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Spinning of PET Fibres Mixed with Calcium Carbonate

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ABSTRACT

The spinning of Poly Ethylene Terephthalate (PET) filament in laboratory-scale was studied. The objective was to study the effect of modified Calcium Carbonate (CC) with vinyltriethoxysilane (VTES) on the melt spinning of PET fibres. The CC was modified with VTES (2% v/v) in diethyl ether at room temperature for 24 h. The modification of CC with VTES improved agglomeration of CC, hydrophobic and heat resistance properties. These properties were expected that modified CC could be used as the filler in melt spinning of PET. The incorporation of modified CC in PET was spinnable. The addition of CC in PET improved its heat resistance. Also, the filler had an effect on the mechanical properties of polyester fibre.

Key words: Fibres, calcium carbonate, composites, polyester, spinning, vinyltriethoxysilane

INTRODUCTION

Polyester fibre is commonly used in the textile industry. The advantage of polyester fibre is highly crystalline, high strength and high tenacity. These properties have encouraged its application in industrial areas (Joseph, 1986).

The modifications of PET fibres improved their physical and chemical properties such as dyeing property, comfort and flame retardant properties. Fibres with a noncircular cross-sectional shape showed properties different from those of fibres with a circular cross-sectional shape, including the bending stiffness, softness, luster, pilling, bulkiness, handle and performance (Karaca and Ozcelik, 2007).

The improvement of fibres may be conducted by addition of a filler. Many fillers were incorporated in the fibres such as AlOH_3 , MgCO_3 and MgOH_2 (Formicola *et al.*, 2009). Incorporation of CC in melt spinning of PET is very interesting. This expects that the CC will improve the heat resistance of PET fibres, also, the adhesion with concrete or the reinforcement of materials.

Calcium carbonate is a chemical compound with the chemical formula CaCO_3 . It is a common substance found in rock in all part of the world and is the main component of shells of marine organisms, snail and pearls. The main use of calcium carbonate is in the construction industry, either as a building material. Also, it is widely used as a filler in plastics (Pradyot, 2003).

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 $(\text{R}'\text{O})_3\text{-O-R}$, where R' is an alkyl group and R is an organo functional group. $\text{R}'\text{O}$ is a hydrolysable group, typically methoxy, 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 trialkoxysilanes are hydrolysed to form silanol-containing species (Si-OH). Reaction of these silanes involve 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 (Arkles, 2011).

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

MATERIALS AND METHODS

This experiment was conducted in the studio of the Faculty of Textile Industries, Rajamangala University of Technology Krungthep, Bangkok, Thailand between September, 2010 and January 2011.

Calcium carbonate was purchased from Fluka. Poly(ethylene terephthalate) chips were supplied by Thai Toray Synthetic Co Ltd. It was the bright PET chips. The properties of the PET chips used in this study are presented in Table 1. Vinyltriethoxysilane was purchased from Aldrich and used as received.

Surface treatment of CC with VTES: VTES (2% v/v) in diethyl ether was applied onto the surface of CC powder (4 g). The mixture was standed at room temperature for 24 h. The dried CC 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 CC/PET composite: The composite of CC-filled PET was conducted in a Rajamangala University of Technology Krungthep Laboratory-scale melt mixer. The CC 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 CC was spun using an equipment in the laboratory scale. A Rajamangala University of Technology Krungthep Laboratory-scale melt spinning unit was employed for this study. A prior to 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⁻¹. The quenching of the filament was achieved in ambient air. The as-spun, undrawn filament was then collected.

Characterization

Hydrophobicity testing of CC: The hydrophobicity of the modified CC was determined by dispersing modified CC and unmodified CC on the water surface and observed the floating of these materials.

Table 1: Properties of the PET chips

Properties	Values
Intrinsic viscosity of the dry chips	0.639 dL g ⁻¹
Moisture of the dry chips	<50 ppm
Density of the chips	1.38 g cm ⁻³
Molecular weight of the polymer	20,000 g mol ⁻¹
Melting temperature of the polymer chips	265°C

Particle size measurement: The particle size distribution of CC was determined by Laser Particle Size Distribution Mastersizer S long bed Version 2.19, Malvern Instrument Ltd., England.

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

Thermogravimetric analysis (TGA): 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 fibre was cut to approximately 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 $20^{\circ}\text{C min}^{-1}$. In addition, the CC was characterized under the same condition.

RESULTS

Figure 1 shows FTIR spectra of unmodified and modified CC with VTES. The FTIR spectrum of CC shows the presence of a strong band centered around 1463 cm^{-1} , characteristics of the C-O stretching mode of carbonate together with a narrow peak around 873 cm^{-1} of the blending mode (Boke *et al.*, 2004). Also, the stretching vibrations of the H_2O molecules in the CC occurred at 3456 cm^{-1} . On the spectrum of the treated sample the fundamental peaks of carbonate can be seen at 1463 and 873 cm^{-1} .

The particle size distribution of CC is shown in Fig. 2. The result shows that modified CC with VTES tended to produce the small particle size. The statistical analysis reveals that the mean diameter of modified particles was 1.70 micron which smaller than unmodified one with the mean diameter 6.31 micron.

Thermograms of CC are shown in Fig. 3. From Fig. 3, it can be seen that CC showed remarkable thermal stability over the temperature range from 25 to 740°C . It exhibited decomposition to calcium oxide and carbon dioxide in the region of 700°C . A similar observation was reported by Deodhar *et al.* (2011). Also, the modified CC showed higher thermal stability than unmodified one.

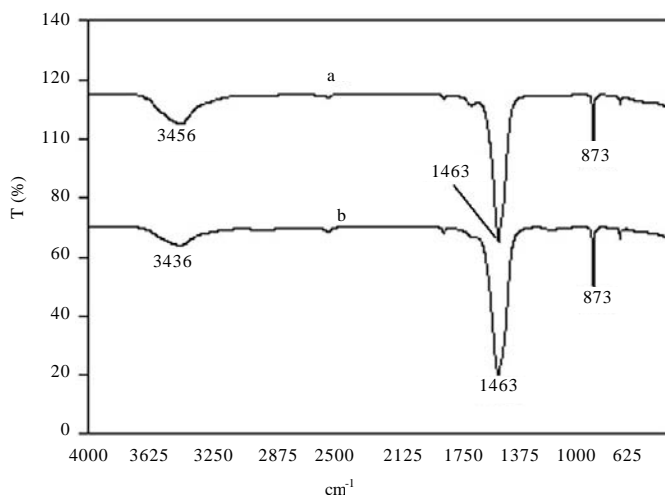


Fig. 1: FTIR spectra of (a) unmodified and (b) modified calcium carbonate

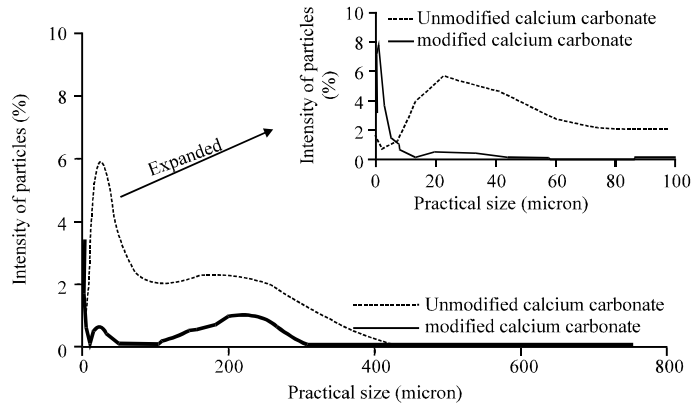


Fig. 2: Particle size distribution of unmodified and modified calcium carbonate in the range of 0.49 to 760 micron

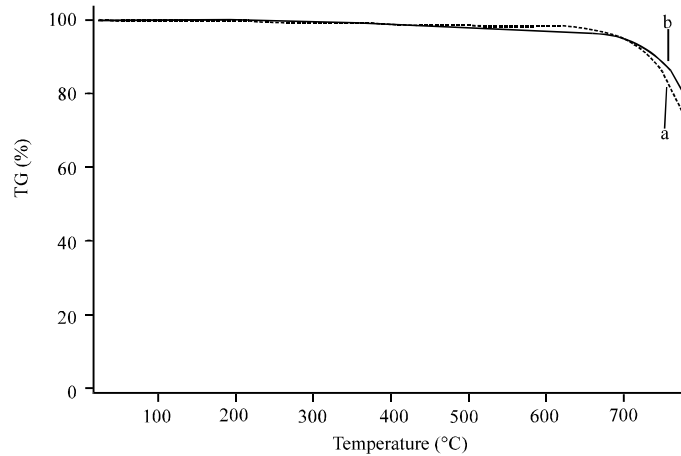


Fig. 3: Thermograms of (a) unmodified and (b) modified calcium carbonate

Effect of CC on spinning of PET fibres: The undrawn filament in this experiment was spun in laboratory-scale at low speed. The size of PET fibre was 116 denier. It exhibited brittle property. However, the effect of CC-containing fibre was examined.

Figure 4 shows FTIR spectra of PET and PET incorporated with CC. It can be seen that the absorption peaks belonging to CC 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 CC treated with VTES.

Thermograms of control and modified PET are shown in Fig. 5. The PET fibre 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 is obtained at 418.8°C with a total weight loss of 84.37%.

Table 2 shows the influence of CC on the elongation and tensile strength of the PET fibres. It can be seen that the addition of particles reduced its mechanical properties.

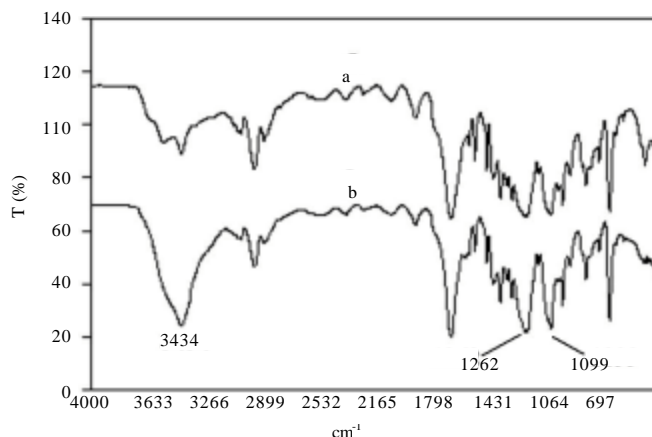


Fig. 4: FTIR spectra of (a) polyester fibre and (b) polyester fibre incorporated with calcium carbonate

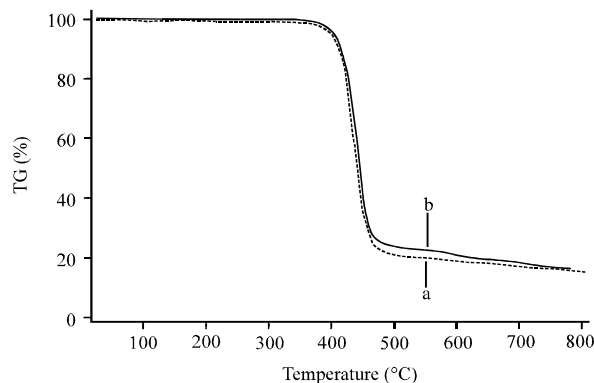


Fig. 5: Thermograms of (a) polyester fibre and (b) polyester fibre incorporated with calcium carbonate

Table 2: Mechanical properties of polyester fibres

Type of PET fibres	Elongation (%)	Tensile strength (mN/denier)
PET	11.0	2.40
PET incorporated with CC	9.9	2.14

DISCUSSION

Surface modification of CC with VTES: CC was modified with VTES. VTES is an organosilicone compound showing $(\text{CH}_3\text{-CH}_2\text{-O})_3\text{-Si-CH=CH}_2$ structure. Alkoxide groups on the silicon are hydrolysed to silanols (Si-OH). In addition, silanol (Si-OH) will condense with each other or with ethoxy silanes to give siloxane bond. Subsequent drying leads to a formation of covalent linkage with treated surface and development of polymeric thin film of silane. The reactions are shown below in Eq. 1 and 2.

- **Hydrolysis reaction:**



- **Condensation reaction:**



Silane that contain three inorganic reactive groups on silicon will bond to most inorganic substrate, such as CC. Therefore a reactive silanol groups can condense with other -OH groups, for example, those on the surface of CC fillers, to form siloxane linkages (Si-O-Metal). Hence in modified CC, the absorption spectrum of OH groups at 3436 cm^{-1} decreased (Fig. 1). This may be due to the effectiveness of the VTES in reacting with CC. The formation of siloxane linkages led to decreasing its water adsorption.

The hydrophobicity of the CC was investigated by dispersing modified and unmodified CC on the water surface. It was found that the modified CC floated on the water surface while the unmodified CC sank immediately. This supported that VTES film was coated on CC surface by coordinate covalent.

In general, CC powder is hydrophilic in nature. This produces an agglomeration of CC particles. Modification of CC with VTES increased its hydrophobicity. This led to decreasing the agglomeration of CC particles. In contrast, the surface-modified CC powder composed of particles with a distribution in size. The effect of VTES on hydrophobicity of materials was reported by Kusktham (2010) in the study of modification of poly(ethylene terephthalate) fabrics with VTES.

The results of treatment effect of CC by VTES must be correlated to density of particles. Modification of CC with VTES inhibited the coalescence of CC particles into higher particle clumps (aggregates and agglomerates). The decreasing of CC particles by surface treatment with chemical was also reported by Dangtungee *et al.* (2005).

Thermogravimetric analysis provides a method for the determination of mass change in the material as a function of temperature. It can be seen from the result that the rate of weight loss of the treated sample was less than untreated one (Fig. 3). Therefore, the coordination between the VTES and CC improved the heat resistance of CC. The result reported by Rahman *et al.* (2009) also indicated that the silane compound improved the thermal stability of materials. However, this result was differ from Dihayati *et al.* (2007) in the study of coated CC with stearic acid. They reported that the coated CC has the same thermal stability with uncoated particles. The mass loss of CC at 300°C is very low (Fig. 3) which allows for it to be melt-blended with high processing temperature polymers like PET.

Effect of CC on spinning of PET fibres: Shapes of thermograms of control PET and modified PET do not differ from each other significantly (Fig. 5). At weight loss over 75%, it can be observed that calcium carbonate-containing PET decomposed less than control sample. It is interesting to note that the addition of CC slightly improved the amount of char. Apparently, some of the polymer dose not undergo thermal degradation upon composite formation. The incorporation of CC in PET, thus, increased the thermal stability of polyester fibres. From the study of Deshmukh *et al.* (2010), the CaCO_3 increased the thermal stability of poly (butylene terephthalate)/calcium carbonate composites. The results reported by many researchers (Costache *et al.*, 2006; Mohaddespour *et al.*, 2007; Sipaut *et al.*, 2007; Abid *et al.*, 2010) also indicated that the addition of fillers such as clay and silica in PET or polymer matrices influenced thermal property.

Incorporation of CC in PET fibre decreased its mechanical properties (Table 2). This may be due to the presence of CC. It inhibited the flow direction and orientation of polymer melt. At above 1%

CC, also, the polymer melt could not flow easily through the spinneret. White and Tanaka (1981) reported that adding small particles in polymer melt could be a “stress concentration” which would lead to premature failure.

CONCLUSION

The surface of CC was modified with VTES at room temperature. The hydrolysis and condensation of VTES formed siloxane onto the surface of CC which improved its particle size distribution, hydrophobic and heat resistance properties. Thus, VTES was the effective surface-modifying agents. In addition, the spinning of PET fibres in laboratory-scale was studied. The addition of modified CC in PET was spinnable. The incorporation of modified CC in PET minimal rose heat resistance of PET fibre. Also, the addition of filler into the fibre decreased its mechanical properties.

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