Interfacial Interaction and Mechanical Properties of Nylon 6–Potassium Titanate Composites Prepared By *In-situ* Polymerization

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ABSTRACT: A new method was proposed for the synthesis of nylon 6–potassium titanate composites with high strength and high modulus. Dispersion quality of potassium titanate whiskers in the polyamide matrix and the degree of interfacial adhesion between polyamide and whiskers are the key points of this composite. A composite with high strength and high modulus was obtained with ϵ-caproamide and potassium titanate whiskers, which were modified by an alkylsilane coupling agent with n-aminocapric acid as initiator through *in-situ* polymerization. The contact angle test showed that the surface energy of modified whiskers is similar to nylon 6's, while that of the unmodified ones was much higher than nylon 6's. These results suggest that the modified whiskers would disperse homogeneously in the nylon 6 matrix. Scanning electronic microscope (SEM) results fortified the above hypothesis. According to infrared (IR) spectra, the sample of whiskers that were separated from the modified composite by formic acid have the characteristic peak of nylon 6's; and the whiskers that were separated from unmodified composite do not have them, which suggested that there are chemical bonds between modified whiskers and nylon 6 matrix, and the whiskers served as chemical cross-link points in the composite. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 2317–2322, 1997

INTRODUCTION

It is well known that the properties of polymers may be improved by the presence of appropriately selected additives.[1–5] These additives usually enhance specific properties of polymers; and the types of additives include fillers, reinforcements, coupling agents, antioxidants, ultraviolet light stabilizers, etc. The final properties of host polymers alter, while the additives vary.[6–9] Small, single crystals,[10–11] such as those of potassium titanate, are being used at an annual rate of over 1000 tons for the reinforcement of nylon and other thermoplastics. Most of these composites were prepared by a twin-screw extruder. Unfortunately, this method may lead to an adverse effect: the crystalline structure of whiskers may be destroyed during processing. In order to avoid this side effect, we used a new method, *in-situ* polymerization, to prepare polyamide–whisker composites in our laboratory.

In-situ polymerization[12] is a method in which fillers or reinforcements were dispersed in monomer first, then this mixture was polymerized using the technique similar to bulk polymerization. It is obvious that the most important factors that affected the properties of composites are the dispersion quality and the adhesion degree at polymer and filler interfaces.[13–17] The addition of surface-active or coupling agents,[18] such as alkylsi-

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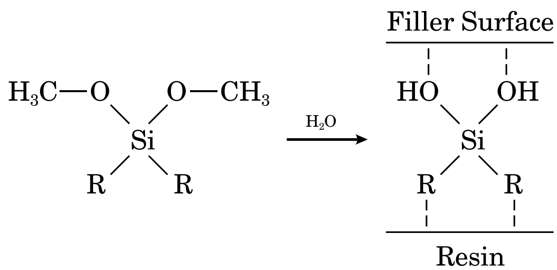
lanes and organotitanates, as well as high-molecular-weight carboxylic acids and esters, which are attracted by both the resin and the fiber surface, was used widespreadly to improve the surface and interface interaction between polymers and fillers. It is believed[19] that coupling agents with two different functional groups could be attracted to the resin with one group and to the filler with the other. For example,[18] dialkyldimethoxysilanes are hydrolyzed to produce dialkyldihydroxysilanes *in-situ,* and the mechanism considered was that the hydroxyl groups bond with the filler surface and that the alkyl groups are attracted to the resin, as follows:



In the present article, the surface energy of modified and unmodified potassium titanate whiskers were investigated. An interfacial structure model was proposed based on this point and other experimental results.

EXPERIMENTAL

Material

ε-caproamide monomer and *n*-aminocapric acid were used to prepare nylon 6. Potassium titanate whiskers (0.1–0.5 μm in diameter and 10–100 μm in length; Jin Jian Fiber Lit. Co.) and γ-(2,3-epoxypropoxy)propyltrimethoxysilane (A-187) were used as the reinforcement and interfacial modifier, respectively.

Preparation of Composites

γ-(2,3-epoxypropoxy)propyltrimethoxysilane (A-187) was dissolved in the ethanol first. Potassium titanate whisker was added slowly in the above mixed solvent under stirring at 80°C. The mixture was dried in an oven when it has been agitated for about 4 h. Modified potassium titanate whiskers were dispersed in ε-caproamide at 90°C, and *n*-aminocapric acid as an initiator was introduced at the same time. Then, this mixture was polymerized using bulk polymerization. The unmodified whisker's composites can also be prepared by this method, while the modified potassium titanate whiskers were replaced by unmodified ones.

Surface Tension Measurement

The surface tensions were measured on a JY-82 Contact Angle (Chengde tester factory) at room temperature. The surface tension of nylon 6 was measured by single liquid method with the reference liquids as water[20,21] and ethylene glycol. The surface tensions of the modified and unmodified potassium titanate whiskers were measured by the double-liquid method[22] according to the Young–Dupre equation and Fowkes theory[23] through the measurement of the contact angle of water drop on the filler in the *n*-hexane, *n*-heptane, *n*-octane, and *n*-decane.

Infrared (IR) Spectroscopic Characterization

Composites were dissolved in formic acid first for 15 days, then the whiskers were separated from the mixture. The whiskers were washed by formic acid and water before testing. A Fourier-transform–infrared (FTIR) tester (PERKIN-ELMER System 2000) was used to determine the components of whiskers. Pure potassium titanate whiskers were also tested in order to determine the changes of whiskers in composites.

SEM Observation

Samples were merged in liquid nitrogen and then fractured at the primed notch. The fractured areas of samples were gilded with gold before testing. A Hitachi S-530 scanning electronic microscope was used to study the morphology of the samples.

Mechanical Property Testing

Tension testing was examined by a CS-183 mechanical tester with the tension rate at 5 rpm.

RESULTS AND DISCUSSION

Interfacial Interaction Between Potassium Titanate Whiskers and the Nylon 6 Matrix

Interfacial forces have been found to be one of the most important factors in determining the mor-

Table I Surface Tension Data at 25°C

Sample	r_s (mJ/m^2)	r_s^d (mJ/m^2)	r_s^p (mJ/m^2)
Nylon 6	38.85	27.61	11.24
Untreated whisker	83.48	45.90	37.58
Treated whisker	39.67	16.40	22.07

Table II Surface Energy Values of the Alkanes and Interfacial Energy Values Between Alkanes and Water

Liquid	r_H (mJ/m^2)	r_{HW} (mJ/m^2)
n-Hexane	18.4	51.1
n-Octane	21.3	51.0
n-Decane	23.4	51.0
n-Hexadecane	27.1	51.3

phology of the polymer blends and composites if the viscosities of the polymers are comparable.[24,25] The contact angle test is a major method to investigate the surface tension of materials, and the results are listed in Table I. In the table, γ_s^d and γ_s^p are the dispersion and polar components, respectively.

In Table I, the surface tension of nylon 6 was obtained by the single liquid method with water and ethylene glycol as reference liquids and was derived from the following equation[22]:

$$\frac{r_L(1 + \cos\theta_{SL})}{2} = (r_S^d r_L^d)^{1/2} + (r_S^P r_L^P)^{1/2} \quad (1)$$

$$r_s = r_S^d + r_S^P \quad (2)$$

In eqs. (1) and (2), θ represented the equilibrated contact angle of the wetting liquid on the solid surface; and r_L, r_L^d, and r_L^P are surface-free energy, dispersion, and polar components of wetting liquid, respectively, while r_s, r_s^d, and r_s^P are those of solid materials.

The surface tension of whiskers, however, was examined by double liquid method with water as the wetting liquid and a series of *n*-alkylane as the reference liquid. According to the theories of Fowkes and the Young–Dupre equation,[23] the surface energy of potassium titanate whiskers can be properly get

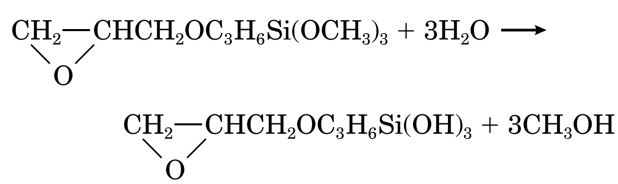
$$r_W - r_H + r_{HW}\cos\theta_{SW/H} = 2(r_S^d)^{1/2}[(r_W^d)^{1/2} - (r_H^d)^{1/2}] + I_{SW}^P \quad (3)$$

$$I_{SW}^P = 2(r_S^P r_W^P)^{1/2} \quad (4)$$

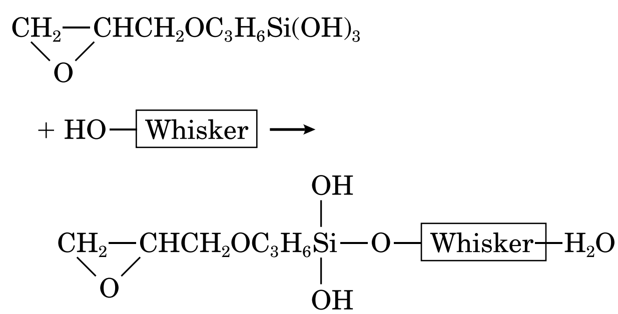
$\theta_{SW/H}$ is the contact angle of water on solid surface in *n*-alkylane. r_W and r_w^d are the surface free energy and dispersion component of water, and r_H and r_H^d are those of the *n*-alkylane. The surface energy values of *n*-alkylane are listed in Table II.

The data of Table I show that the surface-free energy of whiskers, which was modified by a coupling agent, is much lower than that of unmodified whiskers; and it is similar to the values of nylon 6. This result can be explained as the reaction between whiskers and coupling agent; the high surface-free energy of potassium titanate whiskers was caused by the hydroxyl on the surface of whiskers. The coupling agent can react with these hydroxyls by hydrolysis when it was added. The procedure can be described as the following process:

(1) Hydrolysis of trianthoxysilane



(2)



As the results, the surface areas of whiskers were surrounded by organic groups, which led to the decrease of the surface energy. Furthermore, to investigate the degree of interfacial interaction between whiskers and nylon 6, the adhesion work W_a, cohesive energy W_c, and interface tension r_{SL} were calculated by the following equations:

$$W_a = 2[(r_S^d r_L^d)^{1/2} + (r_S^P r_L^P)^{1/2}] \quad (5)$$

$$W_c = 2r_{LV} \quad (6)$$

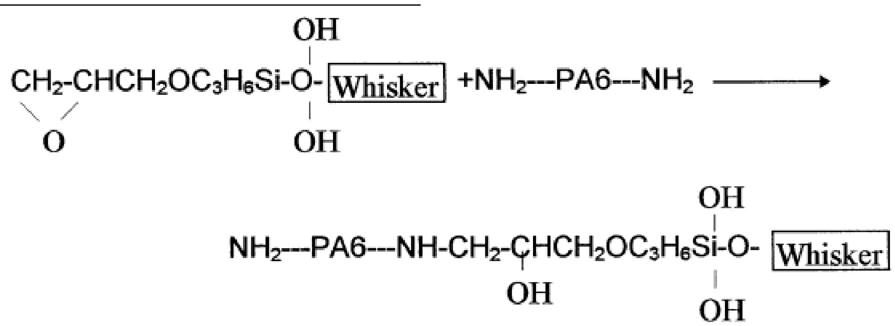
Table III(a) Values of W_a, W_c, and r_{SL} of the Potassium Titanate Whisker-filled Nylon 6

	W_a (mJ/m^2)	W_c (mJ/m^2)	r_{SL} (mJ/m^2)	σ_B (MPa)
PA6–whisker (untreated)	112.3	77.70	10.04	52.10
PA6–whisker (treated)	74.48	77.70	3.43	86.03

$$r_{SL} = [(r_S^d)^{1/2} - (r_L^d)^{1/2}]^2 + [(r_S^P)^{1/2} - (r_L^P)^{1/2}]^2 \quad (7)$$

Table III(a) shows the calculation results of interface thermology. It revealed that the interfacial tension force between nylon 6 and the modified whisker is much smaller than that of nylon 6 and the unmodified one, suggesting that the wetting quality of polyamide molecular and modified whisker is improved and provides the possibility of good interfacial adhesion between them.[26] Although the adhesion between the unmodified whisker and nylon 6 is higher than with the modified whiskers, the dispersion quality of the unmodified filler in polyamide matrix is worse. This difference results from the high interfacial tension force between unmodified whisker and polyamide 6. It can be inferred that the interfacial interaction force between the whiskers and matrix is a main factor in determining the dispersion quality. The tension strength σ_B of modified composites is greater than unmodified ones according to the data in Table III(a). It also confirmed that the degree of interfacial adhesion of modified composite is deeper.

Infrared spectroscopic characterization was undertaken to clarify the types of interfacial connection between whiskers and polymers. Comparing the IR spectra, potassium titanate whiskers separated from modified composites have four peaks at 3437.53, 3300, 2926.34, 2855.18, 1724.25, and 1548.70 cm^{-1}; while the other two do not have, as shown in Figure 1. These peaks represented the —OH, —CH_2, —C=O, and —NH groups, respectively, and suggest that the surface areas of modified whiskers were covered with nylon 6 molecules. Considering that the samples were washed many times before testing, we concluded that the nylon 6 molecule connected with the surface of potassium titanate whiskers by chemical bonds instead of physical absorption.[27,28] We conclude that the whiskers served as cross-linking points in composites. The connection of the whisker and polymer can be schematized, as the following:



SEM micrographs of the fracture surface of nylon 6–whiskers composites are shown in Figure 2. The configuration of whiskers in modified composites is vague, and most of the whiskers in composites are emerged in the matrix, which made the whiskers hard to discriminate. The whiskers of unmodified composites can be identified clearly in contrast, and their configurations are smooth and well defined. This suggests that the potassium titanate whiskers of modified composites have good dispersion qualities and adhesion degree with the nylon 6 matrix, and those of whiskers in unmodified ones are much worse. The deterioration of interfacial adhesion of unmodified composites can be explained by the previous statement we made that the high interfacial tension forces between whiskers and polymers decrease the wetting ability of whiskers in polymers, leading to the lowered

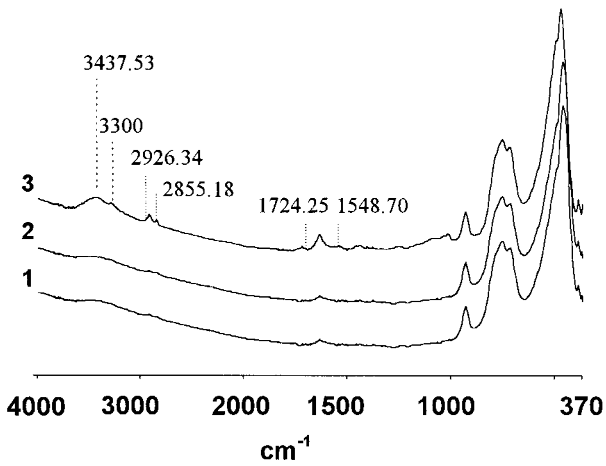


Figure 1 Infrared spectra of potassium titanate whiskers: (1) pure whiskers; (2) whiskers separated from unmodified composites; and (3) whiskers separated from modified composites.

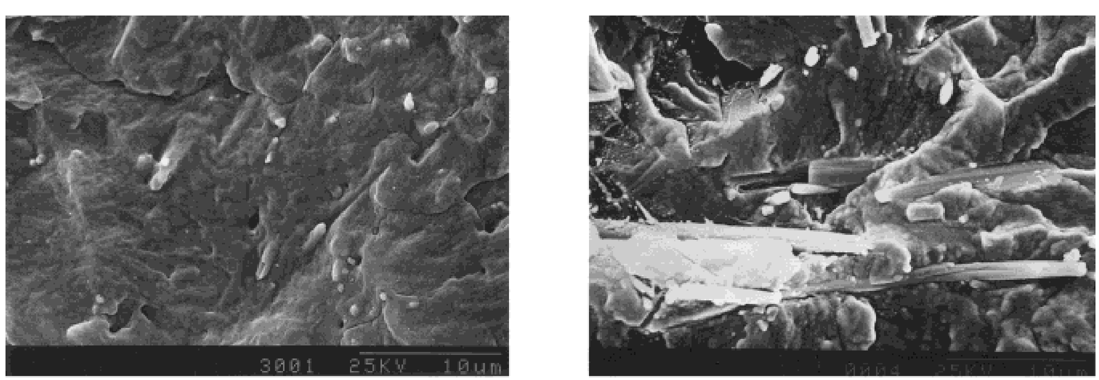
adhesion qualities. The better adhesion of coupling agent modified composites also supports the results of surface tension measurements and IR spectroscopic characterization.

Interfacial Effect on Mechanical Properties of Nylon 6–Potassium Titanate Whiskers Composites

The mechanical properties of the nylon 6–whiskers composites were examined, and the outcomes were shown in Table III(b). From the table, it can be seen that the tensile strength, modulus, and impact strength of modified composites are increased remarkably with the content of the whiskers rise, while the tendencies of unmodified composites are reversed. According to the above analysis, modified composites have good dispersion quality and interfacial adhesion degree between whiskers and polymers; so when under tensile stress, the force was transferred to the whiskers through interphase, and the whiskers become the receptor of the foreign force. According to the FT-IR results mentioned previously, the connection type between the polymer and coupling agent treated potassium titanate whisker is via convalent chemical bonds. If the tensile stress added on the composites is beyond a critical value, the damage of composites results from the destruction of the chemical bond between nylon 6 and the whisker, whose strength is much higher than the strength of cohesion between the whisker and polymer; this is the reason why the addition of coupling agent modified whiskers can improve the mechanical properties of composites. The deterioration of mechanical properties of unmodified composites appears to be related mainly to the high interfacial tension force between whiskers and polymers, which led to many defects and flaws in the areas of interphase and make the damage of composites consequently easier.

CONCLUSIONS

A composite with high modulus and high strength was obtained by *in-situ* polymerization, and dispersion quality of potassium titanate whiskers in the polyamide matrix and good interfacial adhesion between the polyamide and whiskers are the key points of this composite.



(a) (b)

Figure 2 Morphology of nylon 6–whiskers composites by SEM: (a) nylon 6–5%-treated whiskers; (b) nylon 6–5%-untreated whiskers.

Table III(b) Mechanical Properties of Nylon 6–Potassium Titanate Whiskers Composites

	Tensile Strength (MPa)	Tensile Modulus (GPa)	Impact Strength (ln-lbs)
Nylon 6	59.39	18.18	4.00
5% (untreated)	55.33	16.84	3.96
10% (untreated)	51.86	14.98	3.00
15% (untreated)	51.10	13.19	2.40
5% (treated)	70.24	23.40	6.74
10% (treated)	79.43	24.68	7.43
15% (treated)	86.03	31.96	7.97

Various characterization techniques have indicated that the interfacial tension forces and connection type between the whiskers and polymers are the two chief factors influencing the dispersion qualities, interfacial adhesion degrees, and mechanical properties of final composites. Furthermore, it also suggested that modified whiskers connected with nylon 6 matrix by chemical bond.

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