International Journal of Adhesion & Adhesives 110 (2021) 102954

Contents lists available at ScienceDirect

International Journal of Adhesion and Adhesives

journal homepage: www.elsevier.com/locate/ijadhadh

Effects of chlorinated polypropylene based-adhesives on the bonding performance of an epoxy core rod and polyolefin sheath for composite insulators

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ARTICLE INFO

Keywords:
Polyolefin
Epoxy
Chlorinated polypropylene
Adhesive
Bonding performance

ABSTRACT

One of the key technologies of composite insulators is the bonding between the core rod and sheath. This paper explores the use of chlorinated polypropylene-based adhesives to bond a polyolefin sheath material and an epoxy core rod. Dye penetration tests, bonding strength tests and water diffusion tests were carried out to evaluate the adhesiveness. The results demonstrated that the sample bonded by the chlorinated polypropylene/γ-methacryloxypropyltrimethoxysilane adhesive had the best interface tightness, and the bonding strength reached 7.34 MPa. Furthermore, the leakage current was as low as 41 μA after the sample was placed in boiling water for 100 h. This work provides a key bonding technology for polyolefin materials used as composite insulator sheaths.

1. Introduction

Composite insulators such as silicone rubber have been widely applied in electrical transmission lines around the world because they are light-weight materials with excellent anti-pollution flashover properties and easy installation [1]. In a composite insulator, the epoxy core rod and sheath are bonded by an adhesive. Excellent bonding performance is of paramount importance for the safe operation of composite insulators. Otherwise, poor adhesiveness may cause debonding, voids, etc., which may lead to interface breakdown [2], local heating [3], or abnormal fracture [4,5] of the core rod after long-term use. Researchers have put significant effort into evaluating and improving the adhesiveness between the core rod and silicone rubber sheath. For example, Gubanski and coworkers [6] designed an experimental set-up to test the impact of adhesion defects at the interfaces between the core rod and silicone rubber sheath in composite insulators. Liang's group [7] further demonstrated that this interface was the initial deterioration area of decay-like fracture. Zhao's group [8] improved the hydrolysis resistance of an epoxy core rod-silicone rubber sheath interface by changing the coating thickness of the silane coupling agent.

Polyolefin materials are commonly used for high-voltage cables [9–11] and dielectric energy storage capacitors [12] due to their excellent mechanical strength, thermal properties, chemical resistance, and electrical insulation. Very recently, our group explored the possibility of using polyolefin materials for the hard shed (sheath) of a composite insulator [13]. To further meet the application requirements of polyolefin materials for composite insulators, effective bonding between the core rod and polyolefin sheath becomes an urgent problem to be solved. This paper proposes the use of chlorinated polypropylene (CPP)-based adhesives to bond an epoxy core rod and polyolefin sheath. The interface tightness, bonding strength, and hydrolysis resistance of the core rod-sheath samples were studied. The results showed that the CPP-based adhesives effectively bonded the epoxy core rod and polyolefin sheath, which provided superior bonding for polyolefin composite insulators.

2. Experimental

2.1. Materials

The polyolefin sheath material was prepared according to a previous procedure [13], and the epoxy core cord was produced by Zhejiang Golden Phoenix Electrical Co., Ltd., China. CPP (containing 24% Cl) was provided by Shanghai Luanding Industrial Co., Ltd., China. γ-Methacryloxypropyltrimethoxy-silane (KH570) was purchased from Nanjing Pinning Coupling Agent Co., Ltd., China. Polymethylene

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https://doi.org/10.1016/j.ijadhadh.2021.102954
Received 18 February 2021; Accepted 7 July 2021

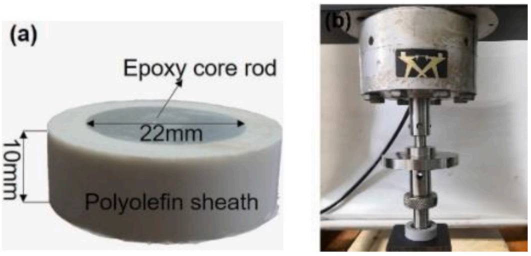

Fig. 1. Photos of bonding strength test: (a) the core rod-sheath sample; (b) the testing setup.

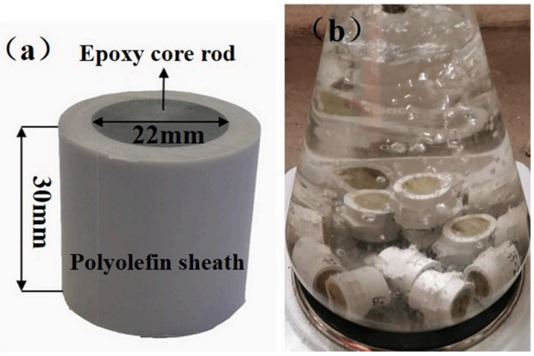

Fig. 2. Photos of boiling test: (a) the core rod–sheath sample (b) the boiling process.

polyphenylpoly-isocyanate (PMDI) was produced by Mitsui Chemicals, Japan. Pentanone solvent was analytical reagent grade and purchased from a commercial source.

2.2. *Preparation of epoxy core rod-polyolefin sheath samples*

Epoxy core rod-polyolefin sheath samples were prepared according to the following procedure. First, CPP was dissolved in pentanone to prepare a 20 wt% CPP solution as the CPP adhesive. The surface of the core rod (22 mm in diameter and 300 mm in length) was coated with the adhesive. The thickness of the adhesive was 15–20 μm. The core rod was dried at room temperature for 10 min and then dried at 90 °C for 2 h. After that, the core rod was placed in the cavity of an injection machine, and the polyolefin material was injected at 200 °C to generate a sheath around the core rod to produce a long epoxy core rod-polyolefin sheath sample. The core rod of sample 1# was coated with the CPP adhesive, the core rod of samples 2# and 3# was coated with CPP/PMDI (100:10) and CPP/KH570 (100:4) mixed adhesive, respectively. Sample 0# was a control sample without adhesive.

2.3. *Dye penetration tests*

The dye penetration tests were carried out according to the National Standard of China (GB/T19519-2014). The length of the core rod-sheath samples was 10 mm and the diameter of the core rod was 22 mm. The samples were placed on a layer of steel balls (diameter: 2 mm) in a tray. A solution of 1 wt% methylene red dye in ethanol was poured into the tray, and its level was 2 mm higher than that of the balls. After dye penetration for 16 min, the core rod-sheath interfaces were examined and photographed. The acceptance criteria for this test is that no dye should rise through the core rod-sheath interface.

2.4. *Bonding strength tests*

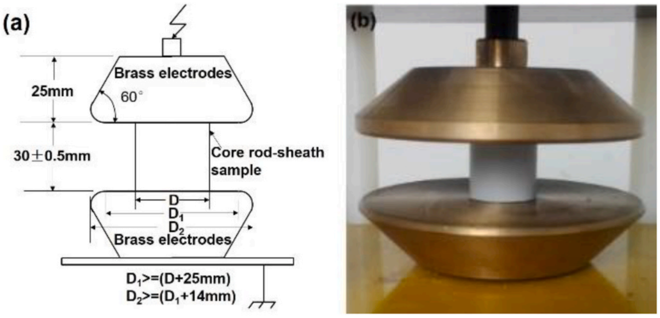

Fig. 3. Instrument for measuring the water diffusion leakage current.

The bonding strength tests of the core rod-sheath samples were carried out in accordance with the National standard of China (GB/T11177-1989). A core rod-sheath sample was fixed on an INSTRON 3366 equipment platform, and a compressive force was applied to the core rod at 2 mm/min to move the core rod down until it was completely detached from the sheath. Compressive shear forces corresponding to different compressive displacements were recorded. The bonding strength was calculated from the maximum compressive shear force per unit bonding area. Fig. 1 shows the core rod-sheath sample used for the bonding strength tests.

2.5. *Water diffusion tests*

According to the National Standard of China (GB/T19519-2014), 100 h water diffusion tests were carried out. The core rod-sheath sample for the water diffusion test and the boiling process are shown in Fig. 2.

Before tests, the surface of the core rod-sheath samples was cleaned with isopropanol and wiped with filter paper. Then, the samples were immersed in a bottle containing deionized water with 0.1 wt% NaCl. After being boiled for 100 h, the samples were cooled in tap water for at least 15 min. Afterwards, the samples were removed from tap water one-by-one, and the surface was dried with filter paper. Immediately, the core rod-sheath sample was tested for leakage current using a brass electrode. The test voltage increased to 12 kV at a rate of 1 kV per second. The test voltage was held at 12 kV for 1 min, and the maximum leakage current was recorded during this period. Five samples were used for each adhesive type to detect the current, and the recorded leakage current was the average value of five samples. The instrument used to measure the water diffusion leakage current is shown in Fig. 3.

2.6. *Scanning electron microscopy (SEM)*

The microscopic morphology of the interface of the core rod and sheath was observed using an S-3400 scanning electron microscope (SEM, Hitachi, Japan).

3. Results and discussion

3.1. *Tightness of the core rod-sheath interface*

CPP is a thermoplastic resin that has been widely used in polyolefin coatings, adhesives, ink carriers, and other fields [14–18]. In this work, CPP was dissolved in pentanone and used as the main component to bond the epoxy core rod and polyolefin sheath. The non-polar part of CPP (polypropylene segments) can infiltrate the polyolefin resin and entangle with the polyolefin molecular chains. Then, CPP and polyolefin simultaneously crystallized [15,19]. The -Cl substituent in CPP was connected with the polar groups of epoxy materials through electrostatic interactions and mutual diffusion [20]. Consequently, the epoxy core rod and polyolefin sheath were bonded by CPP. We also added some PMDI and KH570 to the CPP adhesive, respectively, to modify the adhesion of CPP to the epoxy core rod. To assess the tightness of the core

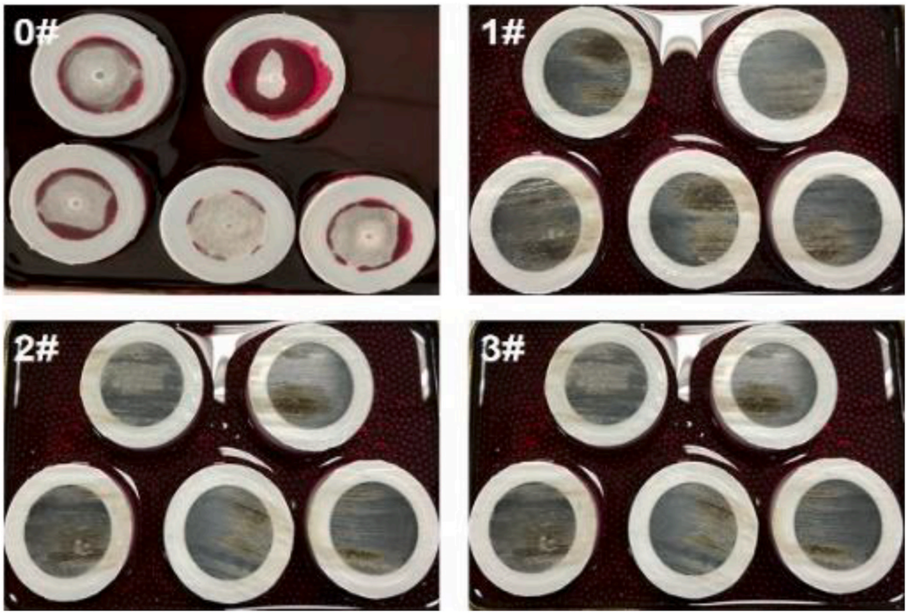

Fig. 4. Dye penetration photos of different core rod-sheath samples.

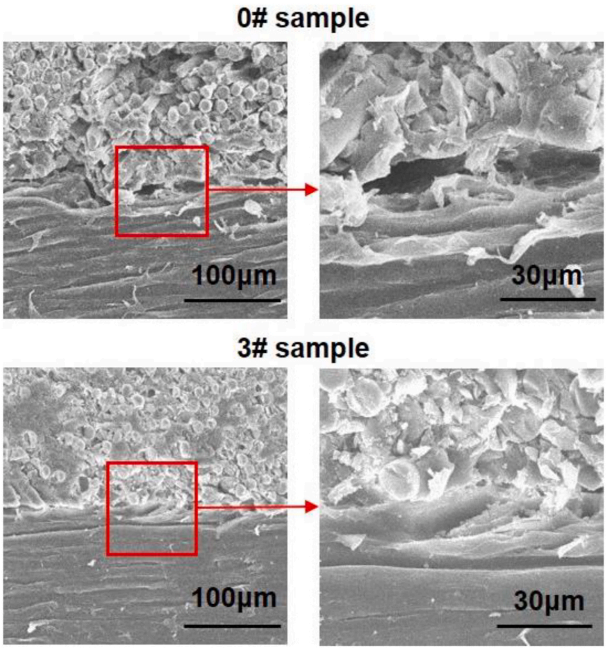

Fig. 5. Micromorphology of the core rod-sheath interface.

rod-sheath interface, the injection-molded core rod-sheath sample was cut into 10-mm-long samples for dye penetration tests. After tests, if no red dye rose through the interface by capillary action, this indicates that the interface tightness is excellent.

The prepared samples were placed in a red dye solution for 16 min, and all the core rod-sheath interfaces were examined carefully. The dye penetration photos of the samples are shown in Fig. 4. In the case of samples without an adhesive (sample 0#), there was obvious red dye exudate on the interface, indicating that the interface tightness was poor, and voids existed at the interface. For comparison, no dye rose through the interfaces of samples 1#, 2#, or 3# due to the following reasons: For sample 0#, after the polyolefin was injected at 200 °C to generate a sheath around the core rod, the shrinkage degree of the inner epoxy core rod and outer polyolefin sheath was quite different due to the different thermal expansion coefficients during cooling. This produced voids at the interface. When the core rod was coated with CPP-based adhesives (samples 1#, 2#, and 3#), the samples shrank in tandem because the interfaces were bonded tightly by the adhesive.

To further discriminate the interfacial tightness of the samples, the micromorphology of the interface was observed using SEM. Here, we selected SEM images of samples 0# and 3# for comparison (Fig. 5). There were obvious voids (about 30 μm in length) at the interface of sample 0#, but the interface of sample 3# was tight with no visible voids. The SEM images confirmed the results of the dye penetration test.

3.2. *Bonding strength*

To evaluate the adhesiveness of the core rod and sheath, we tested their bonding strengths. The compressive shear force-displacement curves of different samples were obtained by the compressive mode on an INSTRON 3366 tester. The bonding strength was calculated by dividing the maximum compressive shear force by the bonding area.

Fig. 6 shows the compressive shear force-displacement curves of different samples, and the obtained bonding strengths are outlined in Table 1. The compressive shear force of all samples remained ~60 N at compressive displacements from 0.1 mm to 0.4 mm, regardless of the adhesive type or without an adhesive (Fig. 6b). This was attributed to the slight deformation of the polyolefin sheath when the compressive displacement was smaller, which produced the same compressive shear force of ~60 N. It can also be seen from Table 1 that the bonding strength of sample 0# was only 0.20 MPa, which may be due to static or dynamic friction. When coated by the CPP adhesive, the bonding strength of sample 1# greatly increased to 3.99 MPa, demonstrating that CPP adhered tightly to both the epoxy core rod and polyolefin sheath. Furthermore, the bonding strength was improved by adding PMDI or KH570 to the adhesive. The bonding strength of sample 3# was highest, reaching 7.34 MPa.

The role of KH570 can be explained as follows: The silane coupling agent was adsorbed on the core rod surface and hydrolyzed to generate silanols $RSi(OH)_3$ in a humid environment. Under heating, the silicon hydroxyls groups reacted with the hydroxyl groups on the core rod surface to form chemical bonds. Meanwhile, the hydroxyl groups of free silanols condensed and oligomerized with each other to form a network structure entangled with CPP, which improved the bonding strength of the sample [21–23].

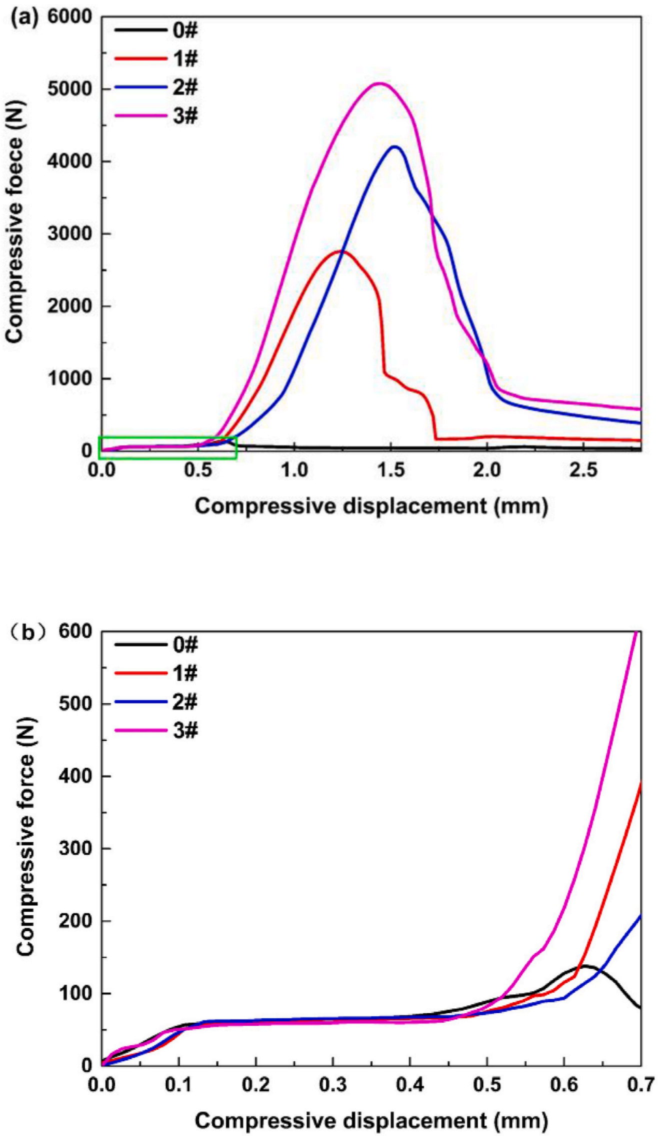

Fig. 6. Compressive shear force-displacement curves of different core rod-sheath samples.

Table 1
Results of the bonding strength tests.

Sample	Adhesive	Bonding strength (MPa)
0#	Without adhesive	0.20
1#	CPP adhesive	3.99
2#	CPP/PMDI mixed adhesive	6.08
3#	CPP/KH570 mixed adhesive	7.34

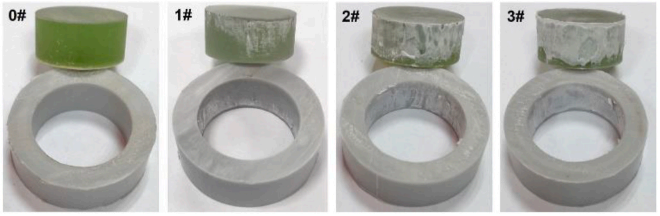

Fig. 7. Photos of the separated core rod and sheath after bonding strength tests.

Table 2
100 h water diffusion leakage currents of the samples.

Sample	Leakage current (μA)	
	Before test	After being boiled for 100 h
Core rod	34	35
Sheath	31	32
0#	38	>2000
1#	39	625
2#	38	105
3#	37	41

Table 3
Water absorption of the adhesives at 25 °C.

Sample	Water absorption (%)					
	1 d	15 d	30 d	45 d	60 d	75 d
CPP film	0.97	6.71	7.45	8.69	9.93	10.5
CPP/PMDI film	0.43	1.2	1.72	1.97	1.97	2.06
CPP/KH570 film	0.35	0.58	0.64	0.70	0.82	0.87

After bonding strength tests, the separated epoxy core rod and polyolefin sheath were observed to evaluate the adhesiveness. The photos of the separated samples are shown in Fig. 7. Except for sample 0#, there was polyolefin residue on the core rod surface, confirming the bonding effect of the CPP-based adhesives. In particular, the inner side of the polyolefin sheath of sample 3# was seriously damaged, which was consistent with the maximum bond strength.

3.3. *Water diffusion tests*

The leakage current of core rod-sheath samples can be used to intuitively characterize the hydrolysis resistance of an interface during water diffusion tests. First, the sample was put into deionized water containing 0.1 wt% NaCl and boiled for 100 h. After cooling in tap water for at least 15 min, the surface of the sample was dried with filter paper. Immediately, the core rod-sheath sample was tested for a leakage current. As a comparison, the separate core rod and sheath were also tested.

Table 2 outlines the leakage currents of the samples before and after being boiled for 100 h. Usually, the total leakage current of a core rod-sheath sample consists of the currents of the sheath surface and interface, along with the volume currents of the core rod and sheath. From Table 2, both the leakage current changes of the core rod and sheath were very small (only increased by 3%), verifying the excellent hydrolysis resistance of the epoxy core rod and polyolefin sheath. However, the leakage current of sample 0# increased dramatically after being boiled, reaching more than 2000 μA. These results indicated that NaCl solution permeated into the interface, and water might be stored in the voids of the interface of sample 0#. Compared with sample 0#, the leakage currents of samples 1#, 2# and 3# decreased significantly. The leakage current of sample 3# bonded by the CPP/KH570 mixed adhesive only achieved a minimum of 41 μA, which was comparable to those of the naked core rod and sheath, exhibiting excellent hydrolysis resistance. This finding revealed that the hydrolysis resistance of the core rod-sheath interface could be greatly improved by adding a silane coupling agent to the CPP adhesive, effectively preventing the NaCl solution from penetrating into the interface.

Table 4
Water absorption of the adhesives at 100 °C.

Sample	Water absorption (%)			
	24 h	48 h	72 h	100 h
CPP film	107	165	188.5	201.6
CPP/PMDI film	36.4	67.1	97	128.3
CPP/KH570 film	23.6	46.8	73.9	91.7

Since the interfacial tightness of samples 1#, 2#, and 3# was similar, as revealed by the dye penetration tests, different leakage currents may result from the water resistance of the adhesives. For this reason, we compared the water absorption of the adhesives. Three CPP-based adhesive solutions were poured onto a Teflon plate and dried at 90 °C for 6 h. After cooling, 20 mm × 20 mm × 2 mm adhesive films were prepared. The films were immersed in water to test their water absorption. Table 3 and Table 4 show the water absorption of the adhesives at different temperatures. CPP/KH570 and CPP/PMDI films absorbed much less water than the CPP film. When the CPP adhesive was modified by KH570, there was more than a 91% and 54% decrease in the water absorption at 25 °C for 75 d and 100 °C for 100 h, respectively. The results revealed that the CPP/KH570 film had the lowest water absorption, indicating the best water resistance.

4. Conclusions

This work investigated the effects of CPP-based adhesives on the bonding performance of an epoxy core rod and polyolefin sheath for composite insulators. The core rod-sheath sample bonded by the CPP adhesive presented excellent interface tightness and high bonding strength. Furthermore, its hydrolysis resistance was significantly improved by the addition of a silane coupling agent. The core rod-sheath sample bonded by the CPP/KH570 mixed adhesive had the maximum bonding strength of 7.34 MPa and the lowest water diffusion leakage current of 41 μA. This work presents a key bonding technology for polyolefin materials used as novel composite insulator sheaths.

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