

## Modification and Properties of Polypropylene Fibers Using Aluminosiloxane

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**Abstract:** Siloxylated polypropylene fibers composed of polypropylene (PP) and aluminosiloxane (AS) were prepared by melt blending followed by spinning. The effects of blend compositions on the thermal behaviors, surface and tensile properties of PP/AS blend fibers were investigated by DSC, WAXD, SEM, static honestometer, etc. The heat of fusion of PP/AS blends decreased with increasing AS contents. In addition, the peak intensity of PP/AS blends in X-ray diffraction patterns decreased with increasing AS contents. It was observed that the silicone molecules exist and well distribute on the surface of siloxylated polypropylene fibers. From the results of the half-life period measurements, the anti-static properties of PP fibers siloxylated with AS was found to be significantly modified.

**Keywords:** Siloxylated polypropylene, Aluminosiloxane, Melt blending, Thermal behaviors, Surface properties

### Introduction

Polypropylene (PP), a class of macromolecules called polyolefin, is widely used because of low density, low cost, easy processing and ability to be modified to meet a variety of performance characteristics [1-4]. Nevertheless, PP without surface modification has difficulty in penetrating the most significant areas of textile materials because of its low hydrophilicity, low anti-static property and poor dyeing property [5,6]. In recent years, only a few studies have been focused to improve the compatibility between polyolefin and polyorganosiloxane segments in polyolefin/polyorganosiloxane system [7,8]. Polyorganosiloxane is the most important type of polysiloxane. Polyorganosiloxanes are composed of two kinds of Si-O and Si-C bonds. Their characteristics on the structure are very similar to ketone compound. They are characterized by high thermal stability (to about 400 °C) due to the strength of Si-O bond, high thermo-oxidative stability (to about 200 °C), and high chemical resistance [9]. Polyorganoaluminosiloxane is a polymer containing siloxane and aluminosiloxane units in the polymer chain, the aluminium also being substituted with organic groups, such polymers may be synthesized by the reaction. Aluminosiloxane (AS) is a low molecular weight polymer of polyorganoaluminosiloxane and has low glass transition temperature and low surface tension and is nonpolar. The excellent overall properties including thermal and oxidation stabilities, gas permeability, biocompatibility, etc. render it to be used in textiles, biomaterials (i.e., implant system, contact lens, and wound dressing), protective coating, photoresist, water repelling agent, etc [10].

The aims of the present work are to prepare PP fibers siloxylated with AS and to investigate the effects of blend compositions on the thermal behaviors, surface and tensile

properties of PP/AS blend fibers.

### Experimental

The polymers used in this study are PP ( $M_n=58200$ ) and AS ( $M_n=1000$ ). PP and AS were dried in a vacuum oven at 60 °C for 48 h before melt blending to remove moisture, completely. PP/AS blends with different compositions were prepared by using a Haake rheomix (600 P, Germany) at 200 °C for 10 min under constant screw speed of 20 rpm. The composition ratios (w/w) of PP/AS blends were 95/05, 90/10, 80/20, 70/30, 60/40, and 50/50. Especially, PP/AS blend pellets at the blend compositions of 95/05 and 90/10 were prepared by using a side feeding twin extruder (Daechang Co.) with continuous process. This was taken into account the spinnability for melt spinning. Direct spin draw melt spinning was carried out using a single screw extruder equipped with a diameter of 0.7 mm and 36 holes (L/D 30) followed by air-cooling. The melt was spun at 200 °C and taken up at 450 m/min. Thermal properties of PP/AS blends were measured using a differential scanning calorimeter (DSC, TA 2100). All the scans were carried out from 0 °C to 250 °C at a heating rate of 10 °C/min under nitrogen atmosphere. Wide-angle X-ray diffractograms were taken with Ni-filtered  $\text{CuK}\alpha$  radiation using a X-ray diffractometer (GADDS, Germany) operated at 45 kV and 200 mA. Scanning electron microscopy (SEM) was performed by a Hitachi Science System (S-300 N). The surface and cross-section features of the samples were sputtered with gold before observation. The half-life period in the test of anti-static properties was measured using a static honesto meter (S-5109, Shishido). Tensile properties of the PP/AS blend fibers (100/0, 95/05, and 90/10, w/w) were measured using a UTM (Lloyd Instrument LR10K) with a load cell of 500 N at a gauge length of 25 mm, and a cross head speed of 10 mm/min.

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## Results and Discussion

### Thermal Behaviors and Crystalline Properties of the Blends

Figure 1 indicates the chemical structures of AS containing organic groups (R). R is most commonly alkyl or aryl group. In particular, AS containing Al-O chemical bonds is very analogous to the chemical structure of conventional polydimethylsiloxane (PDMS, R = CH<sub>3</sub>). To the best of our knowledge, the number of repeating units of AS is n=6 and the molecular weight of AS is 1000, respectively.

DSC curves of PP and AS polymers are shown in Figure 2. The melting temperature (T<sub>m</sub>) of pure PP polymer is 166.9 °C. However, pure AS polymer does not show melting behavior. The heat of fusion (ΔH<sub>f</sub>) of pure PP polymer is 87.4 J/g.

Figure 3 shows DSC curves of PP/AS blends with different blend compositions of 95/5, 90/10, 80/20, 70/30, 60/40, and 50/50 (w/w). The T<sub>m</sub> of the blend was observed as some as that of pure PP, regardless of AS content. On the other hand, the heat of fusion of the blends gradually decreased with increasing AS content.

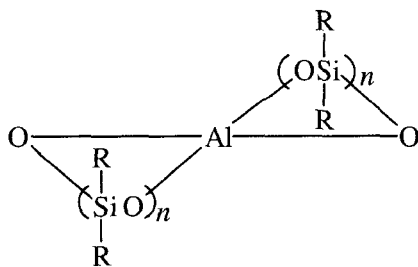


Figure 1. Chemical structure of aluminosiloxane.

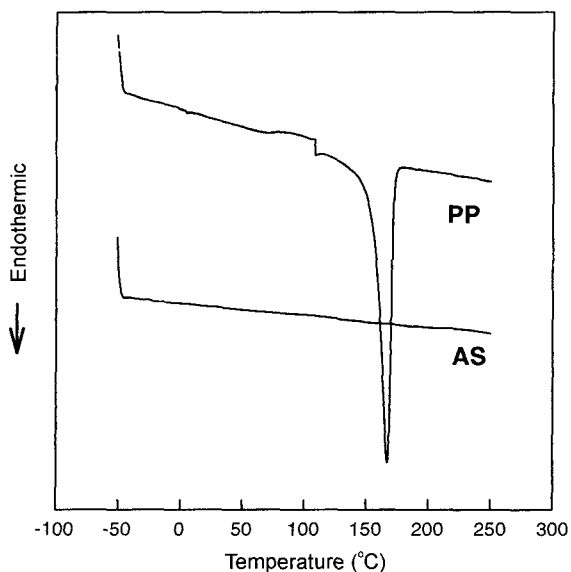


Figure 2. DSC curves of polypropylene and aluminosiloxane.

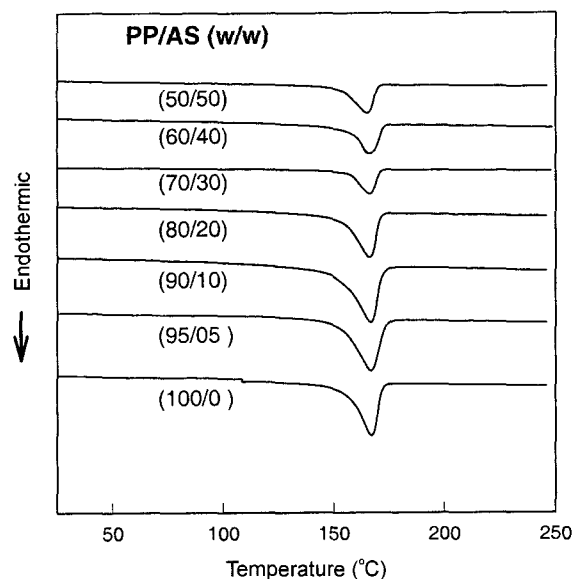


Figure 3. DSC curves of PP/AS blends with different blend compositions.

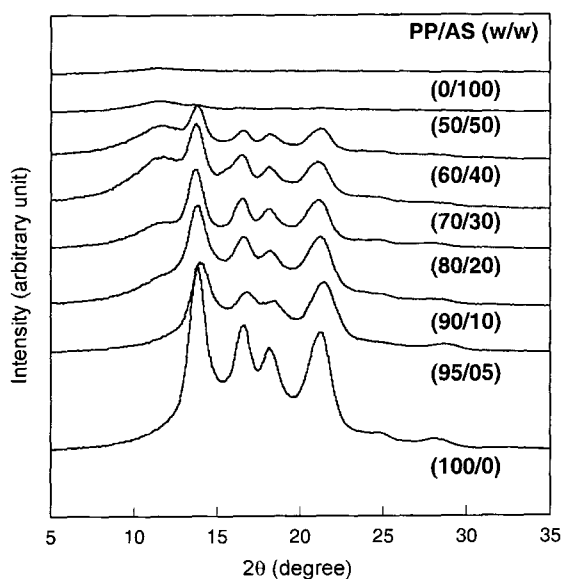
Generally, the miscibility of two polymers is determined by the thermodynamics of the interaction between the blend components. In other words, two polymers are considered to be miscible if there is a chemical reaction between the two, or if specific interactions occur between them on the basis of dipole-dipole attraction, hydrogen bonding, etc [11,12]. Perhaps the most unambiguous criterion of polymer miscibility is the detection of a single glass transition whose temperature is intermediate between those corresponding to the two component polymers.

However, from the result of thermal properties in this study, the chemical reaction in respect of thermodynamic miscibility was not occurred between PP and AS. As shown in Figure 3, not only the T<sub>m</sub> of the blend was observed as some as that of pure PP, regardless of AS content, but also the T<sub>g</sub> of the blend was not observed due to T<sub>g</sub> of AS is very low (about -100 °C). Therefore, because the discussion by T<sub>m</sub> and T<sub>g</sub> on the miscibility of PP/AS blend is difficult we shall discuss here it by the heat of fusion of blends. Accordingly, the decrease of heat of fusion in PP/AS blends is considered to be caused by the glass transition temperature and the surface tension of aluminosiloxane lower than those of PP.

Figure 4 shows the X-ray diffraction patterns of pure components and PP/AS blends. PP shows well-developed crystalline structure, while AS shows amorphous structure. The peak intensity of PP gradually decreased with increasing AS contents due to the effect of amorphous scattering in the blends. The blends showed no crystallinity above 50 (wt%) of AS content.

### Surface and Tensile Properties of the Blend Fibers

SEM photographs in Figure 5 show the features of PP and

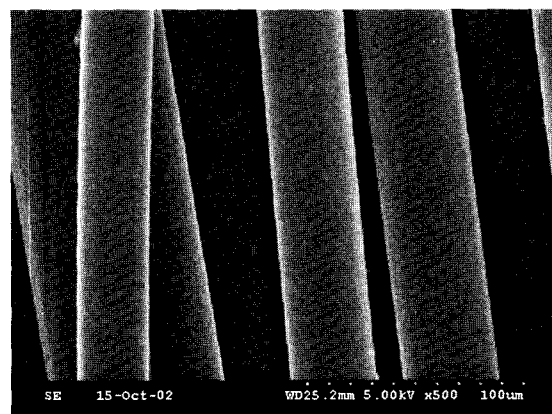


**Figure 4.** X-ray diffractograms of PP/AS blends and each component.

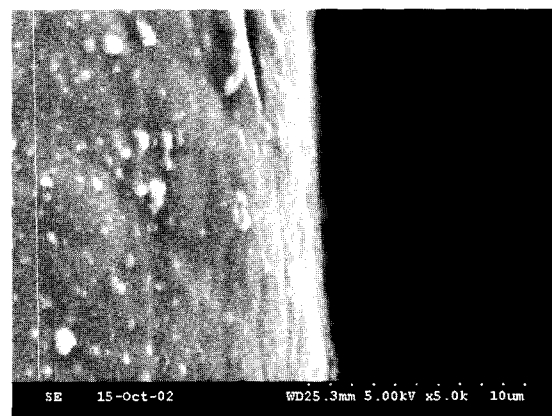
PP/AS blend fibers, respectively. The surface of pure PP fiber in Figure 5(a) appears smooth, while the surface of PP/AS (90/10) blend fibers in Figure 5(b) clearly showed that the silicone molecules in PP/AS blend fibers are well distributed on the surface of blend fibers. On the other hand, in Figure 5(c), the cross-section of PP/AS (90/10) blend fibers did not show the silicone molecules. From this result, it was assumed that the microphase separation between PP and AS domains has occurred due to their different solubility parameter and surface energy [10,13]. That is, AS domains, which have lower surface energy than PP domains, migrated onto the surface of PP/AS blend fibers, therefore, silicone molecules could not be observed in the cross-section of the blend fibers as shown in Figure 5(c). In general, it is well known that the components of siloxane having nonpolar and low surface energy in the polymer compounds modified with polyorganosiloxanes migrated onto the surface of the compounds [9,10,14]. Also, conventional methods to coat the inorganic silicone on the surface of the organic polymers usually go through at least two processes, such as dip-coating. But, the melt blending method used in this study didn't go through the multi-coating process as the in-situ process using physical properties of silicone.

The measurements of the half-life period of PP/AS blend fibers were examined for anti-static properties. The effects of AS contents on the half-life period of PP/AS blend fibers are shown in Figure 6. The half-life period of PP fibers is 180 sec. However, the half-life period of PP/AS blend fibers greatly decreased by about 63-55.8 sec. Therefore, the half-life period of PP/AS blend fibers decreased 65-69 % compared with pure PP fiber.

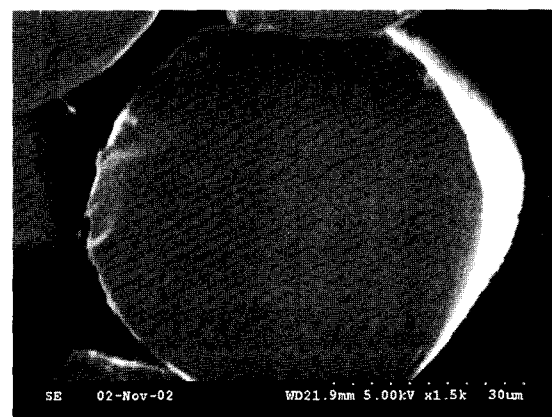
From the results of Figures 5 and 6, it was confirmed that



(a)



(b)

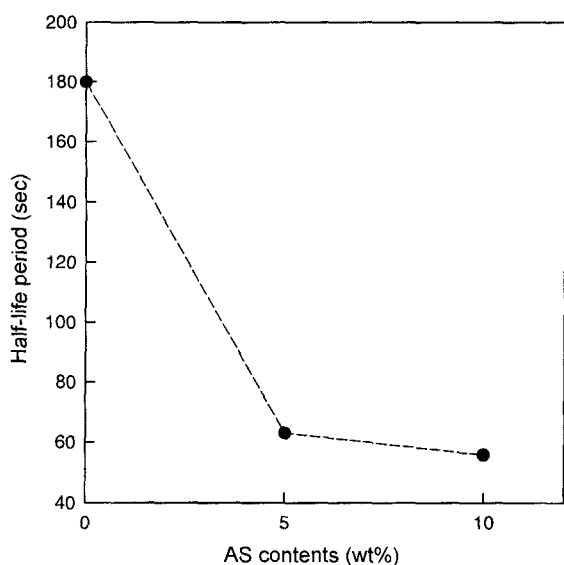


(c)

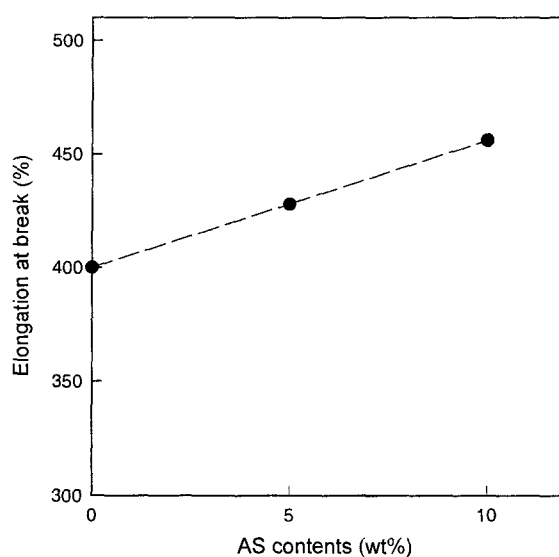
**Figure 5.** SEM photographs of PP and PP/AS (90/10, w/w) blend fibers; (a) surface of pure PP ( $\times 500$ ), (b) surface of PP/AS (90/10) ( $\times 5000$ ), and (c) cross-section of PP/AS (90/10) ( $\times 1500$ ).

the anti-static properties of PP fibers siloxylated with AS was found to be significantly modified.

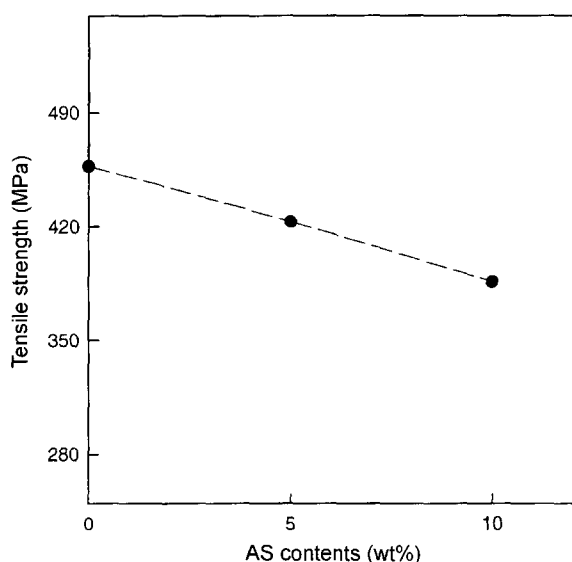
Figure 7 shows the effects of AS contents on the tensile strength of PP/AS blend fibers. The tensile strength of the blend fibers decreased with increasing AS content.



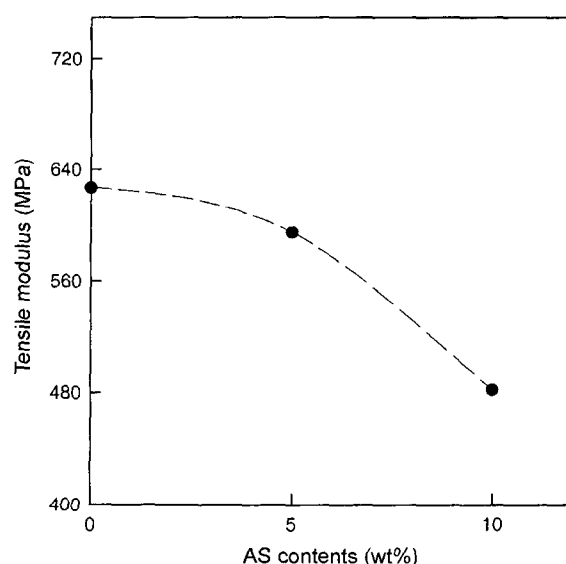
**Figure 6.** Effect of aluminosiloxane content on the half-life period of PP/AS blend fibers.



**Figure 8.** Effect of aluminosiloxane content on the elongation at break of PP/AS blend fibers.



**Figure 7.** Effect of aluminosiloxane content on the tensile strength of PP/AS blend fibers.



**Figure 9.** Effect of aluminosiloxane content on the tensile modulus of PP/AS blend fibers.

It is generally known that crystallization improves the strength and modulus of polymers [4]. Therefore, it is assumed that the strength of PP/AS blend fibers was decreased with increasing AS contents due to decrease of crystallinity of PP blended with AS.

The effects of AS contents on the elongation at break of PP/AS blend fibers are shown in Figure 8. The elongation at break of the blend fibers appeared about 428-456 %, respectively. This result is that the rate of increase of the elongation at break compared with pure PP fiber of 400 % is about 7-14 %.

Figure 9 shows the effects of AS contents on the tensile modulus of PP/AS blend fibers. The tensile modulus of the blend fibers decreased by about 5-23 % compared with 627 MPa of pure PP fiber.

Consequently, from the results in this study, it was confirmed that PP was siloxylated with AS due to mechanically compatibility [15,16].

## Conclusions

PP/AS blends were prepared by melt blending. The effects

of blend compositions on the thermal behaviors, surface and tensile properties of PP/AS blend fibers were investigated.

It was confirmed that PP could be siloxylated with AS due to mechanical compatibility. The peak intensity of PP/AS blends in X-ray diffraction patterns decreased with increasing AS contents due to the effect of amorphous scattering in the blends. As AS contents increased from 5 to 10 wt% at blending time of 10 min and heating temperature of 200 °C, the elongation at break of PP/AS blend fibers increased, while the tensile strength and modulus decreased. In addition, silicone molecules existed and well distributed on the surface of siloxylated polypropylene fibers. Also, the half-life period of PP/AS blend fibers decreased with increasing AS contents. In the long run, it was confirmed that the surface properties of PP fibers modified with AS was found to be greatly improved.

### Acknowledgements

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