FABRICATION OF POROUS POLYPROPYLENE FIBERS EMBEDDED WITH NANOSILICA BASED ON IMMISCIBLE POLYMERS BLEND BY MELT SPINNING AND SELECTIVE EXTRACTION

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ABSTRACT

Development of methods for the functionalization of fibrous materials to improve properties meets the increasing demand for technological needs in various fields. The use of a combination of two immiscible polymers in a filament can allows new high added-value advanced structures. In this study, melt spinning technology was adopted for the polypropylene/polyvinyl alcohol (PP/PVA) blends containing silica nanoparticles, aimed at fabricating biphasic fibers with unevenly distributed silica nanoparticles. The localization of silica nanoparticles has been revealed mainly due to the thermodynamic factors, and the design can help produce a surface-decorated fibrous scaffold with embedded nanoparticles after the selective extraction. The fiber morphology was also investigated by Scanning Electron Microscopy (SEM). Its mean diameter of PVA dispersed phase within PP matrix can reach submicron scale, with the specific interface area over 3.2 m^2/g, which can provide a fiber porous structure. In addition, the mechanical properties of the multifilament fibers were studied via tensile test as well, and the interface-located silica nanoparticles has the slightest impact. Its mechanical properties can be maintained to a great extent as well, which gives a premise for further textile utilization.

Key Words: Porous fibers, polypropylene (PP), polyvinyl alcohol (PVA), melt spinning, silica nanoparticles, polymer blend.

1. INTRODUCTION

Immiscible polymer blending is a common strategy to endow the material with synergetic properties [1]. It is also a strategy for fabricating porous materials, if one of the phases can be removed by with solvent. Different melt-processing techniques (extrusion [2], injection molding [3], compression molding [4], etc.) endow the blends with more specific roles. As a bridge between polymer and textile field, melt spinning can be utilized as well to produce polymer blend fibers [5]. Certainly, the porous fibers are obtained via the selective extraction of the dispersed phase by solvent, if the matrix phase can offer a robust enough scaffold.

The morphology of the dispersed phase undergoes significant change mainly due to the elongational flow field rather than shear flow [6], which is fiercely elongated. Meanwhile, the interconnectivity is also enhanced reflected in the increment of accessibility of the soluble phase. There are variety of water-soluble polymers, including poly(ethylene) (PEO), sulfopolyester (SP), polyvinyl alcohol (PVA), etc, among which PVA has a good fiber-forming property.

In our previous study [7], silica nanoparticles have been localized in different positions of the biphasic phase, by the thermodynamic control. It was realized by the modification of the wettability of the silica nanoparticles. The efforts were made to extend the corresponding research into textile field by melt spinning. The application of polypropylene is ubiquitous for its production simplicity, physicomechanical performance and chemical resistance. 70wt.%/30wt.% in PP to PVA is an ideal formula for fabricating the PP-PVA fibers with satisfactory mechanical properties and high PVA accessibility degree. To realize the surface decoration of the porous fibers, silica nanoparticles were introduced in the blends as well to be induced towards different localizations.

In our study, the fibers from binary blend PP-silica and ternary blend PP-PVA-silica were fabricated. The aim is to investigate the influence of the silica nanoparticles upon the porous structure inside PP fibers as well as their mechanical properties, via SEM observation and tensile test.

2. EXPERIMENTAL SECTION

2.1 Materials

Melt spinning grade polypropylene (PP) was utilized, which was manufactured from Total Enterprise (Courbevoie, France). The melting temperature of PP is 168 °C. Polyvinyl alcohol (PVA) was purchased from Nichigo Gohsei (Osaka, Japan). The melting point is 179 °C.

Three kinds of silica nanoparticles were separately introduced into the biphasic system of PP-PVA. The pristine silica nanoparticles (Sigma-Aldrich® S5505, St. Louis, USA) exhibit hydrophilic properties. In addition, two hydrophobic silica nanoparticles were also adopted (Aerosil® R816: partially hydrophobic, modified with hexadecylsilane; Aerosil® R972: hydrophobic, modified with dimethyldichlorosilane). The denotions are simplified as Si_{S5505}, Si_{R816}, Si_{R972}, respectively. The sizes of the nanoparticles are about 12-16 nm.

2.2 Fabrication of the extrudates

All the blends were compounded by the means of a co-rotating intermeshing twin-screw extruder (Thermo Haake) with the screw diameter of 16 mm and L/D of 25. The raw materials were dried overnight to get rid of the moisture. The temperature profiles were ranged from 160 °C to 200 °C with the rotational speed of 100 rpm.

For the binary blends without fillers as well as the PP blended with silica nanoparticles, two constituents were directly compounded. The ratio of PP to PVA was 70wt.% to 30wt.%, and the ratio of PP to silica nanoparticles was 99wt.% to 1wt.%. The prepared pellets were denoted as PP_{70}-PVA_{30}, PP-Si_{S5505}, PP-Si_{R816}, and PP-Si_{R972}, respectively.

For the ternary blend PP-PVA-silica, PP was pre-compounded with silica nanoparticles into pellets. Afterwards, the pellets were compounded with PVA. The ratio of PP to PVA was still 70wt.% to 30wt.%. Besides, the ratio of the polymeric constituents to silica nanoparticles was 99wt.% to 1wt.%. The prepared pellets were denoted as PP_{70}-PVA_{30}-Si_{S5505}, PP70-PVA30-Si_{R816}, and PP_{70}-PVA_{30}-Si_{R972}, respectively.

2.3 Fabrication of the multifilament yarns

Multifilament yarns were made by melt spinning on the machine named Spinboy 1 (Busschaert, Belgium). The temperature profiles were controlled from 180 °C to 207 °C, and the flow rate of volumetric pump was 52.5 cm^3/min. The molten polymers went through the dies containing 80 holes, and followed with drawing. The draw ratios were adjusted as 2 and 3. The suffix -DR_2 and -DR_3 was placed after the denotion of the extrudates to represent the corresponding multifilaments. For example, PP_{70}-PVA_{30}-Si_{R972}-DR_3 represents the fibers manufactured from the PP_{70}-PVA_{30}-Si_{R972} with the draw ratio of 3.

2.4 Selective extraction

The obtained fibers were immersed into the hot water at 80 °C to get rid of the removable PVA phase, and then placed in the oven to get rid of the moisture. Thus the porous PP fibers was obtained.

2.5 Scanning electron microscopy (SEM)

The multifilament yarns from PP-PVA blends were cut along the cross-sectional direction, right after the immersion inside liquid nitrogen. The cross-section was metalized for SEM observation (Inspect F, USA).

2.6 Tensile test

A Zwick 1456 tensile testing machine was utilized for the mechanical measurement of the monofilaments from the yarns. The deformation rate was 20 mm/min with the gauge length of 20 mm, under a standard atmosphere (20 °C; 65%HR).

3. RESULTS AND DISCUSSION

For the immiscibility of PP and PVA, the PVA nodules were detached and replaced by the related holes. Therefore, more than 500 PVA nodules were taken into account for the calculation of the average diameter of PVA. The mean diameter of PP-PVA blend fibers with draw ratios of 2 and 3 was about 68.1 and 56.4 μm, respectively. Referred to these values, the representative monofilament was selected for the observation, for the huge deviation of the monofilament diameter could not be ignored. SEM observation of the cross-sectional morphology of PP-PVA fiber with different ratios is shown in Fig. 1. The specific interface area A can be estimated by Eq.1.

$$A = \frac{\sum_{i=1}^{N_s} \pi d_i \delta_H}{\sum_{i=1}^{N_s} \pi \left(\frac{d_i}{2}\right)^2 \delta_H \rho_{PVA} (1/\omega_{PVA})} = \frac{4\omega_{PVA}}{\rho_{PVA}} \frac{\sum_{i=1}^{N_s} d_i}{\sum_{i=1}^{N_s} {d_i}^2} \quad \textbf{Eq. 1}$$

Where N_s represents the number of the PVA nodules, d_i represents the bottom areas of the i-th PVA nodule, δ_H represents the layer thickness (close to zero), ρ_{PVA} represents the PVA density (1.3 g/cm^3), and ω_{PVA} represents the PVA mass fraction. In addition, the mean diameter $d_s = \frac{\sum_{i=1}^{N_s} {d_i}^2}{\sum_{i=1}^{N_s} d_i}$ can be defined for calculating the specific interface area, exhibiting a negative correlation.

It is found that unlike the significant impact of silica nanoparticles upon the morphology of extrudates, the small amount of silica nanoparticles does not give a fierce change in the mean diameter of PVA nodules. The specific area is tightly relevant to the mean diameter and not impacted drastically by the nanofillers. The dominant influence lies in the different draw ratios. The mean diameter of PVA phases is 0.29 μm for PP_{70}-PVA_{30}-DR_2, and further decreased to 0.26 μm when the draw ratio is increased to 3. From Eq.1, we can conclude that the specific interface areas are 3.2m^2/g and 3.6m^2/g, respectively.

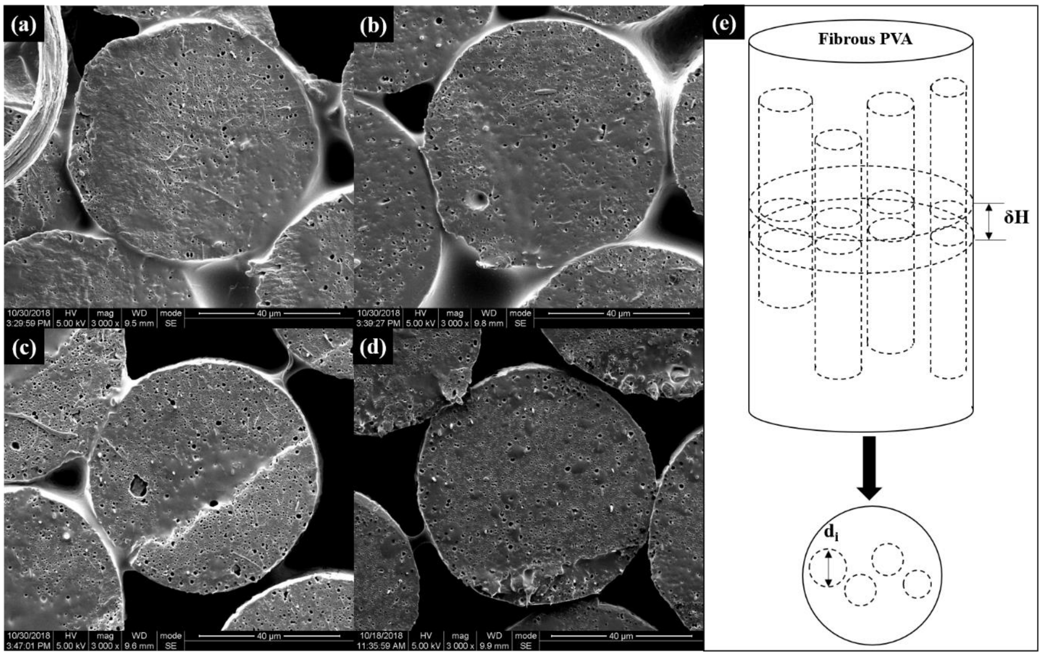

Figure 1 SEM observation of the morphology of PP-PVA fiber with different ratios

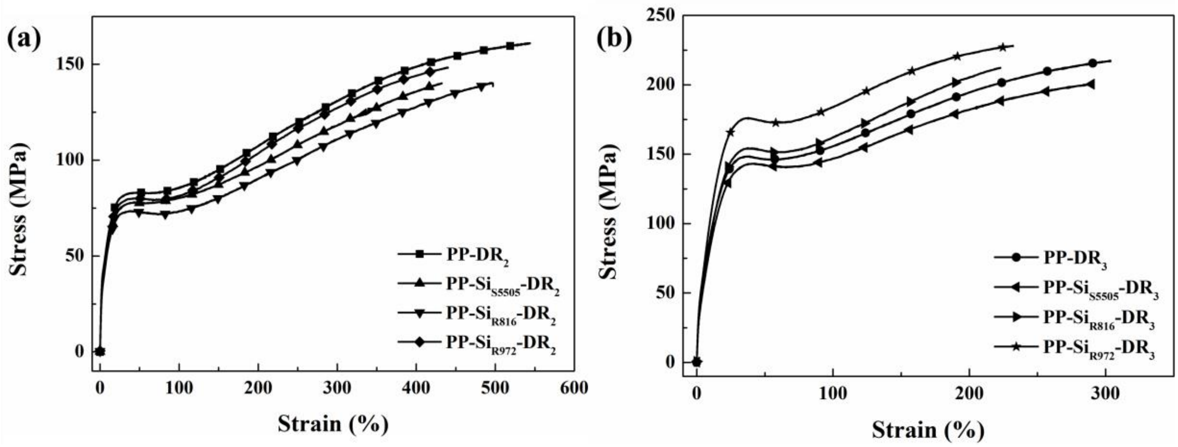

Figure 2. The stress-strain curves of PP fibers without/with different silica nanoparticles (a) DR=2; (b) DR=3.

Table 1. The mechnical properties of PP fibers without/with silica nanoparticles

	DR=2			**DR=3**		
Fibers	**Young's modulus (MPa)**	**Tenacity (cN/Tex)**	**Breaking elongation (%)**	**Young's modulus (MPa)**	**Tenacity (cN/Tex)**	**Breaking elongation (%)**
PP	2174±238	17.9±2.2	516±66	2951±322	24.2±2.1	302±100
PP-Si$_{S5505}$	1759±188	15.3±1.5	436±71	2376±148	21.5±0.9	301±26
PP-Si$_{R816}$	1657±366	14.2±3.4	507±84	2552±349	23.4±2.6	227±32
PP-Si$_{R972}$	1819±295	17.0±1.5	433±43	2750±243	25.4±1.6	226±21

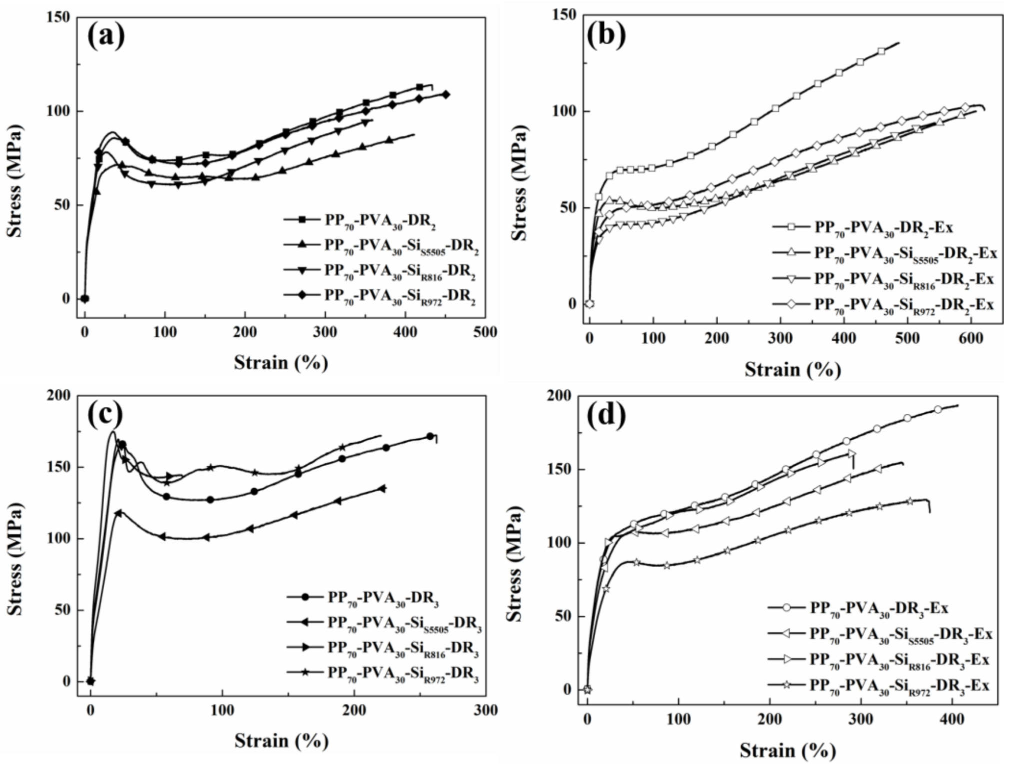

Figure 3. Stress-strain curves of PP_{70}-PVA_{30} fibers without/with silica nanoparticles (a) DR=2 before extraction; (b) DR=2 after extraction; (c) DR=3 before extraction; (d) DR=3 after extraction.

Table 2. The mechanical properties of the blend fibers without/with silica nanoparticles.

Fibers	**Before extraction**			**After extraction**		
	Young's modulus (MPa)	**Tenacity (cN/Tex)**	**Breaking elongation (%)**	**Young's modulus (MPa)**	**Tenacity (cN/Tex)**	**Breaking elongation (%)**
PP_{70}-PVA_{30}-DR_2	1853±249	12.3±1.7	449±51	1570±389	13.1±2.9	547±65
PP_{70}-PVA_{30}-DR_3	2871±617	16.7±2.6	256±108	2012±220	20.9±2.5	371±74
PP_{70}-PVA_{30}-Si_{S5505}-DR_2	1658±236	8.5±1.5	372±58	1265±205	10.7±1.7	575±66
PP_{70}-PVA_{30}-Si_{S5505}-DR_3	1796±182	13.8±0.8	224±25	1564±227	15.2±1.8	373±99
PP_{70}-PVA_{30}-Si_{R816}-DR_2	1638±135	9.6±0.9	375±23	1109±327	9.8±2.8	497±66
PP_{70}-PVA_{30}-Si_{R816}-DR_3	3350±394	17.3±1.7	111±83	1891±226	16.9±2.8	299±89
PP_{70}-PVA_{30}-Si_{R972}-DR_2	1851±167	11.4±0.8	443±68	1207±195	10.9±1.9	643±118
PP_{70}-PVA_{30}-Si_{R972}-DR_3	2839±561	16.2±3.5	211±127	1238±185	13.9±2.0	349±66

The introduction of silica nanoparticles inevitably influences the mechanical behaviors of the fibers. In order to make in-depth investigations, the PP with silica nanoparticles without PVA was also melt-spun. The strain-stress curves of the fibers were illustrated in Figure 2, and the mechanical properties were listed in Table 1. The introduction of the silica nanoparticles

weakens the mechanical behaviors of the PP fibers with DR=2 in different degrees, among which hydrophobic Si_{R972} silica nanoparticles has the slightest influence. What's more, if the draw ratio is elevated to 3, the introduction of Si_{R972} even has a further enhancement for the PP fibers. It gives a strong evidance that the dispersion of Si_{R972} within PP is very excellent.
The stress-strain curves of fibers from PP_{70}-PVA_{30} were displayed in Figure 3, as well as the mechanical properties in Table 2. Similarly, silica nanoparticles influence the mechanical properties of fibers from PP_{70}-PVA_{30} in different degrees as well. However, there is almost no distinct difference between those of PP_{70}-PVA_{30}-DR_2 and PP_{70}-PVA_{30}-Si_{R972}-DR_2, reflected in almost unchanged Young's modulus, tenacity and breaking elongation, even if the draw ratio is elevated towards 3. It may be ascribed to not only the good dispersion of silica nanoparticles, but also the localization of the biphasic interface. The selective extraction process decreases the Young's modulus and increases the breaking elongation, and the tenacity is kept. The mechanical results prove that the obtained PP porous fibers can serve as a scaffold in the common use for its mechanical properties.

CONCLUSION

The study reveals the method of fabricating nanoparticle-decorated porous PP fibers, and the localization of the filler is controlled due to the thermodynamical factors. The diameters of PVA nodules are submicron in the obtained filaments, and not altered significantly by a small amount of filler additions. As for mechanical properties, the interface-localized Si_{R972} silica nanoparticles have the slightest impact upon the PP-containing fibers, for its good dispersion inside PP and the localization at the interface of PP and PVA. Furthermore, the selective extraction leaves the porous fibers with good mechanical maintains. Generally speaking, Si_{R972} is a potential good candidate for manufacturing the surface modified PP fibers.

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