

Spinning of Poly(ethylene terephthalate) Fibers Incorporated with Modified Calcium Silicate

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ABSTRACT: The spinning of poly(ethylene terephthalate) (PET) filaments in laboratory-scale was studied. The objective was to study the effect of modified calcium silicate (CS) with vinyltriethoxysilane (VTES) on the melt spinning of PET fibers. The CS was modified with VTES (2% v/v) in diethyl ether at room temperature for 24 h. The modification of CS with VTES improved agglomeration of CS, hydrophobic, and heat-resistance properties. These properties were

expected that modified CS could be used as the filler in melt spinning of PET. The incorporation of modified CS in PET was spinnable. The addition of CS in PET improved its heat resistance. Also, the filler had an effect on the mechanical properties of polyester fibers. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 699–705, 2012

Key words: extrusion; fibers; fillers; polyester

INTRODUCTION

Polyester fiber is commonly used in the textile industry. The advantage of polyester fiber is highly crystalline, high strength, and high tenacity. These properties have encouraged its application in industrial areas.

The modifications of polyester fiber were studied in previous reports.^{1–3} Many methods had been successfully used for modifying the polyester fibers such as blend with other polymers,⁴ produced bicomponent fibers⁵ and nanocomposite fibers,^{6,7} and changed the cross-section shape.^{8,9}

These modifications improved their physical and chemical properties such as dyeing property, comfort, and flame-retardant properties. Fibers with a noncircular cross-sectional shape showed properties different from those of fibers with a circular cross-sectional shape, including the bending stiffness, softness, luster, pilling, bulkiness, handle, and performance.

The improvement of fibers may be conducted by addition of a filler. Many fillers were incorporated in the fibers such as AlOH_3 , MgCO_3 , and MgOH_2 .¹⁰ To derive the maximum benefit from the fillers, several factors must be considered such as particle size, filler loading, and interaction between polymer matrix and inorganic filler. Also, good (uniform) dispersion must

be considered. This is normally obtained by controlled addition of the filler during melt mixing. White et al.¹¹ reported that highly filled compounds exhibited instability in elongational flow for both simple stretching of filaments and melt spinning. Existing polymers must be modified by the addition of fillers. Zhang et al.¹² reported that polypropylene fibers filled with fumed silica increased crystallization velocity of the polymer melt. The fumed silica increased the thermal stability and charred residue of polypropylene after 500°C.¹³ High density polyethylene with CaCO_3 had better thermal stability than the neat HDPE.¹⁴ Fei et al.¹⁵ found that magnesium hydroxide eliminated the melt chips and improved the flame retardancy of the polyamide. Incorporation of CS in melt spinning of poly(ethylene terephthalate) (PET) is very interesting. This expects that the CS will improve heat resistance of PET fibers and also the adhesion with concrete or reinforcement of materials.

Calcium silicate (CS) is one of group of compounds obtained by reacting calcium oxide and silica in various ratios. It is a white powder with a low density and high physical water absorption. It is used in roads, insulations, and fire protection material. It may be used as a filler in polymeric materials.¹⁶ However, the hydrophilic character of CS appears to be a disadvantage because of its incompatibility with hydrophobic polymeric matrices. This causes poor adhesion between CS and PET matrix, making the dispersion of the CS into polymeric matrices difficult and leading to composites of poor final properties. The use of surface-modifying agents is very interesting for enhancing the bond between a filler and a polymer matrix.

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Silanes are a broad class of surface-modifying chemicals. These compounds are silicon chemicals that possess a hydrolytically sensitive center. A typical general structure is $(R'O)_3-O-R$, where R' is an alkyl group and R is an organo functional group. $R'O$ is a hydrolyzable group, typically methoxy and ethoxy. Most of the widely used organosilanes have one organic substituent and three hydrolyzable substituents. In the vast majority of surface treatment applications, the alkoxy groups of the trialkoxy-silanes are hydrolyzed to form silanol-containing species ($Si-OH$). Reaction of these silanes involves four steps. Initially, hydrolysis of the three labile groups occurs. Condensation to oligomers follows. The oligomers then hydrogen bond with OH groups of the substrate. Finally, during drying or curing, a covalent linkage is formed with the substrate with concomitant loss of water. Also, these compounds can react with inorganic substrates such as glass to form covalent bonds and possess an organic substitution that alters the physical interactions of treated substances. Although the methoxy and ethoxysilanes are not the most reactive organosilanes, they are the most widely used organofunctional silanes for surface modification. The reasons for this include the fact that they are easily handled and the alcohol byproducts are noncorrosive.¹⁷ The low toxicity of ethanol as a byproduct of the reaction favors the ethoxysilanes for modification of CS. Most filler materials have very different physical natures to the polymer matrices in which they are used; for example, fillers usually have polar surface that often must interact with nonpolar polymer matrices such as PET. Consequently, the weakest point in a filled composite is often at the PET-filler interface. Interactions between the PET and filler such as CS may be enhanced with a filler surface modifying agent.

The present study was carried out to study the effect of modified CS on spinnability of polyester fibers. CS was modified with VTES. The spinning of PET fibers with the addition of 1% CS (by weight of polyester chips) was conducted at temperature of 265°C. The characteristics of CS and polyester fibers were also present.

EXPERIMENTAL

Materials

CS was purchased from Fluka. PET chips were supplied by Thai Toray Synthetic Co. It was the bright PET chips. The PET chips had intrinsic viscosity of 0.639 dL/g and density of 1.38 g/cm³ with a weight-average molecular weight of 20,000. Vinyltriethoxysilane was purchased from Aldrich and used as received.

Surface treatment of CS with VTES

VTES (2% v/v) in diethyl ether was applied onto the surface of CS powder (4 g). The mixture was kept constant at room temperature for 24 h. The dried CS was washed with diethyl ether for three times and dried at temperature of 110°C for 2 h and subsequently cooled in desiccator.

Preparation of CS/PET composite

The composite of CS-filled PET was conducted in a Rajamangala University of Technology Krungthep Laboratory-scale melt mixer. The CS was 1% by weight of PET. The temperature in mixer was 265°C, and the final composite extruded was cooled in-line in a water-bath, dried, and granulated.

Laboratory spinning of PET into filaments

PET with or without CS was spun using an equipment in the laboratory scale. A Rajamangala University of Technology Krungthep Laboratory-scale melt spinning unit was used for this study. Before melt spinning, the polymer chips were dried by heating at temperature of 110°C for 8 h. Molten polymer was forced through a single-hole spinneret with capillary diameter of 0.5 mm. The conditions of spinning were maintained constant at temperature of 265°C and spinning speed 200 m/min. The quenching of the filament was achieved in ambient air. The as-spun, undrawn filament was then collected.

Characterization

Hydrophobicity testing of CS

The hydrophobicity of the modified CS was determined by dispersing modified CS and unmodified CS on the water surface and observed the floating of these materials.

Particle size measurement

The particle size distribution of CS was determined by laser particle size distribution Mastersizer S long bed Version 2.19, Malvern Instrument, England.

FTIR measurement

The FTIR spectra of CS and PET filaments were recorded using Perkin-Elmer FTIR Spectrophotometer System 2000.

Morphology

The surface morphology of CS and PET fibers was observed with a scanning electron microscope (SEM, JEOL JSM-5410LV, Japan). Also, the PET fibers were

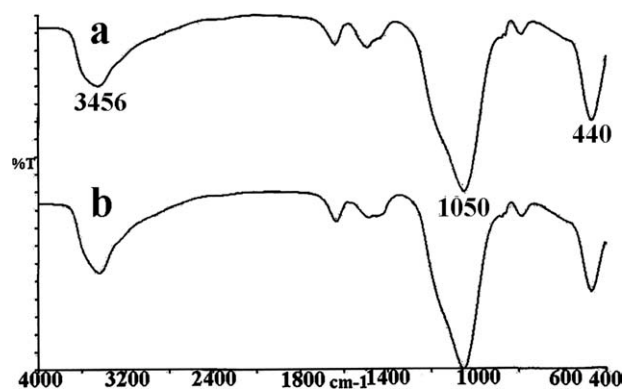


Figure 1 FTIR spectra of unmodified (a) and modified calcium silicate (b).

observed with an optical microscope (Optical Microscope Motic BA 300).

Thermogravimetric analysis

The thermogravimetric analysis was carried out using Netzsch Simultaneous Thermal Analyzer STA 409 C Jupiter, which recorded the mass change as a function of temperature. The fiber was cut to ~1–2 mm length and a 17 ± 3 mg of sample was analyzed under nitrogen atmosphere from room temperature to 800°C at a heating rate of 20°C/min. In addition, the CS was characterized under the same condition.

RESULTS AND DISCUSSION

Surface modification of CS with VTES

CS was modified with VTES. VTES is an organosilicone compound showing $(\text{CH}_3-\text{CH}_2-\text{O})_3-\text{Si}-\text{CH}=\text{CH}_2$ structure. Alkoxide groups on the silicon are hydrolyzed to silanols (Si–OH). In addition, silanol

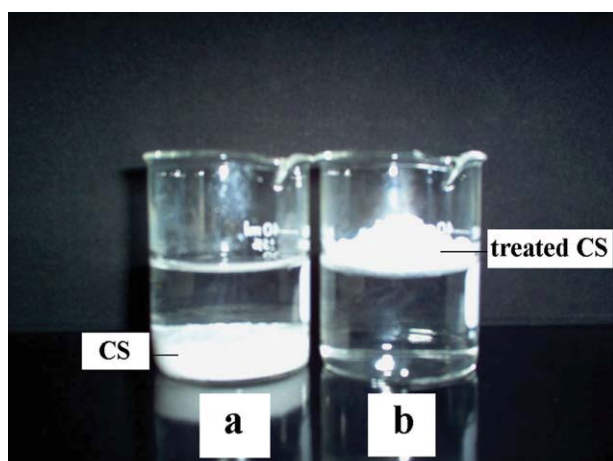


Figure 2 Hydrophobicity testing of unmodified (a) and modified calcium silicate (b).

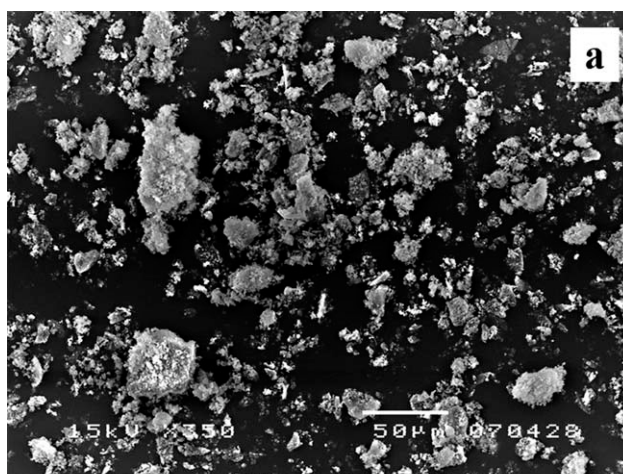


Figure 3 SEM micrographs of unmodified (a) and modified calcium silicate (b).

(Si–OH) will condense with each other to give siloxane bond. The reactions are shown below.

Hydrolysis reaction

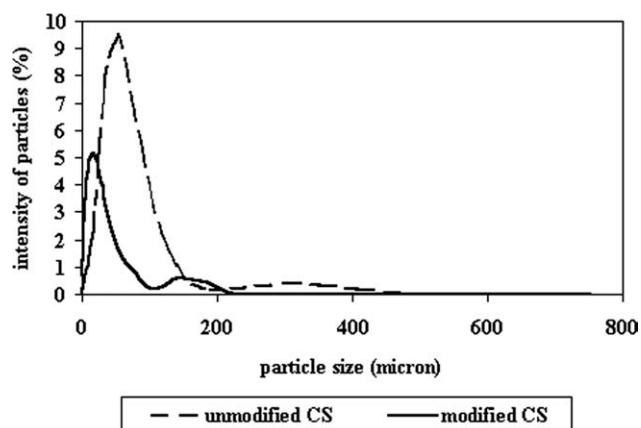
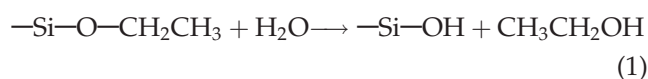
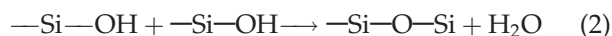


Figure 4 Particle size distribution of unmodified and modified calcium silicate.

TABLE I
Average Particle Size of CS particles

Statistical analysis	Diameter (μm)	
	Calcium silicate	Calcium silicate treated with VTES
At 10%	12.15	2.71
At 50%	46.59	15.66
At 90%	99.65	271.77
Mean diameter	19.15	6.87

Condensation reaction



Silane that contains three inorganic reactive groups on silicon will bond well to most inorganic substrate, especially if the substrate contains silicon such as CS. Therefore, a reactive silanol groups can condense with other silanol groups, for example, those on the surface of CS fillers, to form siloxane linkages. Subsequent drying leads to a formation of covalent linkage with treated surface and development of polymeric thin film of silane.

Figure 1 shows FTIR spectra of unmodified and modified CS with VTES. In the FTIR spectrum of untreated CS [see Fig. 1(a)], the absorption band at 3456 cm^{-1} attributed to the absorbance of $-\text{OH}$ functional groups of $\text{Si}-\text{OH}$ in CS; at 1050 cm^{-1} is due to $\text{Si}-\text{O}$ stretching; at $440\text{--}450 \text{ cm}^{-1}$ is silicate chain structure.¹⁸ Modification of CS with VTES increased the intensity peak of $-\text{OH}$ functional groups [see Fig. 1(b)], which resulted from the silanol groups of VTES.

The hydrophobicity of the CS was investigated by dispersing modified and unmodified CS on the water surface. The result obtained is shown in Figure 2. The modified CS floated on the water surface while the unmodified CS sank immediately.

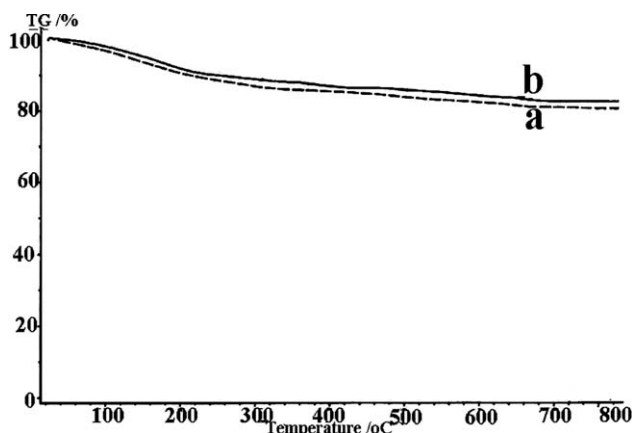


Figure 5 Thermograms of unmodified (a) and modified calcium silicate (b).

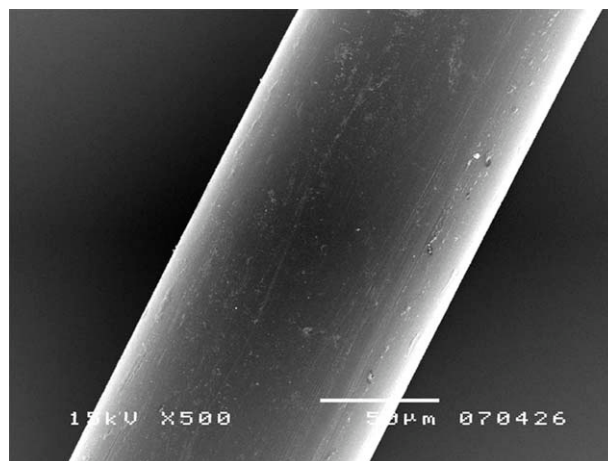


Figure 6 Polyester fiber product at spinning speed 200 m/min.

This supported that VTES film was coated on CS surface by coordinate covalent.

In general, CS powder is hydrophilic in nature. This produces an agglomeration of CS particles. Modification of CS with VTES increased its hydrophobicity. This led to decreasing the agglomeration of CS particles as shown in Figure 3. Scanning electron micrographs showed the different appearance between them. The result shows that unmodified CS composed of small primary particles. Some of these particles fused to each other, forming larger aggregates. In contrast, the surface-modified CS powder composed of particles with a distribution in size. The particle size distribution of CS is shown in Figure 4 and Table I. The result shows that modified CS with VTES tended to produce the small particle size. The statistical analysis reveals that the mean diameter of modified particles was smaller than that of unmodified one (see Table I). The results of treatment effect of CS by VTES must be correlated to density of particles. Modification of CS with VTES inhibited the coalescence of CS

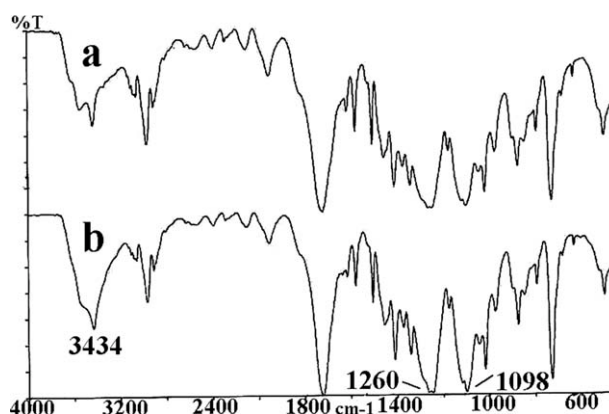


Figure 7 FTIR spectra of polyester fiber (a) and polyester fiber incorporated with calcium silicate (b).

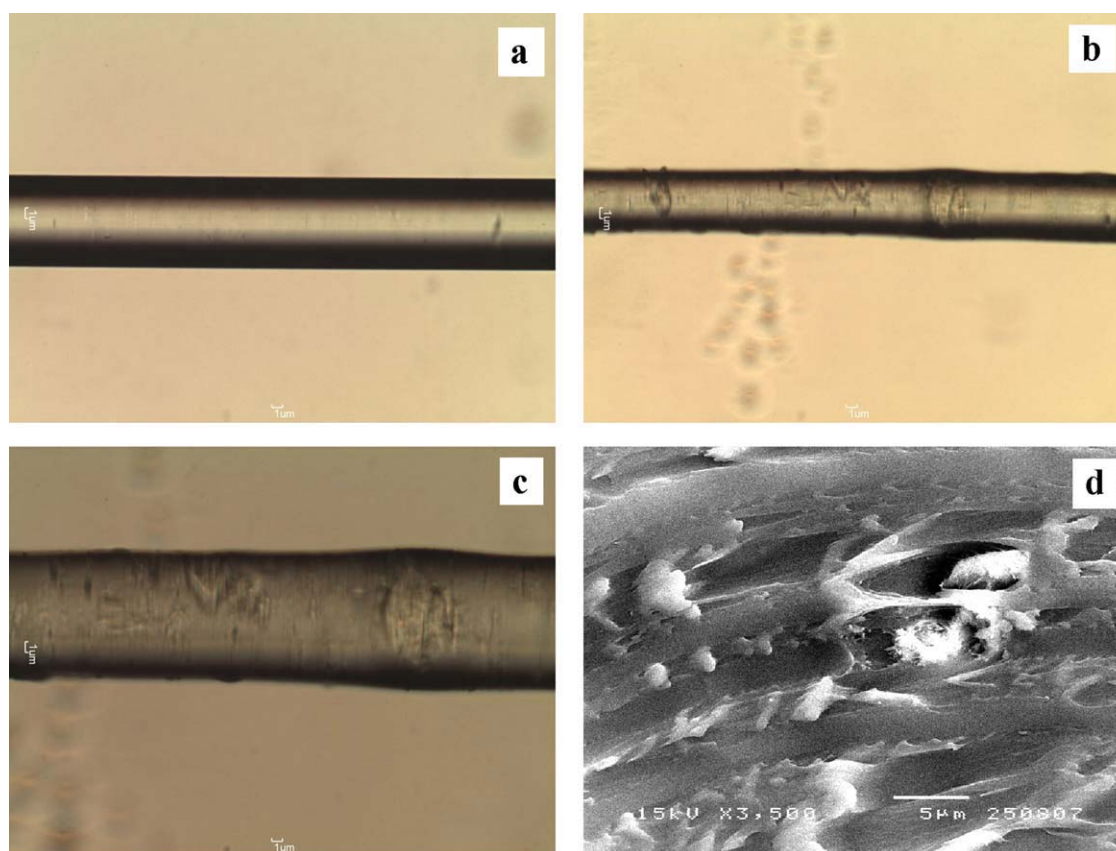


Figure 8 Optical microscope images of polyester fiber (a), and polyester fiber incorporated with calcium silicate (b–d); (b) surface, (c) surface, and (d) cross-section from SEM image. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

particles into higher particle clumps (aggregates and agglomerates).

Thermogravimetric analysis provides a method for the determination of mass change in the material as a function of temperature. Thermograms of CS are shown in Figure 5. From Figure 5, it can be seen that CC showed remarkable thermal stability over the temperature range from 25 to 740°C. At temperature of 25–100°C, it was the dehydration of pore water

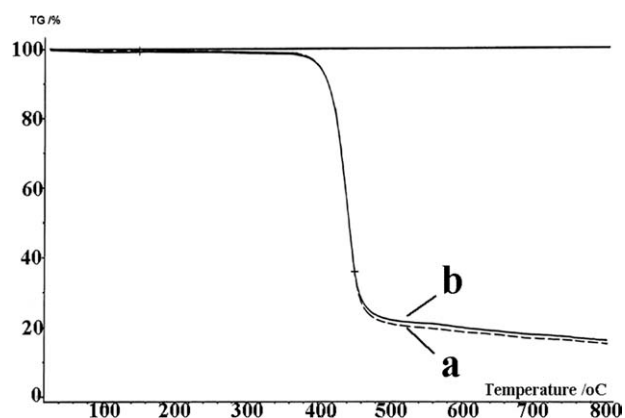


Figure 9 Thermograms of polyester fiber (a) and polyester fiber incorporated with calcium silicate (b).

between particles. The dehydration of CS hydrates occurred at temperature of 100–400°C. At temperature of 400–600°C, it showed the dehydration of calcium hydroxide. Also, decarbonation of CaCO_3 occurred at temperature of 600–730°C.¹⁹ The rates of weight loss of the treated sample were less than untreated one. The coordination between the VTES and CS improved the heat resistance of CS. The mass loss at 300°C being less than 15% allows for it to be melt-blended with high-processing temperature polymers like PET.

Effect of CS on spinning of PET fibers

The undrawn filament in this experiment was spun in laboratory-scale at low speed. It showed a smooth surface with the regular shape (see Fig. 6). The size of PET fiber was 116 denier. It exhibited brittle

TABLE II
Mechanical Properties of Polyester Fibers

Type of PET fibers	Elongation (%)	Tensile strength (mN/denier)
PET	11	2.4
PET incorporated with CS	9.4	2.05

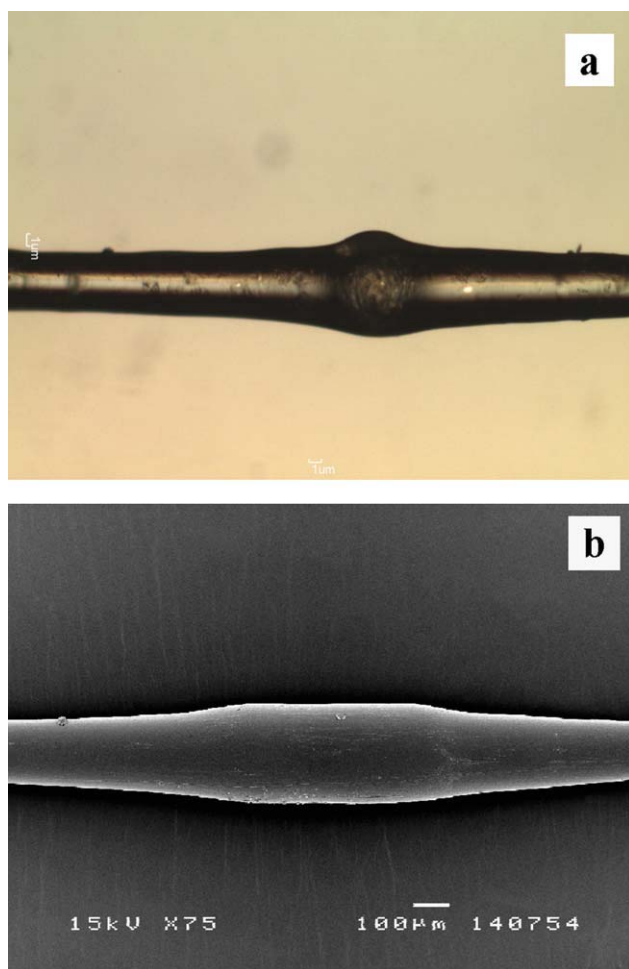


Figure 10 Optical microscope image (a) and SEM image (b) of knot in polyester fiber. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

property. However, the effect of CS-containing fiber was examined.

Figure 7 shows FTIR spectra of PET and PET incorporated with CS. It can be seen that the absorption peaks belonging to CS incorporated in PET were confirmed. The absorption band at 3434 cm^{-1} corresponded to the absorption of Si—OH functional groups. Also, in modified PET, the intensity peaks at about $1100\text{--}1000\text{ cm}^{-1}$ increased. The peaks in this region can be assigned to Si—O—Si stretching of CS treated with VTES. Figure 8 shows optical microscope images and SEM image of PET and PET incorporated with CS. It can be seen as the CS in the fiber. Therefore, incorporation of CS in polymer melt of PET was spinnable.

Thermograms of control and modified PET are shown in Figure 9. The PET fiber exhibited a simple thermal decomposition mass loss beginning at 415.6°C and with a total weight loss of 84.75%. In contrast, the decomposition of the modified PET was obtained at 414.2°C with a total weight loss of

83.64%. Shape of thermograms of control PET and modified PET does not differ from each other significantly. When comparing the temperature of 50% mass loss, no marked change is obtained between the pure polymer and its composite; the presence of the CS appears to have no marked influence. At weight loss over 75%, it can be observed that CS-containing PET decomposed less than control sample. It is interesting to note that the addition of CS slightly improved the amount of char at 800°C from 15% in the case of virgin PET to 16% for the composite studied. Apparently, some of the polymer does not undergo thermal degradation upon composite formation. The incorporation of CS in PET, thus, increased the thermal stability of polyester fibers. Table II shows the influence of CS on the elongation and tensile strength of the PET fibers. It can be seen that the addition of particles reduced its mechanical properties. This may be due to the presence of CS inhibited the flow direction and orientation of polymer melt. At above 1% CS, also, the polymer melt could not flow easily through the spinneret. White and Tanaka¹¹ reported that adding

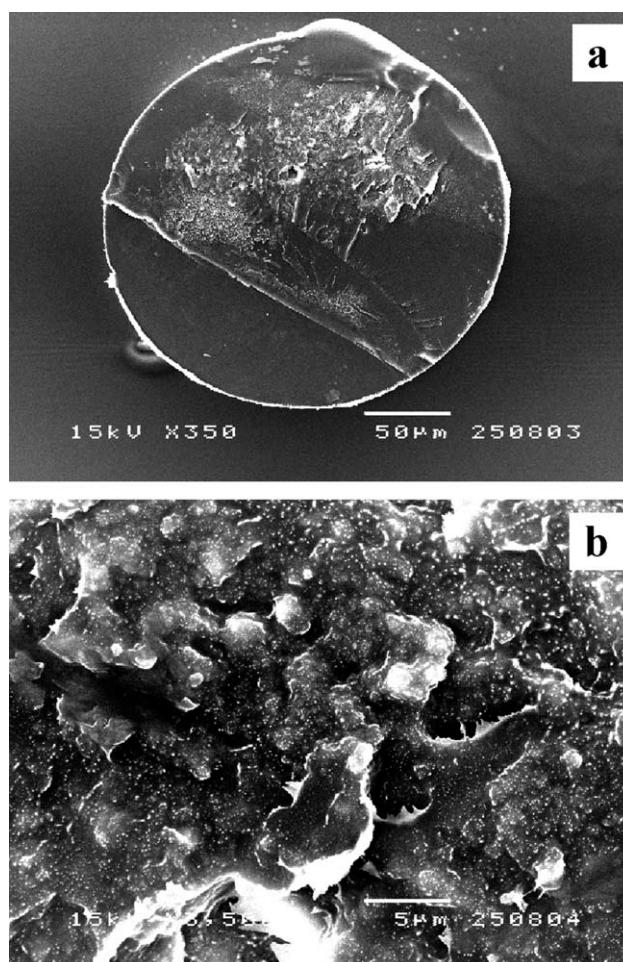


Figure 11 Cross-section of knot in polyester fiber (a and b); (a) low magnification, (b) high magnification.

small particles in polymer melt could be a “stress concentration,” which would lead to premature failure. Nachtigall et al.²⁰ reported that the addition of rigid particulate materials to thermoplastics tended to increase stiffness and decreased mechanical properties. In addition, it was quite obvious that all heterophase in the spinning melt (solid particles) should produce knots, that is, short irregular sections in undrawn fibers. The knot in polyester fibers resulted from the agglomeration of CS as shown in Figures 10 and 11. The effects of particle size and degree of agglomeration on the properties of materials were reported.²¹ Therefore, CS increased the thermal property and decreased mechanical property of PET fiber.

CONCLUSIONS

The surface of CS was modified with VTES at room temperature. The hydrolysis and condensation of VTES formed siloxane onto the surface of CS, which improved its particle size distribution, hydrophobic, and heat resistance properties. Thus, VTES was the effective surface-modifying agent. In addition, the spinning of PET fibers in laboratory-scale was studied. The addition of modified CS in PET was spinnable. The incorporation of modified CS in PET minimal rose heat resistance of PET fiber. The agglomeration of CS had an opportunity to occur. Also, the addition of filler into the fiber decreased its mechanical properties.

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