Effect of Coupling Agents on Mechanical Property of AN/PU Energy Composite

DU SHIGUO, CHE JIANFEI, XIAO YINGHONG, JI FAXIANG, and JIN XIAOYING

Department of Polymer Material Science, Nanjing University of Science and Technology, Nanjing, 210014, China

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ABSTRACT: Silicon and titanate coupling agents are used to process the surface of ammonium nitrate (AN) particles in order to decrease their surface tension, improve affinity to the adhesive and the adhesive strength of the surface, and improve the mechanical property of an AN/polyurethane (PU) energy composite. SEM and ESCA analyses verify the effect of coupling agents on the mechanical property of the AN/PU energy composite. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 1259–1263, 1997

INTRODUCTION

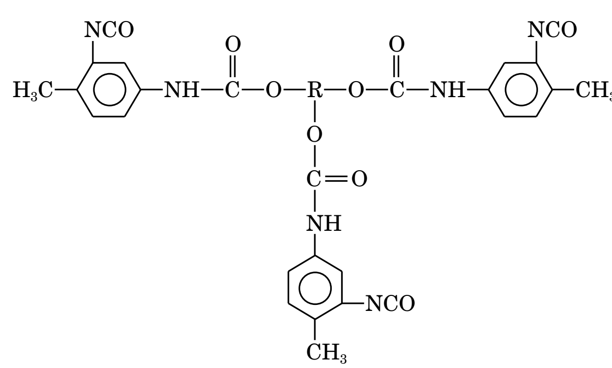
Ammonium nitrate/polyurethane (AN/PU) energy composite is a kind of high solid loading propellant with a low burning rate. It withstands great pressure in use. To avoid deformation and breakage, we must assure that it has good mechanical properties. The properties of AN, PU, and the interaction between them influences the properties, especially the mechanical property of AN/PU energy composite. PU adhesive is a kind of hydrophobic substance with low surface energy, and AN particles are hydrophilic with high surface energy. The difference results in strong interfacial tension and incompatibility in the interfacial zone. Therefore, the adhesive effect is not ideal on the interface of the whole composite.

To improve the mechanical property of an AN/PU energy composite, one method is to improve the adhesive strength by changing the properties of the adhesive, such as blending modification. This was studied in the previous investigation. We found that adding hydroxy-terminated polybutadiene (HTPB) to PU can obviously improve the adhesive strength. The other method is to utilize coupling agents to process the surface of the AN particles to improve the compatibility between the inorganic filler and the polymer adhesive. Therefore, interfacial adhesive effect is enhanced. This article mainly studies the effect of coupling agents on the mechanical property of an AN/PU energy composite.

EXPERIMENTAL

Materials

An isocyanate-terminated PU (ITPU) prepolymer had a molecular weight (MW) of 4500. It was synthesized with copolyether casting PU and toluene-2,4-diisocyanate.



Correspondence to: J. Faxiang

Table I Contact Angles of AN Particles in Different Kinds of Test Liquids

Coupling Agent (wt %)	Ethylene Glycol	Glycerol	Formylamine
—	15	30.5	11
A-1100 (0.5)	33	43	28
A-1100 (0.7)	42	66	40.5
A-1100 (1.0)	43	70	44.5
A-187 (0.5)	43	59	42
A-187 (0.7)	53	68.5	53.5
A-187 (1.0)	54	67	53
9S (0.5)	32	48	28
9S (0.7)	66.5	75	65
9S (1.0)	70	78.5	68
KR-138S (0.5)	40	56	37.5
KR-138S (0.7)	55	67	56
KR-138S (1.0)	57.5	72	59

Methylene-bis-*ortho*-chloroaniline (MOCA) was from Suzhou Advanced Chemical Factory (Jiangsu, China).

HTPB, MW 3000, was provided by Lanzhou Resin Factory (China).

AN was processed for anticrystal changing.[2]

Silicon coupling agents were γ-aminopropyltriethoxysilane (A-1100; Nanjing Chemical Factory, China) and γ-glycidoxypropyltrimethoxysilane (A-187; U.C.C).

Titanate coupling agents were isopropyl tridodecylbenzene sulfonyl titanate (KR-9S; Kenrich) and titanium di (dioctylpyrophosphato) oxyacetate (KRx138S; Kenrich).

Preparation

ITPU was blended with HTPB at room temperature. The benzene solvent and MOCA solidifying agent were added and mixed. Then residual solvent was removed under a vacuum condition. The blend was kept solidified at 50°C for about 36 h. An adhesive matrix blend sample was obtained after being demolded.

A coupling agent was added into the AN particles with toluene as the solvent. The mixture was refluxed, stirred for 2 h, distilled, suction filtered, and dried in a vacuum. AN samples with different surface properties were obtained.

The above AN particles and adhesive blend were mixed and molded. The correspondant AN/PU composite was thus prepared.

Test Methods and Instruments

According to Young's equation and the geometric-mean method,[3] the surface tension of the AN particles (γ_s) was calculated. The formula is as follows:

$$\gamma_{L1} - \gamma_{L2} + \gamma_{L1L2}\cos\theta = 2(\gamma_{L1}^d)^{1/2}[(\gamma_{L1}^d)^{1/2} - (\gamma_{L2}^d)^{1/2}] + 2(\gamma_s^p)^{1/2}[(\gamma_{L1}^p)^{1/2} - (\gamma_{L2}^p)^{1/2}],\ \gamma_s = \gamma_s^d + \gamma_s^p,$$

where γ_{L1} and γ_{L2} refer to the surface tension of testing liquid 1 and 2, respectively; $\gamma_{L1}\ \gamma_{L2}$ refers to the interfacial tension between liquid 1 and 2; and the superscripts d and p refer to dispersion (nonpolar) and polar components, respectively.

The contact angles of the AN particles were tested by the biliquid method.[4]

The tensile strength of the energy composite was tested according to GB 1040-79 (China).

A PHI 5300 ESCA system energy spectrum (Perkin–Elmer Corp.) was used to test the binding energy (O_{1s}, N_{1s}, C_{1s}) of the adhesive blend and the AN/PU energy composite.

RESULTS AND DISCUSSION

Effect of Coupling Agents on Contact Angles of AN Particles

The contact angles of AN particles are listed in Table I. The AN particles were processed by several different coupling agents. It is obvious that the contact angle changed with different coupling agents. This shows that the surface of the

Table II Surface Tension of AN Particles (10^{-3} N/m^2)

Coupling Agent (wt %)	γ_s	γ_s^d	γ_s^p
—	81.5	60.0	21.5
A-1100 (0.5)	76.2	58.4	17.8
A-1100 (0.7)	73.0	59.7	13.3
A-1100 (1.0)	71.1	59.5	11.6
A-187 (0.5)	61.5	47.7	13.8
A-187 (0.7)	54.5	43.4	11.5
A-187 (1.0)	56.9	45.3	11.6
9S (0.5)	70.2	53.8	16.4
9S (0.7)	52.3	42.9	9.4
9S (1.0)	50.6	41.9	8.7
KR-138S (0.5)	66.1	51.9	14.2

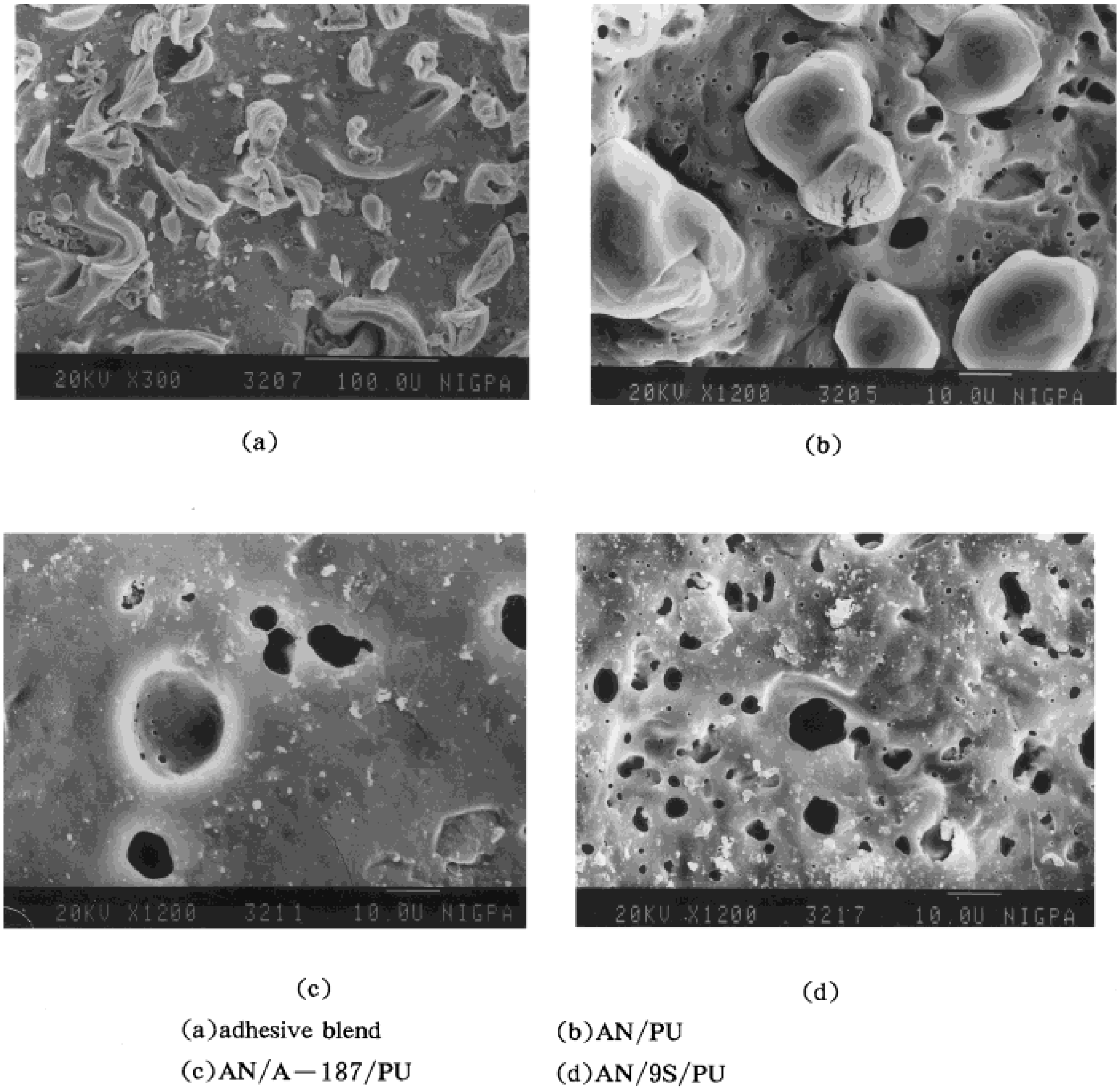


Figure 1 The SEM pictures of the adhesive and the energy composite: (a) adhesive blend, (b) AN/PU, (c) AN/A-187/PU, and (d) AN/9S/PU.

Table III σ_b**,** M_a**, and** W_a **of AN/PU Propellant**

Sample	Propellant	σ_b (MPa)	M_a	W_a (mJ/m^2)
1	AN/PU	3.08	1.33	100.6
2	AN/A-1100/PU	5.76	1.85	97.2
3	AN/A-187/PU	5.12	1.88	85.9
4	AN/9S/PU	3.81	1.72	81.8
5	AN/KR-138S/PU	3.48	1.48	80.3

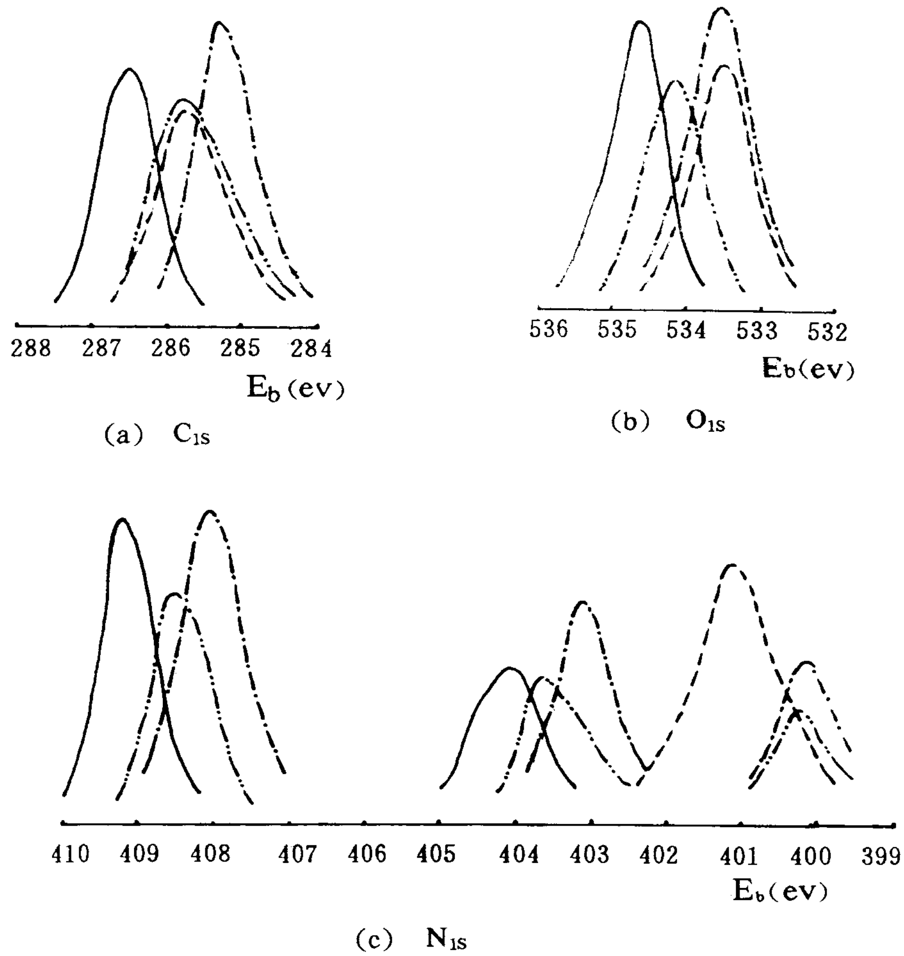


Figure 2 The ESCA spectrum of the adhesive and energy composites: (a) binding energy of C_{1s}, (b) binding energy of O_{1s}, and (c) binding energy of N_{1s}. (—) An particles, (– – –) HTPB-PU system, (– · –) AN/HTPB-PU energy composite; and (– · · –) AN/9S/HTPB-PU energy composite.

AN particles was covered with coupling agents and was converted to a hydrophobic substance. This resulted in the enlargement of the contact angle. The more the coupling agent was used, the larger the contact angle became. But excessive coupling agents will form multilayer physical adsorption, and this can decrease the strength of the material. Studies show that the best amount of coupling agent is 0.7–1.0 wt %.[5]

According to composite interfacial theory, surface tension is one of the important parameters that affect wetting absorptivity and adhesion, etc. The surface tension of AN particles is given in Table II (surface tension is calculated by contact angle).

Table II shows that the surface tension of AN particles decreased after coupling agents were used. This was because the polar groups of the AN surface reacted with the coupling agents, and AN surface was covered with the organic groups of the coupling agents. Therefore, surface polarity and surface tension decreased. Lowering the AN surface tension can improve the interaction with polymer adhesives and further improve the mechanical property of the AN/PU energy composite.

Mechanical Property of AN/PU Energy Composite

Tensile strength (σ_b), apparent crosslinking density (M_a), and adhesive work (W_a) of the AN/PU energy composite are given in Table III. These values were after blending modification of the adhesive (ITPU + HTPB) and processing of the AN particle surface.

According to surface wetting theory, the adhesive strength of an AN/PU energy composite without coupling agents is low although its adhesive work is high. This is because the surface energy of AN particles does not match that of the adhesive, so the interaction is weak. After processing with silicon coupling agents, the tensile strength of the propellant increases because AN particles have a better wetting effect and stronger chemical bonds with the adhesive.[6]

Concerning AN particles processed by titanate coupling agents, titanate coupling agents form one layer of molecules on the surface of the AN particles and long chains are vertical on the surface of the AN particles. This results in the fact that the surface of the AN particles changes to hydrophobic from hydrophilic; therefore, the interfacial compatibility is improved.[7] The enhancement effect of coupling agents is proportional to the apparent crosslinking density and adhesive work ($1.72 : 1.48 \approx 81.8 : 80.3 \approx 3.81 : 3.48$).

Interaction at Interface of AN/PU Energy Composite

The phase structures of the adhesive blend and the interfacial state were observed by SEM. The SEM pictures of the samples are given in Figure 1.

Figure 1(a) indicates that the adhesive blend is composed of discontinuous phase HTPB and continuous phase ITPU. The dispersion effect is fine. The two phases partially diffuse to each other. This shows that they have partial compatibility. Figure 1(b) is an AN/PU energy composite without any coupling agents. In the picture it can be observed that there is a definite phase interface between the AN particles and the adhesive, so the interfacial adhesion is not ideal. Figure 1(c,d) shows the AN/PU propellant processed by different coupling agents. The interface of the AN and the adhesive becomes ambiguous, and more AN particles are covered with adhesive. There is a transition layer between the two phases. AN particles also disperse more evenly. Therefore, coupling agents can reinforce the interaction between the AN particles and the adhesive.

The binding energy of the adhesive blend and energy composite were tested by ESCA. The results in Figure 2 shows that the nitrogen atoms of NH_4^+ and the adhesive yielded chemical shifts [Fig. 2(c)]. This means that the NH_4^+ group forms a chemical bond with the —NCO group. Additionally, oxygen atoms yielded a chemical shift. This probably resulted in a chemical effect between the —NCO groups and the coupling agents. It was also observed that not only the AN particles had interfacial effects with adhesive but the coupling agents also improved the adhesive strength [Fig. 1(d)]. This was one of the important reasons that the mechanical property of the AN/PU energy composite was improved.

CONCLUSION

Silicon and titanate coupling agents were used for processing the surface of AN particles, because can reinforce the interaction between the AN particles and the adhesive. After modification, the contact angle of the AN particles increased and surface tension decreased obviously. Then the dispersion of the AN particles was improved. The SEM and ESCA analyses proved the effect of the coupling agents. Using coupling agents is one of the important ways to improve the mechanical property of an AN/PU energy composite.

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