Synthesis of Boron-Containing Coupling Agents and Its Effect on the Interfacial Bonding of Fluoropolymer/TATB Composite

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ABSTRACT: The four kinds of boron-containing coupling agents were synthesized, which were applied to improve the interfacial bonding of fluoropolymer/1,3,5-triamino-2,4,6-trinitrobenze (TATB) composite. The boron atom of the coupling agent molecule can form coordinate bond with the fluorine atom of fluoropolymer; and hydrogen atom in its amino group can form hydrogen bond with oxygen atom in nitro-group of TATB. The interfacial performance of the composite was investigated by the measurement of contact angle, surface and interface tension, and adhesive work, and the interfacial bonding mechanism was studied by FTIR and XPS analysis. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 777–782, 2007

Key words: boron-containing coupling agent; fluoropolymer; interfacial bonding

INTRODUCTION

Fluoropolymers, especially only containing carbon and fluorine element, have low intermolecular cohesion force, weak interfacial bonding with gas, and very low surface tension, which leads to very poor compatibility with other materials.[1–3] 1,3,5-tri-amino-2,4,6-trinitrobenze (TATB) is a triclinic crystal with two molecules in a unit cell,[4] whose crystal structure is graphite-like with hydrogen-bonded sheets of molecules along the plane of the *a* and *b* crystallographic axes. There are very strong intra-molecular and intermolecular hydrogen bonds in its molecules, resulting in the very low surface energy and poor adhesive performance.[5] Adhesion between two phases relies on the property of interface, and forms an interface layer different from the bulk phase, which has significant influence on the mechanical properties of materials. Coupling agent, usually with organophilic and inorgano-philic terminals, can improve affinity between organic and inorganic components in the composite as a form of so called "molecular bridge" by the chemical and physical interactions. According to the coordinate bond theories, the molecules of fluoropolymer only have electron-donating ability, which shows very strong repulsive effect toward most materials with capability of donate electrons and very weak capability of accepting electrons, resulting in the chemical inertness. But for the materials with capability of providing the electron orbit, it can form a coordinate bond firmly with fluoropolymer. The boron is exactly the atom that can provide the empty orbit but form a coordinate bond with fluorine atom in the fluoropolymer.[6,7] In this work, the boron-containing coupling agents were synthesized, which were applied to improve the interfacial bonding of fluoropolymer/TATB composite.

EXPERIMENTAL

Materials

Fluoropolymer used in this work is a copolymer of vinylidene difluoride and chlorotrifluoroethylene. Both fluoropolymer and TATB used in this study were supplied by China Academy of Engineering Physics (Mianyang, China). Boric acid, *n*-octanol, ethanolamine, diethanolamine, lauric acid, butyl acetate (BA), and ethyl acetate (EA) were all supplied by Bodi Chemical (Tianjin, China), and silane coupling agent KH550 was a commercial product and supplied by Chengguang Chemical Research Institute (Chengdu, China).

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Preparation of the coupling agents

Trioctyl borate (CA-1)

The appropriate amount of boric aid and *n*-octanol were added to a flask with water separator, and benzene as azeotrope. The reacting system was heated to 140°C and kept reacting until no water came out. Then the product was purified by distillation under reduced pressure to remove benzene, water, and residuary *n*-octanol.

Boric acid/KH550 complex (CA-2)

Boric acid and KH550 with weight ratio 1:10 were dissolved in alcohol, and heated to 80°C while stirring under reflux condition. This reaction lasted about 2 h.

Triethanolamine borate (CA-3)

The appropriate amount of boric acid and ethanolamine were added to a flask with water separator, and toluene as azeotrope. The reacting system was heated to 110°C and kept reacting until no water came out. Then the product was purified by distillation under reduced pressure to remove toluene, water, and residuary ethanolamine.

Lauric acid diethanolamine borate (CA-4)

Lauric acid and diethanolamine with mole ratio 1 : 1.3 were added into a flask with stirrer, condensation tube, and thermometer, and were heated to 150°C and stirred for 2 h for conducting amidation reaction. The intermediate product diethanol-lauramide was obtained, which was purified through distillation under reduced pressure by using benzene as azeotrope. The appropriate amount of boric acid and the above synthesized diethanol-lauramide were added into a flask, and benzene was used as azeotrope. The reaction was conducted at 110°C under reflux condition for 3 h. The product was obtained after distillation under reduced pressure to remove benzene.

Preparation of the modified samples

Modified TATB

TATB (5 g), 1 g coupling agent, and 20 mL EA were added to a flask, heated to 80°C, and stirred for 20 min. After filtrating and washing, TATB was dried at 60°C under vacuum.

Modified fluoropolymer

The BA solution with 4 wt % fluoropolymer was prepared. Coupling agent with the content of 5 wt % of fluoropolymer was added into the solution, and

was heated to 80°C while stirring, and refluxed for 3 min at this temperature. The modified fluoropolymer solution was eventually obtained.

Flouropolymer/TATB composite

TATB was first dispersed in water. The above prepared BA solution with 4 wt % fluoropolymer was added into the water, and TATB can be capsulated by fluoropolymer. The Flouropolymer/TATB composite molding powder was obtained by distillation and drying.

Measurements

Contact angle

The contact angles of fluoropolymer solution in the presence of coupling agent on TATB tablet were measured by TY-82 contact angle test apparatus.

By using water and glycerol as testing liquids, the contact angles of TATB tablet modified by coupling agents with them were measured by ErmaG-1 contact angle test apparatus of Japan at room temperature by sessile drop method. The testing liquids, water and glycerol, had different dispersion and polar components for their known surface tension. The surface tension of TATB and flouropolymer was then evaluated from the measured contact angles with the testing liquids through the geometry average method.[8] Both polarity component (γ_s^p) and dispersion component (γ_s^d) contributions to the total surface energy (γ_s) were calculated.

Fourier-transform infrared spectrometer

The compositions of the synthesized compatibilizers were analyzed by Nicolet-560 Fourier-transform infrared spectrometer (FTIR), USA.

XPS

The electron binding energy (BE) of TATB surface elements before and after modified by coupling agent was measured by XSAM800 (UK) X-ray photoelectron energy spectrum with monochromatic MgK_α X-rays (1253.6 eV). All binding energies values were calculated relative to the carbon (C_{1s}) photoelectron at 284.8 eV. Spectrum background was subtracted according to Shirley. Spectra analysis was conducted with spectra deconvolution software XPSPEAK95 version 3.1 (Hong Kong). BE, height, full width at half maximum, and the Gaussian–Lorentzian ratio of component peaks were free parameters.
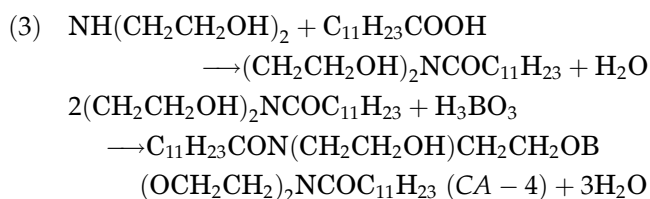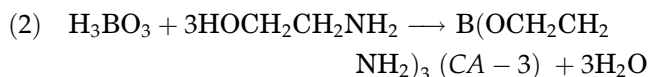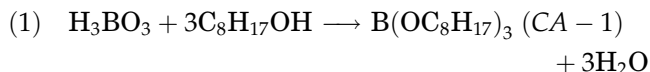
Brazil test

The compression strength, fracture strain, and compression modulus of the fluoropolymer/TATB composite

were measured by Brazil disc test; temperature 22°C, humidity 50%, and test speed 0.5 mm/min.
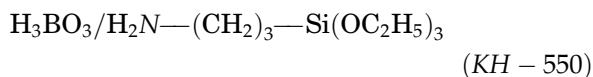
RESULTS AND DISCUSSION

Preparation of coupling agents

The reaction equations of synthesis of the boric-containing coupling agent are shown as follows:

(1) $H_3BO_3 + 3C_8H_{17}OH \longrightarrow B(OC_8H_{17})_3\ (CA-1)$
$$+ 3H_2O$$

(2) $H_3BO_3 + 3HOCH_2CH_2NH_2 \longrightarrow B(OCH_2CH_2$
$$NH_2)_3\ (CA-3)\ + 3H_2O$$

(3) $NH(CH_2CH_2OH)_2 + C_{11}H_{23}COOH$
$$\longrightarrow (CH_2CH_2OH)_2NCOC_{11}H_{23} + H_2O$$
$$2(CH_2CH_2OH)_2NCOC_{11}H_{23} + H_3BO_3$$
$$\longrightarrow C_{11}H_{23}CON(CH_2CH_2OH)CH_2CH_2OB$$
$$(OCH_2CH_2)_2NCOC_{11}H_{23}\ (CA-4) + 3H_2O$$

(4) CA-2 is the complex of boric acid /KH550 as follows:

$$H_3BO_3/H_2N\!-\!(CH_2)_3\!-\!Si(OC_2H_5)_3$$
$$(KH-550)$$

The composition of above synthesized coupling agents was analyzed by FTIR. As shown in Figure 1, for CA-1, the absorbance peaks at 2927.00 cm^{-1} and 2856.09 cm^{-1} were attributed to the stretching vibration of saturated methylene, the peak at 722.23 cm^{-1} was attributed to the characteristic absorbance of long chain alkyl, and the peaks at 1418.03 and 1068.05 cm^{-1} were attributed to the stretching vibration of B—O and C—O of borate group. For CA-3, the absorbance peaks at 3314.78, 3291.83, and 1566.97 cm^{-1} were attributed, respectively, to the stretching vibration and bending vibration of primary amino group H—N—H; the peaks at 1424.48 and 1076.95 cm^{-1} were attributed to the stretching vibration of B—O and C—O of borate group. For CA-4, the absorbance peak at 3360.15 cm^{-1} was attributed to the stretching vibration of hydroxyl group; the peaks at 2924.44 and 2895.99 cm^{-1} attributed to the stretching vibration of saturated methylene; peak at 717.7 cm^{-1} was attributed to the characteristic absorbance of long chain alkyl; the peak of stretching vibration of acrylamine C=O appeared at 1626.43 cm^{-1}; and the peaks at 1463.05 and 1073.50 cm^{-1} were attributed to the stretching vibration of B—O and C—O of borate group.

The effect of coupling agents on the interface of fluoropolymer/TATB composite

As shown in Figure 2, the boron atom of the coupling agent molecule can form coordinate bond with the fluo-
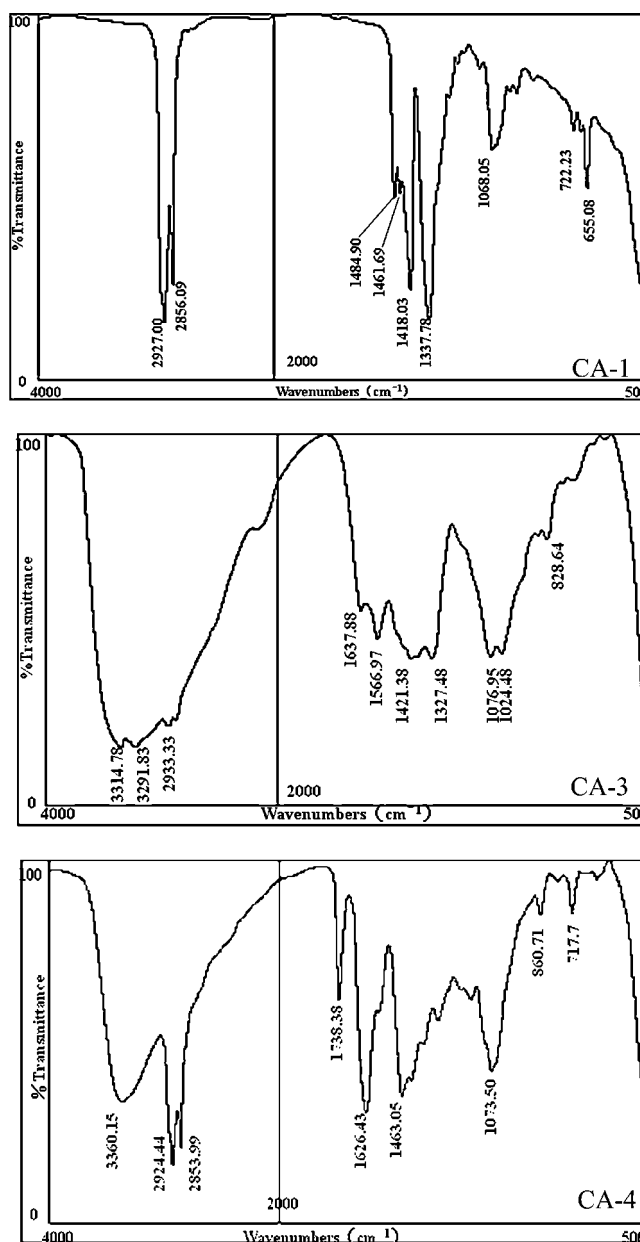

Figure 1 FTIR of the coupling agents.

rine atom of fluoropolymer;[6,7] and hydrogen atom in the amino group of the coupling agent molecule forms hydrogen bond with oxygen atom in nitro-group of TATB. By molecule design, octyl group was introduced into CA-1 to improve compatibility with fluoropolymer. CA-2, the complex of boric acid and KH550, contains both boron atom and amino group in the molecule. By replacing octyl group of CA-1 with ethanolamine, the amino group can be incorporated into CA-3 molecule. CA-4 molecule contains both amino group and long alkyl chain group in the molecule in the meantime.

Contact angle

As listed in Table I, after modified by the coupling agents, the contact angle of fluoropolymer solution on
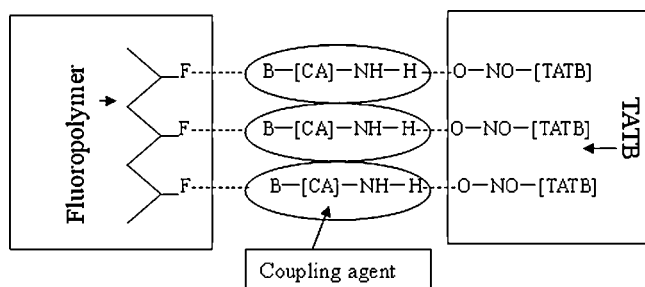
Figure 2 Schematic illustration of the effect of coupling agent on fluoropolymer/TATB composite.

TATB tablet changed compared with the blank sample in absence of coupling agents. CA-1 and CA-2 made the contact angle increase, CA-3 makes it remarkable decrease, and for CA-4, there was only a small increase of the contact angle. Contact angle characterizes the spreading ability of the solution on solid surface; for all solutions in presence of the coupling agents, the contact angles were below 90°, indicating that fluoropolymer solution modified by the coupling agents can spread well on TATB tablet; and it was substantially important for polymer composites.

Table II lists the contact angle of the testing liquids (water and glycerin) on fluoropolymer and TATB before and after modified by coupling agent. After modified by coupling agent, the contact angles of TATB with water all decreased and the contact angles with glycerin all increased except TATB/CA-4, which are more close to those of fluoropolymer.

Surface tension

Surface tension of solid (γ_s) contains both polarity component (γ_s^p) and dispersion component (γ_s^d).[9,10]

$$\gamma_s = \gamma_s^p + \gamma_s^d \tag{1}$$

The surface tensions of TATB and fluoropolymer can be calculated by the equation of geometry average method.[8]

$$\cos\theta = 2/\gamma_1 \times [(\gamma_1^d \gamma_s^d)^{1/2} + (\gamma_1^p \gamma_s^p)^{1/2}] - 1 \tag{2}$$

In the equation, θ is contact angle; γ_l is surface tension of liquid; γ_l^d and γ_l^p are, respectively, dispersion

TABLE I
Contact Angle of the BA Solution of Fluoropolymer/Compatibilizer on TATB

Coupling agent	Contact angle (°)
Blank	56.6
CA-1	73.2
CA-2	85.7
CA-3	39.6
CA-4	59.4

TABLE II
Contact Angle of Testing Liquids on TATB and Fluoropolymer

	Contact angle (°)	
	Water	Glycerin
TATB	65	50
TATB/CA-1	60	51
TATB/CA-2	53	57
TATB/CA-3	49	52
TATB/CA-4	54	43
Fluoropolymer	58	69

component and polarity component of liquid; γ_s^d and γ_s^p are, respectively, dispersion component and polarity component of solid. Equations (1) and (2) thus allow us to estimate γ_s via measurement of the contact angles of two liquids (water and glycerin) for which we know the values of γ_1, γ_l^d, and γ_l^p.

According to the above measurement values of the contact angle of testing liquids on TATB and fluoropolymer, and the surface tension of the testing liquids as listed in Table III, the surface tension of TATB and fluoropolymer can be calculated by eqs. (1) and (2), as displayed in Table IV.

After modified by the coupling agent, the dispersion component of TATB surface tension decreased, while the polarity component increased and the total surface tension had a large increase, indicating that modified with the coupling agents, the surface activity of TATB was improved, and can be adjusted to match with fluoropolymer, and their interfacial bonding was enhanced.

Interfacial tension and adhesive work

For the material with low surface tension, the interfacial tension γ_{12} can be calculated by harmonic average eq. (3) and adhesive work and be calculated by the eq. (4).

$$\gamma_{12} = \gamma_1 + \gamma_2 - [4\gamma_1^d\gamma_2^d/(\gamma_1^d + \gamma_2^d) + 4\gamma_1^p\gamma_2^p/(\gamma_1^p + \gamma_2^p)] \tag{3}$$

$$W_a = \gamma_1 + \gamma_2 - \gamma_{12} \tag{4}$$

in which γ_{12} is interfacial tension, γ_1 and γ_2 are surface tensions of two phases, d is dispersion component, and p is polar component.

Table V lists the results of the interfacial tension and adhesive work of TATB and fluoropolymer calculated by eqs. (3) and (4).

TABLE III
Surface Tension of Testing Liquids (20°C)

Testing liquid	γ_1 (mN/m)	γ_l^d (mN/m)	γ_l^p (mN/m)
Water	72.8	21.8	51.0
Glycerol	63.4	37.0	26.4

TABLE IV
Surface Tension of TATB and Fluoropolymer

Surface tension (mJ/m^2)	γ_s^d	γ_s^p	γ_s
TATB	30.1	13.2	43.3
TATB/CA-1	20.9	21.5	42.4
TATB/CA-2	6.7	41.7	48.4
TATB/CA-3	8.4	42.6	51.0
TATB/CA-4	24.2	23.5	47.7
Fluoropolymer	6.8	27.9	34.7

As shown in Table V, the interfacial tension of fluoropolymer/TATB in presence of the coupling agents decreased and adhesive works increased. CA-2 and CA-3 were more effective, resulting in the remarkable decrease of the interfacial tension of fluoropolymer/TATB, and the adhesive work increased to above 80 mN/m. Both CA-2 and CA-3 contained the same amino group with TATB; CA-1 without amino group had poor interaction with TATB molecule and showed strong interfacial bonding, while the hydrogen atom in the amino group of CA-4 was replaced by long alkyl chain group, which led to the decrease of the hydrogen-bond interaction with TATB.

The chemical stability of TATB

The chemical stability of TATB is important for its application, and it's necessary to consider if the change of the surface behavior of TATB affects its chemical stability. Figure 3 showed the FTIR of TATB modified by the coupling agents. Compared with TATB in absence of the coupling agent, no new absorbance peak appeared, indicating that coupling agents would not affect the chemical structure of TATB.

The interface bonding of fluoropolymer/TATB

XPS can detect the change of electron BE of elements on the TATB surface to probe out the bonding mechanism of fluoropolymer/TATB interface.

Table VI showed that after modified by the coupling agents, the electron binding energies of nitro-
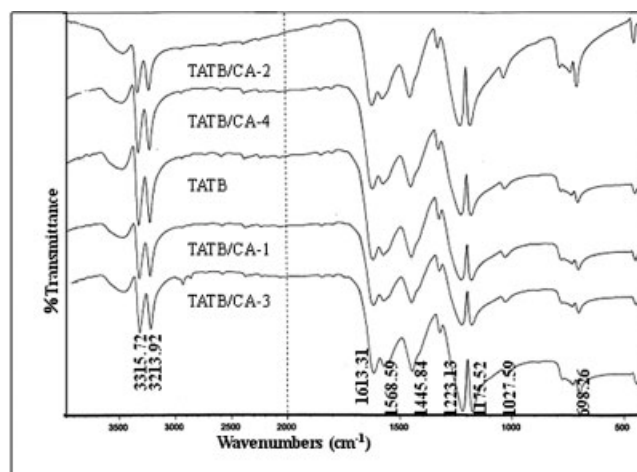

Figure 3 IR of TATB.

gen atom and oxygen atom on amino and nitro-group of TATB decreased, indicating that electron cloud flew toward TATB from the coupling agent molecule, and TATB withdrew the electrons of the coupling agents. The density of electron cloud of the external electron orbit of the atom increased, resulting in the decrease of the BE of electron on the internal orbit. The decrease of the BE of N and O belonging to NO_2 of TATB also led to the decrease of the BE of N belonging to NH_2 of TATB due to the induction effect of the benzene ring.[11–13] Especially, the decrease trend of the electron BE of oxygen atom of TATB facilitated the form of hydrogen bond between TATB and the coupling agents, and the hydrogen atom in amino group of the coupling agent molecules may form hydrogen bond with oxygen atom in nitro-group of TATB.

To further confirm the strong hydrogen bond between TATB and coupling agent, the mole ratio of amino-group and nitro-group of TATB surface (NH_2/NO_2) before and after modifying by the coupling agents were calculated, as shown in Figure 4.

The NH_2/NO_2 ratio of TATB surface in presence of CA-1 kept almost the same as the blank one, while it increased for other coupling agents, especially for CA-2 there was a remarkable increase of NH_2/NO_2 ratio, resulting from the strong hydrogen bond interaction. For CA-1, trioctyl borate, there was no amino-group in its molecule, and cannot form hydrogen bond with TATB.

Mechanical property

As shown in Table VII, CA-4 can improve break strength, compression strain, and modulus of fluoropolymer/TATB composite, which was an effective coupling agent for the composite. For CA-1 and CA-2, there was little change for the mechanical property of the composite, and for CA-3, compression strain and

TABLE V
Interfacial Tension and Adhesive Work of TATB and Fluoropolymer

Sample	Interfacial tension (mN/m)	Adhesive work (mN/m)
TATB	19.9	58.2
TATB/CA-1	8.0	69.2
TATB/CA-2	2.7	80.5
TATB/CA-3	3.2	82.6
TATB/CA-4	10.1	72.4

TABLE VI
The Electron Bonding Energy of TATB Surface Elements

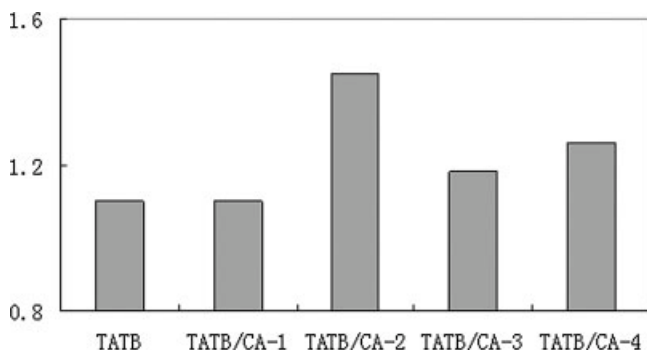| Bonding energy (eV)	N$_{1s}$		C$_{1s}$			O$_{1s}$
	NH$_2$	NO$_2$				
TATB	399.829	405.530	287.638	286.203	284.726	532.525
TATB/CA-1	399.804	405.502	287.655	286.210	284.800	532.507
TATB/CA-2	399.494	405.080	287.450	286.210	284.740	532.134
TATB/CA-3	399.544	405.239	287.466	286.180	284.710	532.254
TATB/CA-4	399.626	405.230	287.390	286.110	284.810	532.240

Figure 4 The mole ratio of NH$_2$/NO$_2$ of TATB surface.

break strength of the composite decreased although it improved the interfacial bonding of the composite remarkably. CA-3 is water soluble and may be easy to dissolve in water and cannot cover TATB particle very well during the preparation of the fluoropolymer/TATB composite molding powder in water.

CONCLUSIONS

Four kinds of boric-containing coupling agents were synthesized, and the modified fluoropolymer/TATB composite was prepared. The interfacial tension decreased, the adhesive work increased, and the interfacial bonding was improved remarkably for the composite through being modified by the coupling agents, in which, CA-2 and CA-3 showed the most obvious effect on the hydrogen bond between amino-group of the coupling agents and nitro-group of TATB, and coordination bond between boric atom of the coupling agents and fluorine atom of fluoropolymer. There was no influence on the chemical stability of TATB when modified with the coupling agents. The fluoropolymer/TATB composite modified by CA-4 showed relatively higher mechanical property.

TABLE VII
The Mechanical Properties of Fluoropolymer/TATB Composite

Sample	Break strength (MPa)	Compression strain (%)	Modulus (GPa)
Fluoropolymer/ TATB	4.62	0.077	12.3
Fluoropolymer/ TATB/CA-1	4.62	0.077	12.3
Fluoropolymer/ TATB/CA-2	4.56	0.078	12.3
Fluoropolymer/ TATB/CA-3	2.72	0.035	13.0
Fluoropolymer/ TATB/CA-4	4.95	0.081	12.9

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