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Note

Preparation of Phytoncide-Emitting Nylon/PP Sheath/Core Fiber and the Release Profile of Phytoncide

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Abstract: Phytoncide, a volatile essential oil produced by plants and trees, has not only anti-microbial activity, but also a stress relieving effect. We prepared a sheath/core type melt-spun fiber that releases phytoncide for a prolonged time. The fiber is comprised of a nylon sheath and a polypropylene (PP) core material. Phytoncide-containing microcapsules are embedded within the core part. The phytoncide microcapsule-containing nylon/PP sheath/core (M-Ny/PP) fiber has suitable mechanical properties for textile application. The phytoncide release from the microcapsule-containing the PP fiber (M-PP) reached a plateau level after 4 days and maintained that level for an additional 7 days, indicating a zero-order release after the initial burst. The M-Ny/PP fiber emitted the volatile phytoncide even though the fiber was spun at 250 ^{o}C. The release of phytoncide decreased in the M-Ny/PP fiber compared to the phytoncide microcapsule-containing PP (M-PP) fiber due to the dense sheath layer.

Keywords: Phytoncide, Sustained release, Microcapsule, Sheath-core Fiber, Health-care

Introduction

In Asia, people visit the forest to rest and refresh themselves by breathing the fresh forest air. This activity is called “forest bathing” or “Sam-rim-yok” in Korean and “Shin-rin-yoku” in Japanese. It has been reported that people not only experience vigor and relief from anxiety, but they also experience relief from depression and anger after forest bathing [1]. It is believed that the phytoncide released from the trees has a positive effect on human health. Phytoncides are volatile essential oils emitted from various trees and plants and that act to protect the trees and plants against harmful micro-organisms, insects, and animals. There are some reports on the physiological effects of phytoncides, such as stress relief [2], skin whitening [3], and anti-oxidant and anti-microbial effects [4]. Many commercial products that release phytoncide are now available on the market.

Health-care textiles are a new trend in the textile industry. Different functionalities can be incorporated into textiles such as insect repelling, temperature regulating, anti-microbial, and aromatic actions. Usually the ingredients responsible for these effects are added during the finishing process by simply dipping the fabrics into solutions containing the active ingredients [5]. However, the active ingredients dissipate or are washed out during storage or laundering. Currently, the encapsulation of active ingredients has been suggested to prolong the service of such textiles. Active ingredients have been encapsulated into nano- or micro-capsules, which were then attached to the textile using various binders [6-8]. The prolonged release of active ingredients was achieved but the capsules were prone to friction. Although rupture of the nano- or micro-capsules is one of the release mechanisms of active ingredients, once these capsules are destroyed, they are no longer effective. In addition, detachment of nano- or micro-capsules could be also occurred via friction. Using a stronger adhesive might be useful to solve this problem but such a solution usually hardens the fabric.

A sheath/core type fiber has been developed in order to compensate for the properties of two different polymers. Generally, polymers of high cost or low strength are uses to form the sheath part, while a polymer of low cost or high strength forms the core part. Mitsubishi Rayon has introduced a novel sheath/core type acrylic fiber, COREBRID® [9]. The sheath part is made of an acrylic polymer, but the core part is filled with microparticles. Conventionally, microparticles are embedded in a single fiber matrix by simple mixing the microparticles with the dope solution before spinning. However, the spinnability decreases because the microparticles may clog the spinneret. Lowering the microparticle content might solve this problem but the intended functionality may not be achieved. The company solved this problem using a bicomponent spinning technique. The microparticles are extruded in the core of the fiber, thereby confining their spatial position to the center of the fiber. As a result, increased spinnability and conserved functionality were achieved. Another benefit is that there is a greater prolonged

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functionality than could be expected when comparing to fibers in which the microparticles were attached on the surface, because the microparticles in the core are protected against friction by the sheath layer.

In this study, we report the sustained release of phytoncide from a sheath/core fiber. Although COREBRID® is a wet-spun fiber, we adopted the same concept used in its manufacture into a melt-spun fiber with some modification. To the best of our knowledge, this is the first report of a volatile substance being incorporated within a nylon fiber.

Materials and Methods

Materials

Heat-resistant phytoncide microcapsules (3.6 μm) were kindly provided by Polychrom, Co., Ltd. (Ansan, Korea). PP (Melt Index, MI 18) was purchased from Honam Petrochemical Co. (Yeosu, Korea). The nylon (Relative Viscosity, RV 2.6) was provided from Hyosung Cooperation (Anyang, Korea).

Preparation of Sheath/core Fiber

Figure 1 shows the overall process for the preparation of the M-Ny/PP fiber. We used a bicomponent spinneret where PP and phytoncide microcapsule were extruded through the core part, and nylon was extruded through the sheath part. The PP and microcapsule are compounded into a master chip before spinning. The spinning temperature was about 250 °C. The M-PP fiber was spun using the general melting spinning process. The content of phytoncide microcapsules was about 2 % for the M-PP fiber and 1 % for the M-Ny/PP fiber.

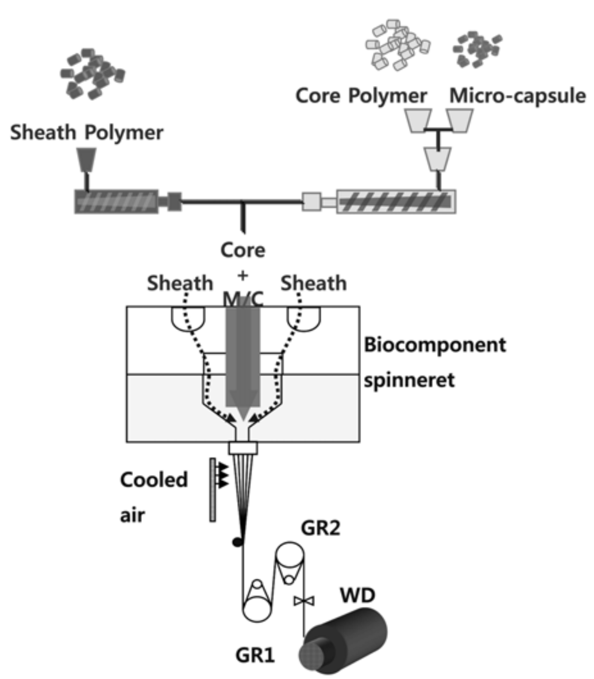

Figure 1. Overall spinning process of the M-Ny/PP fiber.

Quantification of Released Phytoncide

The released amount of phytoncide was measured with gas chromatography after collecting the phytoncide released from the fibers. Fibers were placed in a 20 *l* chamber where the temperature and relative humidity were controlled at 25 °C and 50 %, respectively. The air in the chamber flowed continuously during the measurement, and the flow rate corresponded to one complete ventilation cycle every 2 hours, which is a typical experimental condition for measuring VOC from construction material. It simulates the ventilation condition in normal houses. The sample air (3.2 *l*) was collected at predetermined intervals and injected into the GC for analysis.

Results and Discussion

Preparation of Phytoncide-Emitting Sheath/Core Fibers

Phytoncide, a complex compound composed of various volatile chemicals, has a boiling point far below than the spinning temperature of melt spun fibers [10]. Therefore, the spinning temperature should be as low as possible in order to prevent loss of the volatile compound during the spinning process. Fragrances have previously been incorporated into melt-spun fiber, but polymers with relative low spinning temperature, such as PP and PLA, were chosen [11].

However, PP and PLA fibers have limited usage in the textile industry. More versatile fibers are PET and nylon. The problem is that these fibers are spun at very high temperature typically above 250 °C. Therefore, volatile chemicals will be lost by evaporation or decomposition during the spinning process. In this study, we used two strategies to prevent the loss of phytoncide during the spinning process. First, we used micro-encapsulated phytoncide. Encapsulation of functional substances is not a new concept in the textile industry; various functional materials such as fragrance, phase change materials (PCM) have been encapsulated and attached onto fibers during the finishing process or mixed with the polymer before spinning [6-8,12,13]. The encapsulated functional material is protected against pre-mature loss and spatially confined by the capsule wall. Here, we used a heat-resistant microcapsule in which the capsule wall may protect the volatile chemicals of phytoncide from heat or at least hinder the release of gaseous materials during the spinning process. In addition, prolonged release is expected after the fiber is prepared. Second, we used bicomponent spinning technology. Even though the phytoncide is encapsulated by the capsule wall, heat transfer through the fiber would be fast due to the small diameter. As mentioned in the Introduction, bicomponent spinning allows us to simultaneously use two different types of polymer. Here, we used PP for the core part and nylon for the sheath part. The PP can act as a second protective layer for the phytoncide next to the capsule wall. In addition, PP has relatively lower melting point which prevents pre-mature loss of phytoncide

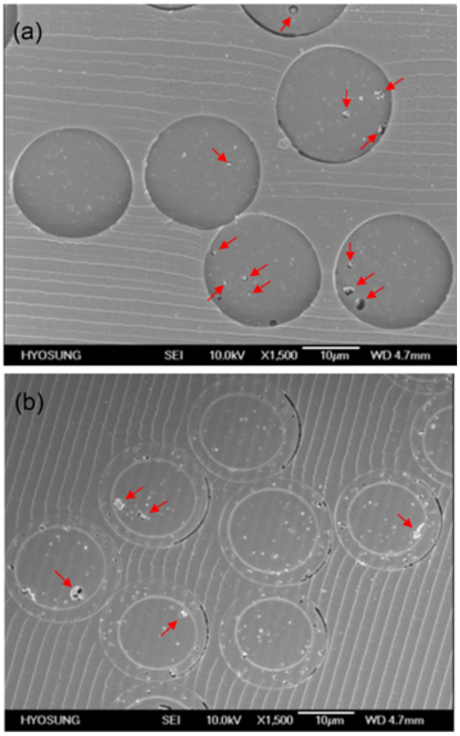

Figure 2. SEM image of the cross-sections of M-PP (a) and M-Ny/PP (b) fiber.

Table 1. Physical properties of M-PP and M-Ny/PP fibers

Sample	Fineness (tex)	Tensile strength (g/d)	Elongation (%)
PP	7.78	3.8	128
M-PP	7.56	3.3	120
M-Ny/PP	6.81	3.2	32

during the master chip preparation. The sheath part can reduce the mass transfer of volatile compounds during the spinning process, because the nylon has a higher density than PP.

First, we examined whether the microcapsules could be embedded into the PP fiber. Figure 2(a) shows the cross-section of the M-PP fiber. As shown with arrows, the microparticles were successfully embedded into the PP fiber. The tensile strength of the microcapsule-containing fiber was sufficient compared to the PP fiber without the microcapsule and the maximum elongation reached 120 % (Table 1). We were initially concerned about the mechanical property of the fiber since the microcapsules may act as a defect. This was the reason why we only added 2 wt-% microcapsules. The result shows that this amount of microcapsule would not cause serious problems for use in textiles. However, the M-PP fiber was too stretchable to be used for knitting.

Figure 2(b) shows the SEM image of the cross-section of the M-Ny/PP fiber. The microcapsules can be observed within the core (arrows), indicating their successful incorporation. The mechanical properties of the M-Ny/PP fiber were within a typical range of general nylon, indicating that the sheath part governs the overall properties (Table 1). In addition, the M-Ny/PP fibers could be successfully knitted into fabric.

Sustained Release of Phytoncide

As mentioned before, phytoncide is a complex compound composed of various chemicals. When the phytoncide is subjected to GC analysis, innumerous peaks are generated, as shown in Figure 3(a). However, once they are passed through the spinneret, only three major peaks were found (Figure 3(b)). These were identified as tridecane, bornyl acetate and tetradecane in the order of elution time. The other chemicals are likely evaporated or decomposed during the spinning process. The boiling points of three substances are 232-236 ^{o}C, 226-231 ^{o}C and 252-254 ^{o}C, respectively, while those of other components in the phytoncide are below 200 ^{o}C.

We used bornyl acetate as a reference substance for detecting phytoncide at it is found in many essential oils of trees. The compound has a pine-like odor and is approved by

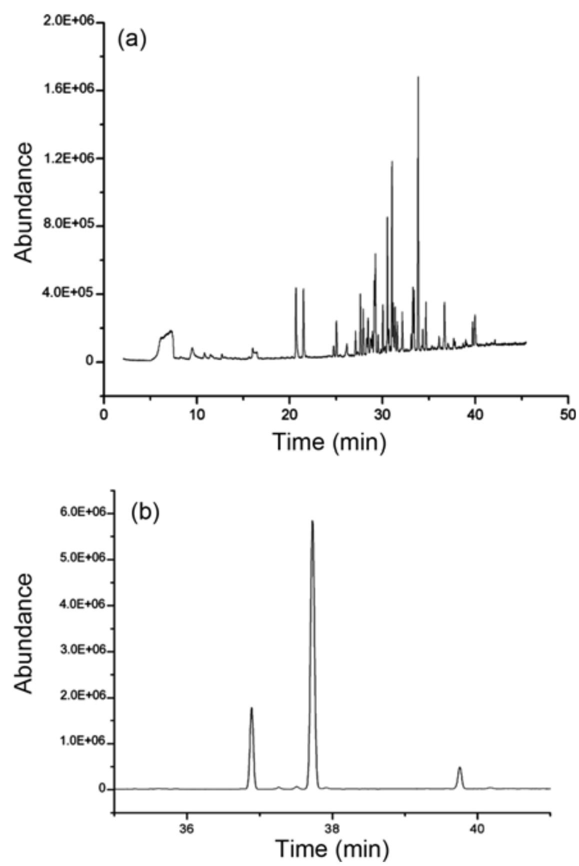

Figure 3. Typical GC analysis results of phytoncide (a) and phytoncide released from M-Ny/PP fiber (b).

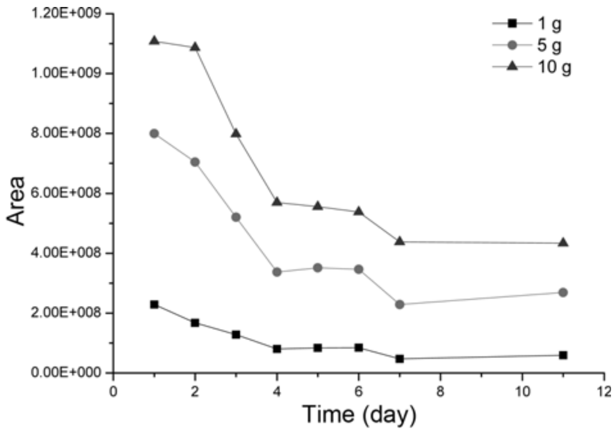

Figure 4. Release profile of bornyl acetate from different weight of M-PP fiber.

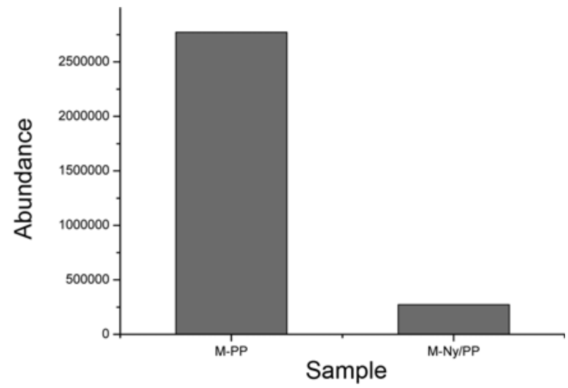

Figure 5. Released bornyl acetate from M-PP and M-Ny/PP fibers after 4 days of incubation in a 20 *l* chamber.

the FDA as a food additive. There are several reports on the anti-microbial activities of plant essential oils, of which bornyl acetate is one of the major components [14,15].

Figure 4 shows the amount of released bornyl acetate from M-PP fiber during the testing period. The released amount of bornyl acetate decreased with time and increased with the loading amount of fiber. When 10 g of sample were placed in the chamber, there was no decrease of released bornyl acetate until two days, indicating the emitted bornyl acetate is sufficient to saturate the chamber. During the first four days, the release of bornyl acetate decreased significantly. However, after four days of testing, the released amount of bornyl acetate reached a plateau, where it remained until the last days of observation. The release profile of bornyl acetate showed an initial burst at the early stage and was followed by a zero-order release. The initial burst might be due to the rupture or decomposition of some microcapsules during the spinning process. Thereby, a large amount of phytoncide is dispersed freely in the fiber matrix rather than remaining in the microcapsule. The zero-order release might be achieved by the release of the bornyl acetate that remained in the microcapsule.

Figure 5 shows the emitted bornyl acetate from 1 g of M-Ny/PP fiber. Although a zero-order release was observed, the amount of emitted bornyl acetate from the M-Ny/PP fiber was significantly reduced compared to the M-PP fiber. However, it should be noted that only half of the microcapsules were embedded in the M-Ny/PP fiber compared to the M-PP fiber. We reduced the amount of loaded microcapsules due to concern of breakage during the spinning process. In addition, the spinning temperature of the M-Ny/PP fiber was much higher than that of the M-PP fiber. Therefore, the M-Ny/PP fiber was subjected to more severe conditions. Nevertheless, it is clear that the presence of the nylon sheath layer reduces the emitted amount of bornyl acetate due to its high density. However, phytoncide is still released from the M-Ny/PP fiber; thus, sustained release of phytoncide from the fiber is achieved even after being subjected to harsh spinning condition.

Conclusion

Here, we report the first melt spun nylon/PP sheath/core fiber emitting a volatile compound, phytoncide. The first and the largest barrier was whether the volatile phytoncide would withstand high spinning temperature. We overcame this problem by two strategies: using encapsulated phytoncide and adopting bicomponent spinning technology. Phytoncide was released from the sheath/core fiber even though it was subjected to high spinning temperature. The mechanical property was also sufficient for textile application. However, there are additional factors that must be improved. Some loss of chemicals occurs during the spinning process, and the released amount of phytoncide is not sufficient, yet. The intensity of the fragrance of M-PP fiber is strong but that of the M-Ny/PP fiber is too weak. However it could be overcome in the future by using a more heat-stable microcapsule and a creating micro-slit in the sheath layer of the fiber.

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