Viser Technology Pte. Ltd.
Research and Application of Materials Science
DOI: 10.33142/rams.v6i2.14586

Research Article Open Access

Surface and Interfacial Bonding with Epoxy Adhesive of Flame Retardent Acrylonitrile-Butadiene-Styrene Copolymers (ABS)

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Abstract

Flame retardants were widely used to expanding applications of acrylonitrile-butadiene-styrene copolymers (ABS) to daily life, heat generation, and energy storage. However, effect of flame retardants on surface properties such as wettability, adhesion and epoxy resins affinity were few studied. In this work, surface, epoxy resin adhesive as well as curing condition of ABS/ FRABS were investigated systematically. Results showed that processing temperature changing the ABS-flame retardant mixing from liquid-solid to liquid-liquid and affect the interface shear bonding strength. Best processing of rebonded ABS samples were curing under 0.7 kg, in 60 ℃ for 2 hours. Adhesion of epoxy to ABS/ FRABS remained for 90 days under soaking in 40 wt% sulfuric acid, showing the obvious chemical stability.

Keywords: *ABS; Flame retardant; Epoxy resin; Surface adhesion*

1 Introduction

As a typical common amorphous plastics, acrylonitrile-butadiene-styrene co-polymers (ABS) was widely-used in automobile, electrical industry, decoration, biology, and aerospace as substrate or sealing materials, which requires tough and robust bonding with heterogeneous materials, including polymethyl methacrylate (PMMA)[1], nylon[2], epoxy resin, nickel[3], silver[4], copper[5], and so on. However, almost all ABS the researches were neat ABS containing few additives. For industrial application, ABS was not fabricated independently, but used as a major component mixed with several chemical agents especially flame retardants, fillers, or other polymers via solution or melting blending. One of the most important components was flame retardant. Flame retardant overcome the drawbacks ABS's burning behaviors to ensure the safety and reduce the risk of fire accidents. Recently, conventional flame retardant like Br-Sb_2O_3 flame retardant systems [6-8] and halogen-free flame retardant systems[9-12] were developed. For combining high properties of ABS, such as toughness, fluidity, heat stability, weatherability, stress crack resistance and heat-sealing adaptability, with flame retardancy, Br-Sb_2O_3 flame retardants were applied for ABS generally.

Therefore, the application of flame retardant ABS (FRABS) was expanded to battery as structural part, which required secondary sealing materials. Between ABS and secondary sealing materials are epoxy resins adhesive usually. As the consequence, the robustness of the battery is linked with the adhesion of ABS-epoxy adhesive and secondary sealing materials-epoxy adhesive intensively. Worse adhesion induces leakage of battery contents or contamination under real circumstances including collision and vibration. However, flame retardants affect the surface condition deeply. ABS commercially adaptable flame retardant contains Br element and aromatic/ heteroaromatic ring mainly. Nowadays, few works evaluated the effect of flame retardant onto the ABS surface, which limited the further applications. In this work, surface, epoxy resin adhesive as well as curing condition of ABS/ FRABS were investigated systematically.

2 Experimental

2.1 Materials

ABS (PA-757) were purchased from Qimei Co. Ltd., China (Taiwan). Tetrabromobisphenol A (FR-1524), was purchased from Dead Sea Mromine Co. Ltd.. Bromotriazine (FR-245) and Decabromodiphenylethane (DBDPE, 4010) were purchased from Albemarle Corporation, U.S.A.. Brominated Epoxy Resin

Received on September 6th, 2024; Accepted on October 16, 2024

(CXB-714C) was purchased from Woojin Copolymer Co., Ltd.. South Korea. Antioxidant 1010 and 168 were purchased from Ciba Specialty Chemicals, Co., Ltd.. Switzerland. Lubricant (EBS) were purchased from Nanjing Guochen Chemical Co., Ltd. China. Mineral oil (O-WO1) were purchased by Liaoning Oxiranchem Inc. China. Anti-dripping agent SN80-SA7 were purchased by Guangzhou Entropy Polymer Technology Co., Ltd.. ABS powder with high rubber (HR-181) were purchased from Kumho, Korea. Sb_2O_3 (S-05N) were purchased from Yunnan Muli Antimony Industry Co., Ltd. China. Epoxy adhesives (5212B) and the hardeners (5212H) were purchased from First Li-Bond (Wuxi), Co. Ltd., China.

ABS and FRABS were prepared via injection molding. First, 0.1 phr of antioxidant 1010, 0.2 phr of antioxidant 168, 0.3 phr of lubricants EBS-50, 0.2 phr of anti-dipping agent SN3306, 0.2 phr white oil were mixed by high speed mixer (Keda Machinery, China) and added with the others according to Table1 into a twin screw extruder (SHJ-30, Nanjing Ruiya, China) with the temperature between 180 to 210 ℃, main engine speed of 1020 r/min, feeding speed of 400 r/min. As-received ABS/ FRABS pellets were dried for 4 hours at 80 ℃. Standard testing samples were formed by an injection molding machine (Un90SK II-V, Yizumi, China).

2.3 Characterizations

Tensile strengths, bending properties, Izod impact strengths were tested according to GB/T 1040—2006, GB/T 9341—2006, GB/T 1843—2008, respectively.

Besides, the adhesive strength were conducted via a self-developed method: standard tensile samples were molded according to GB/T 1040.2-2022, with the thickness of 3.2 mm, the width of 12.7 mm in narrow part and 19.0 mm in wide part, the gauge length of 60 mm and the total length of 220 mm.

Evaluation of adhesive strength were conducted as below shown in Figure 1: After molding, ABS/ FRABS tensile samples were cut into two parts evenly and epoxy adhesives were coated onto the surface near the cutting sides. The two parts were rejointed and cured under heating. The prepared samples were tested with tensile strength (fracture). The adhesive strengths were defined as the tensile strength/ coated area. Contact angle were tested by a an optical contact angle meter (OCA35, Dataphysics) with water and diiodomethane. Besides, critical surface tensions were calculated by extrapolation method based on the contact angle results.

Anti-chemical properties were conducted as below: The re-bonded FRABS were cured under the load of 0.5 kg, after curing in an oven at 60 ℃ for 2 hours. After placing into standard environment 24 hours, the samples were transferred into a vessel containing 40% sulfuric acid solution. Then the vessel was placed in an oven at different temperatures for different aging time. A tensile test (5% tensile rate) was carried out after being cleaned and placed for 24 hours.

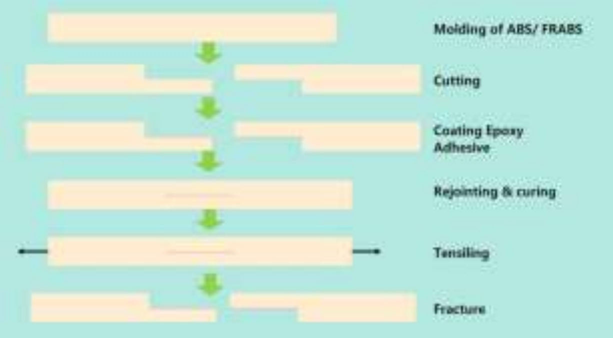

Figure 1 Illustration of the evaluation of adhesive strength

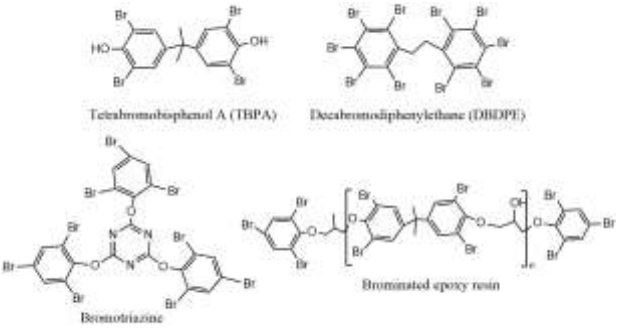

Figure 2 Chemical structure of flame retardants used in this work

Table 1 Major formula of prepared samples

	Content/ phr						
	ABS PA-757	HR-181	FR-1524	FR-714C	FR-245	FR-4010	S-05N
ABS	90	10					
TBPA	65	10	20				5
Br-Epoxy	65	10		20			5
Br-Triazine	65	10			20		5
10-Br	65	10				20	5

3 Results and Discussions

3.1 Surface adhesion of ABS/ FRABS onto epoxy adhesive

As Figure 3a showed, flame retardants affected the interfacial bonding deeply, for the interfacial shear binding strength of groups of Br-Triazine and 10-Br increased increased obviously white TBPA and Br-Epoxy not. Segments of ABS including were with middle polarities and providing hydrophilicity as well as adhesive capability, which were inferior to oxygen groups. There was a probable reason: Hydroxyl groups of TBPA and Br-epoxy existed. However, surface wettabilities and critical surface tensions displayed in Figure 3b showed that there were alomst no obvious differences between different FRABS; Therefore, the surface functional groups were not the dominant factors.

Another explanation was the gap of melting points of the four flame retardants: Br-epoxy (100～110 ℃ liquid in 200 ℃), TBPA (178～181 ℃ (Br-epoxy, liquid in 200 ℃), Br-Triazine (220～230 ℃, solid in 200 ℃), 10-Br (357 ℃, solid in 200 ℃), which resulted in the transformation of ABS-flame retardant surfaces from liquid-liquid to liquid-solid. As for ABS matrix, liquid-liquid interfaces improved the disaggregation and the effect of two-screw shearing undoubtedly. However, for surface, liquid-liquid interfaces formed smoother surface and molecular chains with higher density. What's more, liquid phase flame retardant occupied the space of electron-rich groups such as -C=C-, -Ar, and -C≡N. In another word, the introductions of Br flame retardant represented that the hydrogen atoms were replaced by the electrophilic bromine atoms, which were harmful for the adhesion from epoxy resins because of weaker Van der Waals force.

For solid-liquid surfaces, because of the internal force, the stress from tougher fillers promoted the relaxation of surface molecular segments. Many researches reported that introduced of fillers lowered the interfacial adhesion. Sb_2O_3 was existed in all the FRABS in this work, however, effect of Sb_2O_3 onto surfaces were limited by the differential of chemical structures between Sb_2O_3 and matrix. The differences of liquid-liquid and liquid-solid were also effected on the mechanical properties. As Figure 3c showed, toughness of FRABS with liquid-solid mixing were weak as the result of segregation and stress concentration. Therefore, for future researches, to realize liquid-solid mixing and avoid large segregation simultaneously were urgent to be solved.

3.2 Curing process

Curing of epoxy is a volume shrinking stage, which induces crosslinking and liquid-solid transformations. As a result, although epoxy net chains can infiltrate ABS/ FRABS, volume shrinking improved the separation of molecular chains from epoxy-ABS/ FRABS surfaces. Thus, there were a conflict tendency: epoxy with higher crosslinking density gave the epoxy resins higher strength but lowered the interfacial shearing strength and vice versa. On the other hand, applying pressures during all the curing stage were a common solution to improve interfacial bonding as well. Density of contact surface of epoxy net chains and ABS net chains was improved, vapor was extruded, separation tendency was restricted because of the pressures. Nevertheless, pressures will extruded epoxy, lowered the thickness of adhesive layers, and restricted the motion of epoxy resins net chains. Therefore, this section would discuss the optimal processes.

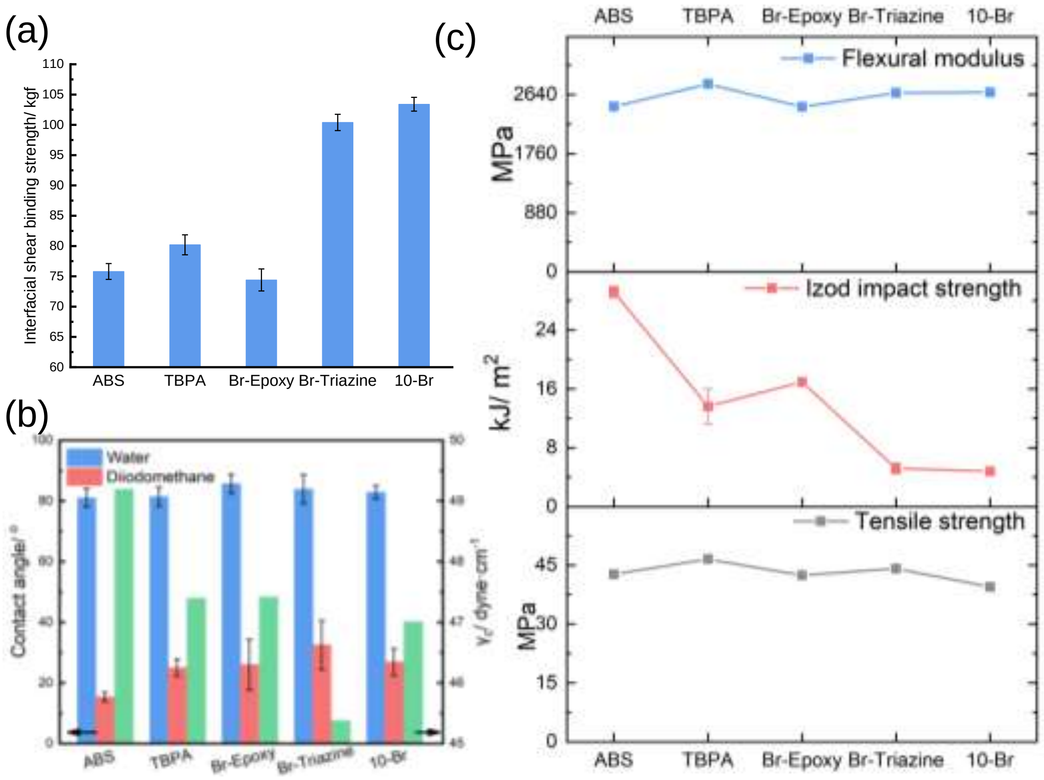

Figure 3 (a) Interfacial shear binding strength (Cured at 60 ℃ for 2 hours under 0.7 kg loading), (b) Water/ diiodomethane contact angle and critical surface tension (γc) (c) Mechanical properties of different ABS/ FRABS

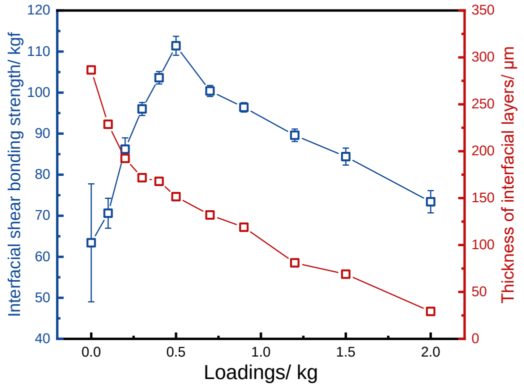

Figure 4 Interfacial shear binding strength and adhesive thickness of different curing load (Cured at 60 ℃ for 2 hours)

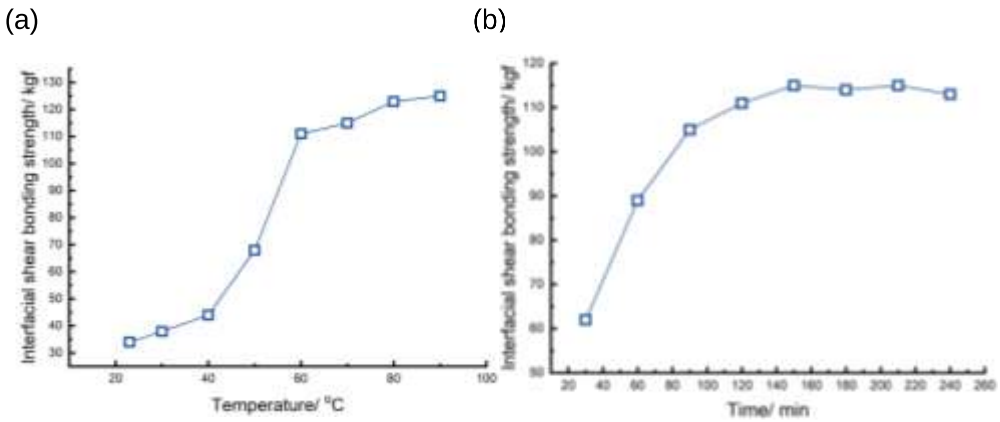

Figure 5 Interfacial tensile and shear binding strength of different curing (a) temperature and (b) time (Cured under 0.7 kg loading)

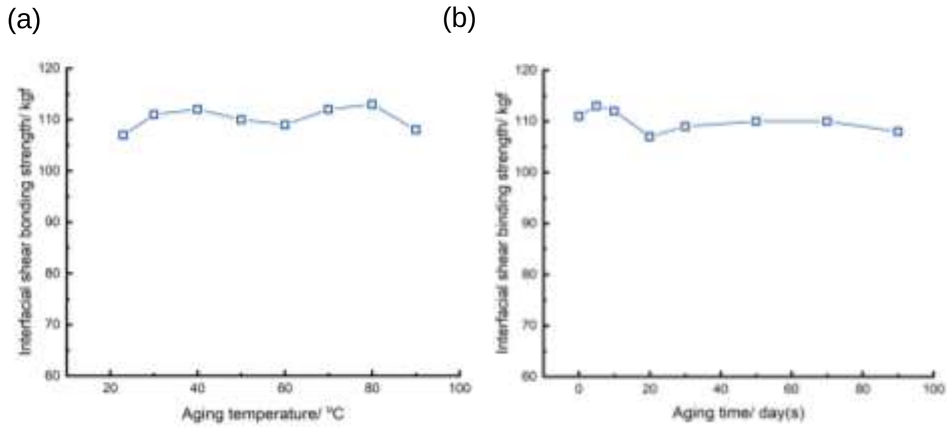

Figure 6 Interfacial tensile and shear bonding strength of different temperature and time under 40% sulfuric acid solution (Cured at 60 ℃ for 2 hours under 0.7 kg loading)

Figure 4 showed the relationships between loading, interfacial shear bonding strength and thickness of interfacial layers. As foresight, the increasements of loadings lowered the thickness of interfacial layers, but the tendency was separated by 0.5 kg into two stages: rapid declining and slow declining. Simultaneously, the interfacial shear bonding strength reached to the peak of 111.4 kgf. Rapid declining stages were attributed to the improvements of contact volumes of epoxy resins and ABS chains, increasing of epoxy crosslinking density and extruded of vapors. In slow declining stage, the extrusion of epoxy resin was the dominant factor.

3.3 Properties in acid environment

Anti-chemicals was the key properties for further applications, like batteries and sealing materials. All the samples were dipped into 40% sulfuric acid with different time and temperature. The results showed that the adhesion was stable even under 60 ℃ or for 90 days.

4 Conclusion

Adhesions of epoxy resins to ABS/ FRABS were evaluated and solid states flame retardant under processing temperature improved the interface shear bonding strength. The surface wettability were not influnced by flame retardant, but the surface distributinons of flame retardant were. Interface shear bonding strength and thickness of epoxy resins were related with pressure, curing time and temperature and the best processing were curing under 0.7 kg, in 60 ℃ for 2 hours. Adhesion remained for 90 days under soaking in 40 wt% sulfuric acid.

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