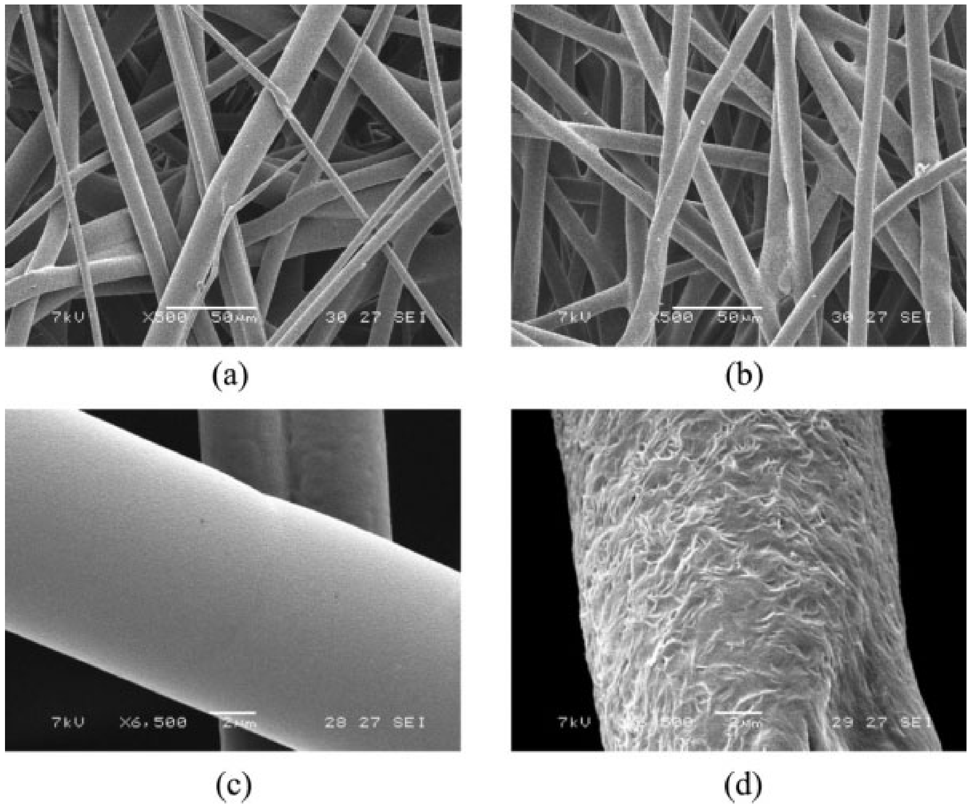


Figure 3 Physical structure and fiber surface morphology of PP1 and PP2 observed by SEM.

NWFs enhances their repellency to water so that water cannot penetrate at all. After plasma treatment, PP films became hydrophilic (with WCA of 13°) and the surface roughness made the two PP NWFs more hydrophilic. However, it was found that this modified hydrophilicity cannot last more than 12 days in the case of PP1 but retained quite well even after 30 days in the case of PP2.

In fact, the surface energy of all the PP samples decreased with increasing of storage time, which was indicated by the increased WCA of PP film. Having the same hydrophobic recovery history, PP1

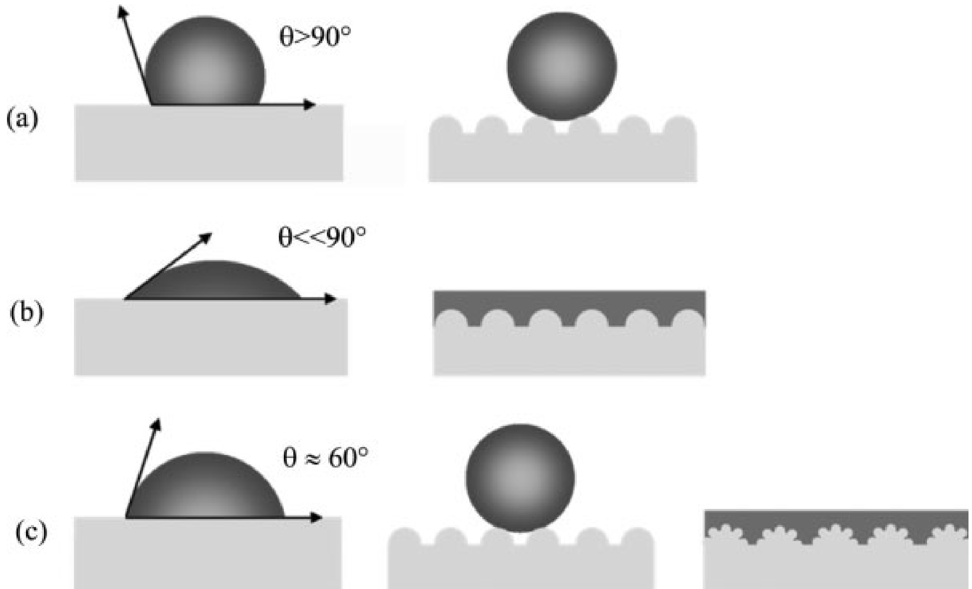
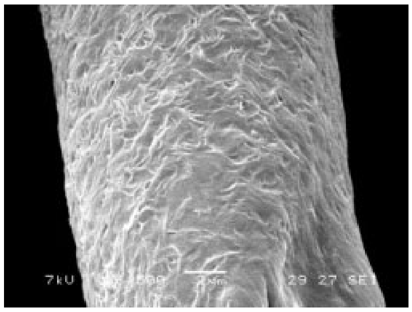
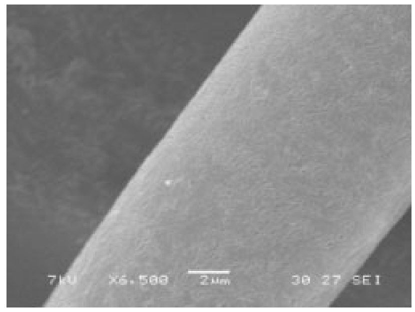
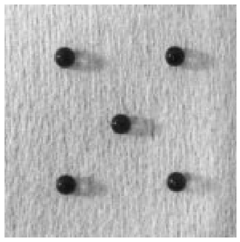
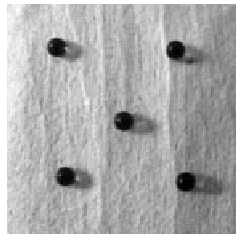
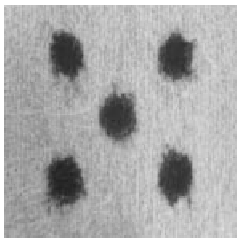
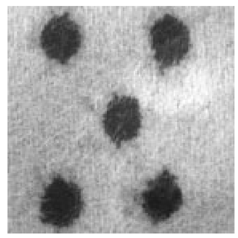
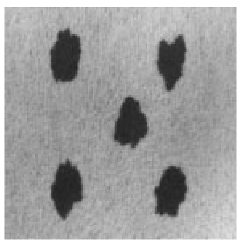
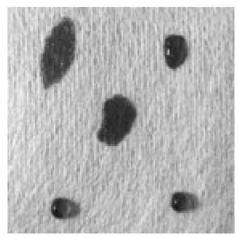


Figure 4 The effect of surface roughness at different scale levels on the wettability: (a) hydrophobic materials with flat and rough surface; (b) hydrophilic materials with flat and rough surface; (c) almost hydrophobic materials with flat surface and rough structure at different scale levels.

TABLE III
The Effect of Fiber Surface Morphology on the Lifetime of Improved Hydrophilicity of PP2

	Untreated	Immersed in decalin for 24 days
SEM pictures		
Before plasma treatment		
Within 5 min after plasma treatment		
30 days after plasma treatment		

show obvious hydrophobic recovery but PP2 retained its wettability. Based on the fiber surface morphology observed by SEM, a schematic picture of PP1 and PP2 was proposed in Figure 4(c) to explain this unique phenomenon. It was thought that the surface roughness at a larger scale level can only help a hydrophilic material behave more hydrophilic, or conversely make an almost hydrophobic material more hydrophobic. But if an almost hydrophobic material contains rough structure at an even smaller scale, like fine concaves and convexes on the PP2 fiber surface, the residual hydrophilicity can be enhanced and the material macroscopically still behaves like a hydrophilic one. It is also obvious that the fine concaves and convexes on the PP2 fiber surface greatly increased the contact area of PP2 NWF with water.

To prove this opinion, a dissolving treatment was imparted to PP2. In the process, PP2 was immersed in decalin at room temperature to smooth the rough fiber surface of PP2. The fiber surface morphology was followed by SEM until it became almost smooth. The sample was then taken out of decalin, washed by acetone to remove residual solvent and dried at room temperature. The solvent-treated PP2 was then treated by oxygen plasma under the optimum condition. It was found that this PP2 cannot absorb water droplets completely anymore 30 days after plasma treatment as shown in Table III. In fact, without a rough surface, solvent-treated PP2 has the similar roughness at both larger and smaller scale to PP1. Therefore, this PP2 show the similar hydrophobic recovery with PP1 over time. This experiment result strongly supported our opinion that fiber surface morphology of PP NWF is the key factor for the lifetime of its improved wettability, which gives a positive solution to overcome the aging effect of hydrophilicity modification by plasma treatment.

In addition, it is worthy to point out that the fine rough fiber surface in PP2 cannot prevent the inherently hydrophobic recovery of the material. Hydrophobic recovery is a thermodynamically driven process, which is inevitable. The difference in retention of wettability between plasma-treated PP1 and PP2 at room temperature over time is mainly caused by their physical structure differences at a microscopic level.

CONCLUSION

Cold oxygen plasma can effectively improve hydrophilicity of originally hydrophobic polypropylene materials. It was found that the fiber surface morphology greatly affect the lifetime of improved wettability of PP NWF. PP1 composed of fibers with smooth surfaces cannot keep its wettability for more than 12 days; while PP2 composed of fibers with fine rough surfaces can keep its wettability for more than 30 days. The interesting phenomenon disclosed in this article could give a positive solution to overcome the aging effect normally shown in polymer materials after hydrophilicity modification by plasma treatment.

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