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Effect of epoxy-silicone copolymer content on the thermal and mechanical properties of cured epoxy resin modified with siloxane

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Abstract: In this research, a bisphenol-A type epoxy resin (DGEBA) was modified with epoxy-block-silicone copolymers and hydroxyl-terminated silicone oligomers by physical blending and chemical reaction, respectively. The chemical structure of siloxane-bridged epoxy resin terminated by -OHs was characterized by Fourier transform infrared spectroscopy (FTIR), ^{1}H-NMR and epoxy equivalent weight (EEW) test. Both the samples show better elongation at break and impact strength than neat resin. TGA–FTIR results revealed that the residue at 600 °C of the modified epoxy resin increased with the increase of siloxane content, but the thermal stability was slightly reduced compared with that of the neat epoxy resin. Morphology studies indicate that the increase in izod notched impact strength are due to the suitable diameter of silicone phases because of the silicone toughening effect. Therefore, it is believed that the modified epoxy resin with good toughness and high thermal residual weight will show potential applications in anti-corrosion coatings and structure bonding materials.

Keywords: Epoxy resin; Epoxy-block-silicone copolymer; Silicone oligomers; Mechanical properties; Thermal stability;

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1. Introduction

Epoxy resin has been widely used in many applications such as composite materials, coatings, structural adhesives and microelectronic [1, 2] due to its good mechanical properties, excellent chemical resistance, heat stability, excellent adhesion characteristics, and high electrical insulation. The major drawback of epoxy resin is the brittleness caused by its high crosslinking degree. This inherent brittleness results in epoxy composites poor impact strength and shear strength of epoxy-based adhesives.

In light of this problem, researchers have incorporated carbon nanotubes [3, 4], liquid crystalline polymer [5, 6], rubber [7, 8, 9], and polyurethane [10, 11] to improve the toughness of the cured epoxy resins. Of all these methods, the most successful one is modified with reactive liquid rubbers, such as carboxyl-terminated butadiene acrylonitrile (CTBN) [12, 13], hydroxyl-terminated butadiene acrylonitrile (HTBN) [14, 15] and amine terminated butadiene acrylonitrile (ATBN) [16, 17]. However, the presence of unsaturated structure in liquid rubbers bring about thermal instability and low oxidation resistance into the epoxy matrix. Hence, such modified resins are not suitable for applications at high temperature levels. In contrast, the modification of epoxy resin with organosilicone polymers can improve the toughness of cured epoxy without damaging to its thermal resistance [18, 19]. However, polysiloxanes have poor compatibility with the epoxy resin due to their varied solubility parameters, which results in a formation of finely phase-separated structure and a considerable sacrifice in glass transition temperatures (T_g) in thermosets [20, 21]. Therefore, much attention has been paid to improve the compatibility between epoxy and silicone resins. For example, the introduction of aramid-silicone block copolymer [22, 23] as compatibilizer, preparation of silicon- and carbon- based block copolymer [24], and synthesis of polysiloxane copolymer which contains epoxide groups on the side chains [19] have been proved to be effective. Studies for enhancing toughness of epoxy resins evaluated in terms of the measurement of impact strength [18, 24, 25, 26] and critical stress intensity factor [22, 23, 27] are reported. So far there has been rare report in the literature focused on the elongation at break aspects of silicone oligomer modified epoxy resins.

In this study, a commercial grade epoxy-block-silicone copolymer and hydroxyl-terminated silicone oligomers of different mass ratios were employed in epoxy resin by physical blending and chemical reaction process, respectively. The mechanical properties, thermal properties and morphology of these modified epoxy resins were studied. Results indicate that the modified epoxy resin exhibit high elongation at break, good impact strength and advanced thermal stability than neat epoxy resin. Therefore, high temperature filler could be introduced to the modified epoxy resins in order to prepare anti-corrosive coatings, electronic packaging and structural adhesive.

2. Experimental

2.1 Materials

Bisphenol-A type epoxy resins (DGEBA) with an epoxide equivalent weight of 185-192 g/eq (n=0.1) were purchased from Wuxi Resin Plant, China. Polypropylene oxide diglycidyl ether (DER732) with an average molecular weight of 640 g/mol was supplied by Dow Chemical Company. DER732 was used to reduce the viscosity in the curing process and to endow the system excellent flexibility, elongation and impact properties. Hydroxyl-terminated silicone oligomer with a brand name Z-6018 was obtained from Dow Corning, which is a mixture of phenyl, propyl silsesquioxanes (>60%) and a hydroxyl-terminated linear siloxane. The curing agent, polypropylene oxide Jeffamine (EC-301) was purchased from BASF Chemical Company (equivalent [H] weight: 61.0). Epoxy-block-siloxane copolymer (SH023) with epoxy value of 0.02-0.07 mol/100g and siloxane content of 70% was purchased from Hubei Zaoyang Company. Dibutyltindilaurate (DBTDL), which was used as catalyst, was purchased from Chengdu Chemical Reagent Company, China. The chemical structure of DGEBA, Z-6018, DER732 and EC-301 is shown as Scheme 1.

These materials were used as supplied without further purification.

2.2 Synthesis of hydroxyl-terminated silicone oligomer-bridged epoxy resins (PSG)

DGEBA was firstly fed into a 250 mL three-neck round-bottomed flask, which was equipped with a mechanical stirrer, a thermometer and a connection to N_2 cylinder. Epoxy resins were preheated to 120 ^{o}C in an oil bath and then a stoichiometric amount of Z-6018 was added and stirred under nitrogen atmosphere. The compositions are illustrated in Table 1. Then a certain amount (0.5% of DGEBA resins) of DBTDL was added as catalyst into the flask after Z-6018 was completely meltdown. The polymerization was carried out at 120 ^{o}C for 2 h under a stirring rate of about 500 rpm. After the reaction completed, the colorless, transparent, viscous and homogeneous products were obtained (Scheme 2). The structure and the equivalent weight of these resultant products were confirmed by flourier transform infrared spectrometer and the hydrochloric acid/acetone method, respectively.

2.3 Curing of silicon modified epoxy resin

The PSDG copolymers were obtained by blending the reaction products of section 2.2 which was used without further purification and 25 wt% DER732 (based on the weight of the reaction resultants). Another kind of siloxane-type epoxy resins (PSHG) were prepared simply by blending alternating block polymers (SH023) with a stoichiometric amount of DGEBA and DER732. The formulation of SH023 and Z-6018 modified epoxy resins is showed as Table 2. Then a stoichiometric amount of curing agents (EC-301) was added to PSDG and PSHG at room temperature. The equivalent ratio between the epoxy resin and curing agent was based on the epoxide equivalent weight of epoxy resin and the amine equivalent weight (A.E.W) of the curing agent. These blends were completely mixed by a mechanical stirrer and degassed in a vacuum oven to eliminate air bubbles. The bubble-free mixtures were poured into 4 mm-thick polytetrafluoroethylene (PTFE) molds which were preheated at 80 ^{o}C to prepare the specimens for mechanical tests. The materials were cured at 80 ^{o}C for 2.5 h and 125 ^{o}C for 3 h in a convection oven.

2.4 Characterization

An fourier transform infrared (FTIR) spectrum was obtained by a (FTIR) (Nicolet 570) using potassium bromide (KBr) pellets to investigate the structure of DGEBA, Z-6018 and PSG. The scans were collected in the range of 4000-400 cm^{-1} wavenumber at room temperature.

Epoxide equivalent weights (EEW) of the PSG systems were determined according to GB 1677-81 standard. The analyses were performed in duplicate. Samples weighed 0.5-1.0 g, which were sufficient to determine the EEW values.

^{1}H-NMR spectra were recorded on a DRX-400 (Bruker Company, Germany) with $CDCl_3$ solvent.

The tensile strength and breaking elongation of the cured specimens were conducted with the help of Universal tensile instrument (INSTRON 5567) according to GB/T 2567-2008. The test was performed under a rate of 10 mm/min at room temperature.

The izod notched impact strength of the cured specimens was tested with an Izod Impact Tester (MTS Co.) according to GB/T 2567-2008. The size of the tested specimen was 4 mm × 10 mm ×80 mm. All mechanical property values were obtained by averaging the five experimental values.

The morphology of the impact fracture surfaces was observed using a scanning electron microscope (SEM: JSM-5900, JEOL Co., Ltd) at an accelerating voltage of 10 KV. Prior to the examination, the fractured surfaces were coated with gold in order to enhance conductivity and prevent charging.

The thermal stability were studied by means of thermogravimetric analysis (TGA: Q500, TA Co, Ltd. USA) coupled with FTIR spectrometer (Nicolet Magna 570, Nicolet Co, Ltd. USA). The samples weight ranges from 5-10 mg were heated from 50 to 600 °C at a rate of 10 °C/min in dry nitrogen atmosphere. The flow rate of gases into the cell for TGA/FTIR experiments was 100 mL /min. The solid weight loss, together with other process variables such as temperature, gaseous species was detected using the FTIR throughout the measurement.

3. Results and discussion

3.1 Characterization of hydroxyl-terminated silicone oligomer-bridged epoxy resins (PSG)

Fig.1 shows the FTIR spectra of neat epoxy resins (DGEBA), and hydroxyl-terminated silicone (Z-6018) and PSG1 (E51/Z-6018=70/10). For PSG1, the characteristic absorption peaks at 1438, 1247, 1133, 913 and 832 cm^{-1} were attributed to the Si-C_6H_5, Si-CH_3, Si-O-C and the terminal epoxy groups, respectively [28-33]. Compared with Z-6018 and DGEBA, these peaks ultimately were nearly the same besides the relative proportions of 832 cm^{-1} peak and 913 cm^{-1} diminished. This indicate that only a small amount of the epoxy groups have reacted with Si-O-H. The strong band in the range of 1035-1165 cm^{-1} become broader after reaction with DGEBA, which was likely the result of the formation of Si-O-C bond. However, the formation of the Si-O-C bond in PSG1 overlapped the Si-O-Si band in the region 1035-1165 cm^{-1} and 1200-1000 cm^{-1} of C-O-C vibration. Moreover, the broad Si-O-H peak of Z-6018 (3140-3590cm^{-1}) changed to a narrow peak (3493 cm^{-1}) of PSG1 attributed to the reaction between Si-O-H and C-O-H of epoxy resin (Scheme2).

Pure epoxy resin (^{1}H-NMR, $CDCl_3$), δ (ppm): 7.14-6.8 (aromatic ring protons), 4.17 (-CH_2-O-Ar), 3.33-3.30 (-CH, oxirane), 2.9-2.7 (-CH_2, oxirane), 1.8-1.6 (-CH_3). The ^{1}H-NMR of PSG1 is shown in Fig.2. The presence of characteristics peaks in ^{1}H-NMR spectra (δ, ppm, 2.2 (CH-O-Si)) of PSG1 attributed to the reaction between Si-O-H and C-O-H of epoxy resin and Z-6018 (Scheme2) [32]. The results further support the formation of the PSG copolymer.

The EEW values of the synthesized PSG copolymer are listed in Table 3. The calculated values based on the weight ratios agree well with the experimental data of PSG copolymer. The opening rate of epoxy ring remains almost unchanged. This further confirms few epoxy groups involve in the ring opening reaction. These results are consistent with theoretical assumption, ^{1}H-NMR and FTIR result.

3.2 Morphology of cured blends

In Fig.3 (a), EG (blank sample) exhibited a smooth, glassy microstructure without any plastic deformation. Fig.3 (b), (c) and (d) show that fine silicone phase was uniformly dispersed in the epoxy matrix by the addition of SH023. The average diameter of the dispersed phases of SH023 was 0.25 μm at the loading of 10 wt% and the size distribution was narrow. Moreover, the diameter of the silicone-dispersed phases increased to 0.81 μm with 40wt% content of SH023. This means SH023 shows good compatibility with epoxy resin.

Fig.3 (e), (f) and (g) show the morphology of the systems with Z-6018 which had a silicone content of about 10 wt%, 20 wt% and 40 wt%, respectively. Bi-phase separation structure was obviously observed through SEM. However, SEM photographs show that better silicone phases could be uniformly dispersed in the epoxy matrix at the Z-6018 addition of 10 wt%, compared with the modified systems with 20 wt% Z-6018 and 40 wt% Z-6018. In particular, the diameter of dispersed phases reached to 2.8 μm in system with 40 wt% of Z-6018.

3.3 Mechanical properties

Fig.4 (a) and (b) show the tensile strength and elongation at break of PSHG systems. The decreased tensile strengths with increasing SH023 content is ascribed to the low strength of SH023. Whereas, the breaking elongation of the systems increased almost seven times to 47% compared with that of epoxy resin when SH023 content increase up to 40 wt%. The increased elongation at break can be attributed to the good compatibility between epoxy-block-silicone copolymers and epoxy resin. Siloxane chain owns better deformability, while for pure epoxy resins, the cross-linked network with poor chain mobility leads to low elongation at break.

The values of tensile strength and elongation at break of PSDG systems are illustrated in Fig.5(a) and (b), respectively. The declined tensile strength with an increase of Z-6018 is due to the presence of the flexible siloxane linkages, free rotation of the Si-O-Si bonds, and weak interface boundaries between the siloxane and epoxy resin. The elongation at break showed little fluctuations until the Z-6018 content reached 40 wt% of the modified epoxy resins. Since the bad compatibility between epoxy and silicone resins in PSDG systems, when a small amount of silicone is added, -Si-O-Si- chains are not enough to change the network of epoxy resin, therefore, the elongation at break remains unchanged.

Fig.6 shows the impact strength of the PSHG systems as a function of SH023 content. As observed, the impact strength values of the systems are significantly raised with increasing the SH023 contents. When the content of SH023 reaches 40 wt%, the impact strength of systems increased nearly three times higher than that of pure epoxy resins. This result can be interpreted in terms of increased energy dissipation induced by addition of siloxane segment into the epoxy network [34-35]. Siloxane chain acts as obstacles in the crack path, and more energy is required for crack propagation.

Fig.7 shows the impact strength values of the PSDG systems as a function of Z-6018 content. It is found that the impact strength of the modified systems has a maximum value when the content of the Z-6018 is 10 wt%. It can be explained that Z-6018 (10 wt%) has a good compatibility with epoxy resin. The silicone segment of Z-6018 is flexible enough to enhance the impact strength by increasing energy dissipation. When the addition of Z-6018 increased to more than 10 wt%, the compatibility of epoxy resins and Z-6018 decreased. In addition, the diameter of the silicone phases became larger and the distribution of silicone phases turns homogeneity, thus resulting in poorer impact strength of the blends.

It has been reported that the fracture toughness of a brittle epoxy is related to the size of the dispersion phase.[36] The impact strength will initially increase with the increasing size of the dispersion phase to a maximum value and after that fall with the further increasing of second phase. Comparison made between the SEM micro-graphs of PSHG and PSDG systems reveal that, in the same dispersed phase content, the dispersed particle size for PSDG system is larger than those observed for PSHG system. Thus, the impact strength values of the PSHG systems are significantly increased with increasing the SH023 contents while addition of Z-6018 increased first and then decreased.

3.4 TGA-FTIR analysis of cured epoxy mixture

In this work, TGA-FTIR was used to analyze the gas product during the thermal degradation process. TGA and DTA curves of PSHG and PSDG systems in nitrogen are presented in Fig.8 (a) and (b) and Fig.9 (a) and (b), respectively. The initial decomposition temperature of samples which was evaluated by the temperature of 5 wt% weight loss ($T_{-5\%}$) [37] and the solid residue left at 600 ^{o}C were obtained from the TGA curve. And the temperature at the maximum weight loss rate (T_{max}1and T_{max}2) of researched samples was obtained from the DTA curve. These data are given in Table 4.

3.4.1 TGA analysis of the cured epoxy mixture

Fig.8 shows that the pure epoxy resin started to decompose at 332.1 ^{o}C, the thermal degradation process of the pure epoxy resin exhibited only two stages and its corresponding T_{max} were 347 ^{o}C and 377 ^{o}C, respectively, and the leaving residual yield was 4.47%. The thermal degradation process of the system with added 40 wt% SH023 in nitrogen mainly experience one step. The composite's initial decomposition temperature was about 316.9 ^{o}C, and degraded mostly at 351.3 ^{o}C. The late residue weight for the system was 13.2%. The solid residue of the system increased with the increasing content of SH023.

However, the thermal stability decreased according to the temperature of thermal degradation. Specifically, when the proportion of epoxy resin decreased, the systems began to lose weight earlier than unmodified epoxy resins due to its lower cross-linking density of the cured systems. On the other hand, the siloxane bond –Si-O- has a binding energy of 445 kJ/mol, which is higher than that of the carbon-carbon bond –C-C- in the epoxy resins. Consequently, higher activation energy is required to destroy the siloxane inorganic polymer skeleton, thus leaving higher solid residue.

As shown in Fig.9 (a), the solid residual yield increased to 33.54% comparing with epoxy resins with 40 wt% Z-6018. From the DTA curves of PSDG systems in Fig.9 (b), it can be detected that the thermal decomposition temperature showed a similar trend for PSDG and PSHG systems. In addition, reduction of mass loss rate was detected with the increase of Z-6018 loading. These results could be explained by the stability of the inorganic nature of the siloxane structure and its partial ionic nature, which stabilized the epoxy resin from the heat. While heating, low surface energy of silicone renders it to migrate to the surface of the epoxy resin by forming a protective self-heating layer with resistance to heat and ability of slowing down the thermal degradation of the polymer. Eventually, we find that epoxy resins modified by Z-6018 show a higher residual yield than epoxy resins modified by the same addition of SH023 caused by the proportion of silicone in Z-6018 is higher than that in SH023.

3.4.2 Species identification and discussions from TGA-FTIR

FTIR spectra of pyrolysis products of EG, epoxy resins with 40 wt% SH023 (PSHG4) and epoxy resins with 40wt% Z-6018 (PSDG4) at different time are shown in Fig.10 (a), (b), (c). Peaks in the regions of around 3500-3900 cm^{-1}, 2800-3000 cm^{-1}, 2200-2400 cm^{-1}, 1450-1800 cm^{-1}, 1000-1250 cm^{-1}, 800-850 cm^{-1}, 670-730 cm^{-1} were noted [38-41]. From the spectra obtained at 28 min (332 ^{o}C) corresponding to the first gaseous decomposition products which indicated that the water vapour was a predominant product. The noise-like bands in these spectra and in the following spectra at 1400-1800 cm^{-1} and 3600-3900 cm^{-1} were due to volatilization of water. These spectra exhibited bands attributed to carbon dioxide at 2360-2340 cm^{-1}, suggesting that little moisture was present in the neat epoxy resin.

During the second step of thermal degradation, the characteristic peak of water still existed until to 55 min (550 ^{o}C). The resultant water could be associated with dehydration of the two hydroxy propyl group of the phenoxy resin. The evolved gases also show bands 2990-3020cm^{-1} and 1000-1300 cm^{-1} which are related to sp^2 and sp^3 C-H stretching vibrations of para-disubstituted aromatic and aliphatic groups. The spectrum also revealed the presence of aldehyde-containing compounds by overlapping (C=O)-H stretches (around 2700 cm^{-1}-2900 $cm^{-1}$and 1724 cm^{-1}) in the IR spectrum. The peak appeared at 3010 cm^{-1} and 1316 cm^{-1} is the characteristic peak of CH_4. The spectrum showed the appearance of bands at 1608 cm^{-1} at 340 ^{o}C and 820 cm^{-1} could be attributed to C=C stretching vibrations and aromatic C-H stretching of para-disubstituted aromatic compounds, respectively. At 55 min (600 ^{o}C) the characteristic peak of CO_2 and N-H appeared and the thermal degradation rate of these products was very low.

As shown in Fig.10 (b) and (c), the evolved gas analysis for PSHG4 or PSDG4 exhibited characteristic bands of compounds containing –OH group (e.g. H_2O, phenol; 3500-3900 cm^{-1}), methyl substituted compounds (CH_2/CH_3 stretching, 2890-3000 cm^{-1}), CO_2 (2330, 2360 cm^{-1}), compounds containing aromatic ring (1320-1580 cm^{-1}, 823 cm^{-1}), hydrocarbons (C-H stretching at 1113 cm^{-1}, 1248 cm^{-1} and 1172 cm^{-1}), N-C (675 cm^{-1}).

From above results, it is noted that the main evolved gas products for EG were different from epoxy resins modified by SH023 or Z-6018. The main evolved gas products of EG were composed of small molecule, such as CO_2. In another aspect, epoxy resins modified by SH023 or Z-6018 released mainly methyl-substituted, carbonyl and aromatic which have higher molecular weight compared with that of EG gas product.

4. Conclusion

In this paper, silicone-bridged epoxy resins were synthesized by reacting Z-6018 with epoxy resins. Epoxy resins blended with two different silicone resins (Z-6018, SH023) were investigated to compare their thermal and mechanical properties. The diameter of the silicone phases considerably increased with the addition of Z-6018 and SH023. The toughness of the silicone modified system increased considerably with a suitable diameter of silicone phases. The results showed SH023 has better enhancement on elongation at break and impact strength of epoxy resins. However, during the thermal degradation, Z-6018 showed better residual yield contribution to epoxy resins than SH023 modified epoxy resins. The neat epoxy resins released compounds containing small molecules (CO_2), methyl-substituted, carbonyl and aromatic ring compounds. The presence of Z-6018 or SH023 could retard the movement and scission of the main chain of EG during thermal degradation process, thus resulted in high residual yield.

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Fig.1. FTIR spectra of DGEBA, Z-6018 and PSG1.

Fig. 2. ^{1}H-NMR spectra of epoxy resin modified with silicone.

Fig.3. SEM micrographs of the fracture surfaces of epoxy resin modified with silicone: (a) EG, (b) PSHG1, (c) PSHG2, (d) PSHG4, (e) PSDG1, (f) PSDG2, (g) PSDG4

Fig.4. Tensile strength (a) and elongation at break (b) of the PSHG systems as a function of SH023 content

Fig.5. Tensile strength (a) and elongation at break (b) of the PSDG systems as a function of Z-6018 content

Fig.6. Impact strength of the PSHG systems as a function of SH023 content

Fig.7. Impact strength of the PSDG systems as a function of Z-6018 content

Fig.8. TGA(a) and DTA (b) cures of PSHG systems under nitrogen at indicated heating rates

Fig.9. TGA (a) and DTA (b) curves of PSDG systems under nitrogen at indicated heating rates

Fig.10. FTIR spectra of volatile products recorded at indicated temperatures for decomposition of silicone modified epoxy resins in nitrogen atmosphere: (a) EG, (b) PSHG4, (c) PSDG4.

Scheme.1. Chemical structure formula of DGEBA, Z-6018, DER732 and EC-301.

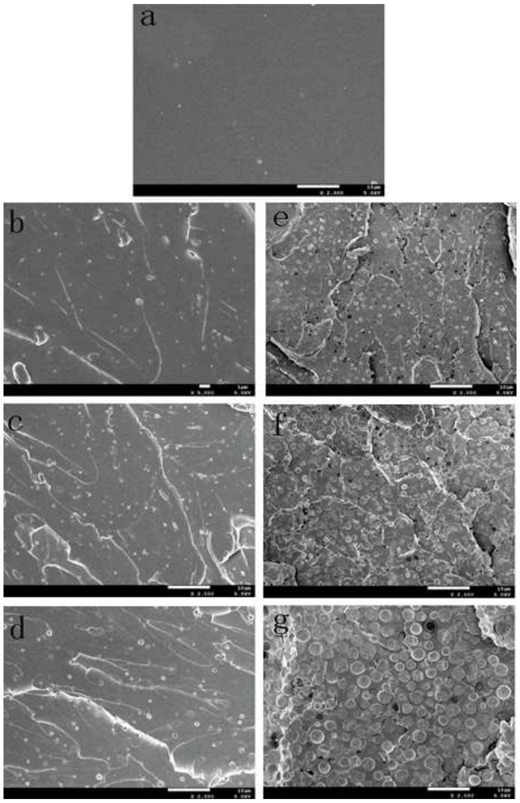
Scheme.2. Synthesis of hydroxyl-terminated silicone oligomer-bridged epoxy resins (PSG)

Table1. PSG produced from DGEBA modified with Z-6018

Table2. The compositions of epoxy resins$^{(a)}$ modified with SH023 and Z-6018

Table3. EEW Values of EP and PSG systems

Table4. Thermal stability factors of the cured PSHG systems and PSDG systems



Siloxane modified epoxy resin with good toughness and high thermal residual weight has been successfully prepared and will show potential applications in anti-corrosion coatings and structure bonding materials.