Effect of the in-situ polymerized polyurethane on laminated epoxy adhesive /aramid fabrics composites

GuangLei Lv and He Rui

CNOOC Safety Technology Services Co., Ltd, Tianjin, China
E-mail: 731735101@qq.com

Abstract: In order to avoid the high brittleness of epoxy resin and the low peeling strength of its laminated composite, polyurethane was synthesized by in-situ polymerization in epoxy adhesive system. The results of IR, SEM and mechanical properties test showed that the peel strength and shear strength of laminated epoxy adhesive /aramid fabrics composites reached the optimum value when the molar ratio of NCO/OH was 1.2, the content of MoCA curing agent was 1.5% and the content of polyurethane prepolymer was 20%. The brittleness of epoxy resin was reduced to a certain degree, and the bonding properties of epoxy adhesive/aramid fabrics composites were improved.

1. Introduction
Because of its high strength, high stability, high insulation and low cost, the epoxy resin has been widely used as adhesive in the fields of architecture, aerospace and integrated circuit. However, because the main drawback of epoxy resin is brittle and easy to fault, it limits its application. To improve its peel strength, shear strength, and broaden its application, improving the toughness of epoxy resin is an important way.

At present, the methods for improving the toughness of epoxy resin are divided into chemical methods and physical methods. The physical method is to mix fillers into epoxy resin for modification. Inorganic particles are dispersed in the cracks of the material by blending with epoxy resin, which restricts the further development of cracks. However, due to the energy absorbed by particles is limited, the modification effect of inorganic particles on epoxy resin is limited, which only restrains the cracks to a certain extent. The chemical method is the essential modification of the rigid chain of epoxy resin. Through the combination of chemical bonds, flexible segments are added into the original molecular chain to achieve the purpose of toughening.

Polyurethane (PU) is composed of polyester or polyether in the soft segment and isocyanate and cross-linking agent in the hard segment. The active isocyanate group can react with the hydroxyl group in epoxy resin, which can make the soft segment in polyurethane bonded on the epoxy resin, increasing the flexibility and toughness of the molecule chain. Therefore, many researchers have focused on epoxy resin toughened by polyurethane in recent years. In order to further explore the toughening effect of PU, different proportion of polyurethane prepolymer, IPDI and polyester polyol, and MOCA curing agent are used in synthesis, and the mechanical properties of modified epoxy resin were explored.

2. Experiment Details

2.1. Raw materials
Epoxy resin E-51 (industrial product), Isophorone diisocyanate (IPDI, analytical pure), polyester polyol (PPG-1000), 3,3'-dichloro-4,4'-diaminodiphenylmethane (MoCA), dibutyltin dilaurate (analytical pure).

2.2. Preparation of polyurethane prepolymer
Polyester polyol is added into a three-port flask to raise the temperature to 80 ℃. After melting, it is continuously heated for 30 minutes to remove water from polyester polyol. And then IPDI was added into the flask with a certain proportion(- NCO and - OH molar ratio are 0.8, 1, 1.2, 1.4, 1.6, respectively), which is continuously heated for a period of time. Finally, a certain amount of MOCA is added into the flask and stirred to the reaction finished, then, it is cooled down naturally to room temperature.

2.3. Preparation of polyurethane modified epoxy resin
The different proportion of polyurethane prepolymer was added into the epoxy resin E-51, stirred until uniformly mixed, and added a certain amount of dibutyltin dilaurate, then it was reacted at 80 ℃ for 20 minutes.

2.4. Preparation of epoxy resin adhesive/aramid fiber laminated composite
The prepared modified adhesive and T-31 curing agent (30%, relative to the adhesive) were well mixed, applied on aramid fiber and steel plate. Then the composite was vacuumed and cured at 80 ℃ for about 6 hours. The epoxy resin adhesive/aramid fiber laminated composite sample was cut into a strip adhesive sample with a length of 40 mm and a width of 25 mm and cured at room temperature for 48 hours. The sample preparation was completed.

2.5. Characterization
FTIR of the PU grafted epoxy resin samples were tested by Fourier infrared spectrometer (Nicolet 6700, Thermo Fisher Technology Co., Ltd.), with a wavenumber range of 600-4000cm⁻¹ and resolution of 4cm⁻¹. The SEM of PU grafted epoxy resin samples were tested by scanning electron microscope with the magnification of 2000. The elongation at the break of the composite, the peel strength and shear strength are tested by the standard adhesive property test method with microcomputer controlled electronic universal testing machine (cmt4503, Shenzhen Xinsansi material testing Co., Ltd.).

3. Results and discussion

3.1. Structure of PU grafted epoxy resin

![Figure 1. FTIR spectra of epoxy resin and modified epoxy resin](image-url)
Fig. 1 shows the FTIR spectrum of epoxy resin and modified epoxy resin. From the E-51 spectrum in Fig. 1, it can be seen that the absorption peak at 3450 cm\(^{-1}\) is the characteristic absorption peak of -OH, and the characteristic absorption peaks of the benzene ring skeleton are 1606 cm\(^{-1}\) and 1508 cm\(^{-1}\), respectively. The adsorption peak at 914 cm\(^{-1}\) is the characteristic absorption peak of an epoxy group, which is consistent with the structure of bisphenol-A epoxy resin. Compared with the FTIR spectrum of pure epoxy resin, the characteristic absorption peak of epoxy group at 914 cm\(^{-1}\) in modified epoxy resin was retained, the characteristic absorption peak at 1730 cm\(^{-1}\) which belonged to -C = O , and -NCO group characteristic peak was not found at 2272 cm\(^{-1}\), which was due to the reaction between -NCO group in PU prepolymer and -OH in epoxy resin. The results of the FTIR spectra showed that PU prepolymer was grafted to the epoxy resin molecular chain.  

![Figure 2. SEM images of epoxy resin (left) and modified epoxy resin (right)](image)

The images in Fig. 2 were the SEM pictures of epoxy resin and modified epoxy resin. It can be seen that the cross-section of epoxy resin without polyurethane particles is smooth and clear, which is a typical brittle fracture; while the cross-section crack distribution of epoxy resin modified with polyurethane particles is relatively dense. The results of SEM analysis indicated that it had more energy absorption after modification and the material toughness is improved.

3.2. Mechanical properties of epoxy resin composite

As shown in Figure 3, the peel strength of modified epoxy resin was increased at first and decreased afterward with the increase of NCO / OH molar ratio. With the increase of the molar ratio, the excessive NCO group becomes the terminal groups at both ends of the polyurethane chain gradually. The -NCO acts as the active group by bonding into the polyurethane elastomer and the epoxy resin. This leads to the toughening effect from two aspects, in which the molecular weight of the modified polymer increased rapidly, and the interpenetrating network structure appeared. In terms of adhesion, epoxy resin has strong adhesion to metal materials, but when a small amount of polyurethane is added, a small amount of hydroxyl reacts with the -NCO group, so the relative density of epoxy group and the adhesion to metal are decreased. With the continued increase of polyurethane content, the ammonia ester group (-NHCO-) which has strong polarity increases more, and it can form the hydrogen bond with metal, which enhances intermolecular force and bonding strength, so the adhesive force increases. When the content of -NCO continues to increase, it reacts with the hydroxyl group in epoxy resin completely, which makes the adhesive force decrease again, and the interpenetrating structure disappears, so the toughening effect weakens. According to the results, the best formula for NCO / OH molar ratio to prepare the polyurethane prepolymer is 1.6.

3.3. Effect of MoCA content on mechanical properties

Figure 4 shows the mechanical properties of modified epoxy resin with the different amount of curing agent MoCA(MoCA wt% = 0.5%, 1%, 1.5%, 2%, 2.5%). It can be seen from the figure that the peel strength, shear strength and elongation at the break all increase at first and decrease...
Figure 3. Effect of n (NCO/OH) on mechanical properties of epoxy resin

Figure 4. Effect of MoCA content on mechanical properties of epoxy resin
afterward with the increase of MOCA dosage. This is because the addition of MoCA changes the curing degree of polyurethane prepolymer. With the increase of curing degree, the toughening mode gradually changes from the way of chemical synthesis of the block copolymer to the way of physical mixing epoxy resin with polyurethane. It can be seen that the toughening effect is best when the MoCA addition amount is 1.5%.

3.4. Effect of prepolymer content on mechanical properties

![Graphs showing mechanical properties](image)

**Figure 5.** Effect of PU content on mechanical properties of epoxy resin

The mechanical properties of epoxy resin with different mixed content of PU prepolymer were shown in Figure 5. The results show that the break elongation keeps increase, but the peel strength and shear strength of the composite increase first and then decrease afterward with the increase of PU prepolymer. It is due to the more prepolymer is added into the epoxy resin, the more NCO group increase, the more complete reaction with -OH in epoxy resin is, the lower adhesion of epoxy resin is. As results shown in pictures The adhesion effect is best when there are 20% PU prepolymer added into epoxy resin.

4. Conclusion

Polyurethane as a soft segment in-situ polymerized in epoxy resin has obvious toughen the composite. When the molar ratio of -NCO/-OH for the prepolymer synthesized is 1.2, the peel strength of the epoxy resin adhesive/aramid fibers laminated composite reaches the expected goal. Moreover, the shear strength and break elongation are improved, the effect of improvement is significant. The addition of MoCA can control the degree and speed of the pre-polymerization of polyurethane. When the amount of MoCA is 1.5wt%, it will not overheat or have a low polymerization degree, which makes the soft segment in-situ polymerized in epoxy resin have the best toughening effect. This formula retains the excellent adhesive properties of epoxy resin while the defects of low peel strength
of epoxy resin in the laminated composite are reduced. It is a kind of modification with practical application significance.

5. References

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