Curing behavior and flexural properties of cyanate composites reinforced with rare earth- and silane-modified basalt fibers

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Abstract. Herein, basalt fibers (BFs) modified by treatment with (3-aminopropyl) triethoxysilane and lanthanum ethylenediaminetetraacetic acid were used to fabricate BF-reinforced bisphenol A dicyanate ester composites via cast molding, and the effects of the modification method on the surface chemical groups and structures of BFs were determined using a range of instrumental techniques. Both modifications increased the number of functional groups on the BF surface. Silane treatment was shown to increase the BF surface roughness to a greater extent than rare earth treatment. Subsequently, we investigated the curing behavior and mechanical properties of BF-reinforced composites, demonstrating that the curing temperature of bisphenol A dicyanate ester was more effectively lowered by the incorporation of lanthanum-modified BFs than by that of silane-modified BFs. Additionally, the composite containing 12 wt% La-modified BFs exhibited flexural strength and modulus that exceeded those of the composite containing 12 wt% silane-modified BFs (by 15 MPa and 0.6 GPa, respectively), which was ascribed to the higher strength of La-modified fibers and the higher extent of curing and moderate interfacial adhesion of the former composites. In summary, lanthanum ethylenediaminetetraacetic acid was proven to be a more effective modifier than (3-aminopropyltriethoxy) silane for improving the curing behavior and flexural properties of the composites.

1. Introduction

Cyanate esters are characterized by high rigidity, good thermal resistance, and low dielectric permittivity and are therefore often used as matrices in fiber-reinforced polymer composites [1–5]. Recently, basalt fibers (BFs) have been widely employed for polymer matrix reinforcement in building material fabrication, sensing, and electrical/packing applications [6–9], exhibiting the advantages of thermal stability, corrosion resistance, environmentally friendly nature, and low cost [6, 10–12]. In contrast to carbon fibers, BFs largely resemble glass fibers, which implies that BF reinforcement of cyanate resins should not significantly affect their dielectric properties [13–16]. Therefore, BFs present a viable alternative to carbon fillers and are viewed as a promising reinforcing filler for cyanate esters.
As the failure of composites often occurs at the fiber-matrix interface, it is important and necessary to modify the fiber surface to enhance the interfacial adhesion [17]. In the past, researchers have proved that acid and alkali modification could improve the roughness of the fiber surface, but at the same time damage the structure and decrease mechanical properties of the fiber itself [18]. Surface modification of BFs (e.g., with silane coupling agents such as (3-aminopropyl) triethoxysilane (KH-550; Figure 1)) can effectively promote their bonding with the polymer matrix and eventually enhance the mechanical and thermal properties of BF-reinforced polymer materials [19–23].

Rare earth-based modifiers were found to be superior to KH-550 for increasing the glass fiber-polytetrafluoroethylene matrix interfacial adhesion and improving the tensile strength of the corresponding composites [24]. In particular, treatment of carbon fibers with lanthanum ethylenediaminetetraacetic acid (La-EDTA) increased the number of carboxyl groups on their surface and improved the interfacial properties of carbon fiber-reinforced polyimide composites [25]. Additionally, modification with La-EDTA has also been applied to inorganic oxides, e.g., Yang [26] prepared La-EDTA-Fe3O4 by a co-precipitation method and used this composite for phosphate removal from aqueous solutions, while Ryczkowski [27] showed that EDTA can form water-soluble complexes with alkaline earth metals and heavy metal ions. Zhou [28] immobilized Fe3O4 nanoparticles on silk fabrics using an aqueous solution of EDTA disodium salt and urea as a swelling agent to prepare fabrics with interesting magnetic properties. Importantly, all these surface modifications relied on the reaction between the hydroxyl groups on the fiber surface and the carboxyl groups of EDTA (structure shown in Figure 1). BFs comprise numerous inorganic constituents such as SiO2, Al2O3, Fe2O3, CaO, MgO, and Na2O [7, 29] and are characterized by the presence of abundant surface hydroxyl groups under humid conditions [30, 31]; therefore, they can react with La-EDTA and thus enhance the BF-resin matrix interface and the mechanical properties of BF-reinforced cyanate esters. However, the modification of BFs by La-EDTA and the properties of the corresponding composites have not been extensively investigated, which limits the application of BFs in many fields, e.g., environmental protection, friction, and magnetization. To address this issue, we have modified BFs with La-EDTA using an improved technique [25] to prevent the deterioration of BF mechanical properties caused by exposure to acidic media, high temperatures, and plasma. On the other hand, the curing of bisphenol A dicyanate ester (BADCy) is catalyzed by active hydrogen ions [32] that can be provided by the BF surface, EDTA, and KH-550. The degree of resin curing is known to inevitably affect the interfacial and mechanical properties of the corresponding composites [33]. Therefore, to compare the mechanical property enhancement of BADCy composites achieved by the incorporation of KH-550- and La-EDTA-modified BFs, one needs to study the effects of the two modifications on the curing behavior of these composites.

![Figure 1. Chemical structures of EDTA and KH-550.](image)
Herein, we compare the effects of KH-550 and La-EDTA modification on the curing behavior and flexural/interfacial properties of BF/BADCy composites prepared by cast molding, characterizing KH-550-modified BFs (KBFs) and La-EDTA-modified BFs (LBFs) by Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and flexural testing.

2. Experimental

2.1. Materials
BFs with an average diameter of 10 μm were obtained from Shanxi Jintou Basalt Fiber Co., Ltd. (Shanxi, China). KH-550 was sourced from Hubei Xin Lan Tian New Materials Co., Ltd. (China), and LaCl₃·nH₂O was procured from Shanghai Shanpu Chemical Factory (Shanghai, China). C₂H₅OH, HNO₃, CO(NH₂)₂, EDTA, and analytical grade NH₄Cl were obtained from Guangdong Chemical Reagent Engineering Technological Research and Development Center (China). 2, 2′-Bis(4-cyanatophenyl)isopropylidene (BADCy) was provided by Yangzhou Tianqi New Material Co., Ltd. (China).

2.2. BF surface modification
Commercially available plain basalt fabric with a surface density of 100 ± 20 g m⁻² and an average fiber diameter of 10–20 μm was washed with ethanol for 5 min to remove surface impurities and then repeatedly washed (10 times) with deionized water to obtain pristine BFs.

LaCl₃·nH₂O, EDTA, HNO₃, NH₄Cl, and CO(NH₂)₂ were dissolved in C₂H₅OH to achieve respective concentrations of ~1, 2, 0.5, 1, and 5 wt%. The obtained solution was blended at ~25 °C for 2 h and filtered to afford an alcoholic solution of the La-EDTA modifier with pH 6–7. Pristine BFs were incubated in the above solution for ~48 h to afford LBFs, which were washed with deionized water for ~10 min (3 × 500 mL) and dried by 4-h heating at 80 °C.

KH-550 was dissolved in 90 wt% aqueous ethanol to achieve a concentration of 5 wt%. After 5 min, BFs were immersed into the above solution for 30 min, and the obtained mixture was heated to 120 °C for 2 h to form covalent bonds between the coupling agent and the basalt fabric. Subsequently, BFs were taken out, washed with deionized water (3 × 500 mL), and oven-dried at 80 °C for 4 h to obtain KBFs.

2.3. Composites preparation
The basalt fabric was cut into pieces of the required size, and the composite material plate was prepared by cast molding. The mold containing a laid-flat piece of basalt fabric was filled with BADCy preheated to 120 °C, and the obtained mixture was put into a preheated mold and degassed at 180 °C for 20 min in a vacuum oven. Finally, the degassed mixture was placed into an oven and cured using the following protocol: 180 °C/1 h + 200 °C/2 h + 220 °C/2 h + 240 °C/2 h. The above process was used to prepare pristine BF-, LBF-, and KBF-reinforced BADCy-matrix composites with fiber contents of 2, 4, 6, 8, 10, and 12 wt%. A similar procedure was used to cure BF-free BADCy.

2.4. Characterization

2.4.1. FT-IR spectroscopy. FT-IR (Nicolet iS50, Thermo Fisher Scientific, United States) spectra were recorded in the wavenumber range of 4000–400 cm⁻¹. BF, KBF, and LBF samples were ground, mixed with KBr powder, and pressed to obtain 1-cm-diameter discs with a fiber loading of 1 wt%.

2.4.2. X-ray diffraction (XRD). The XRD patterns (PANalytical B.V., Xpert PRO MPD, the Netherlands) of pristine BFs, LBFs, and KBFs were recorded in a 2θ range of 20–70° at a scan rate of 4° min⁻¹ using Cu Kα radiation. The grain size (D) of short-range-ordered structures was estimated by the Scherrer equation as D = λ/(βcosθ) (Equation (1)), where λ is the measurement wavelength, θ is the
half-width at half-maximum of the main amorphous band, and $\theta$ is the diffraction angle at the band maximum [29].

2.4.3. Scanning electron microscopy (SEM). The microstructures of pristine BFs, KBFs, and LBFs as well as the microstructures and fracture surfaces of the corresponding composites were observed by SEM imaging (Hitachi SU-8010, Tokyo, Japan).

2.4.4. Differential scanning calorimeter (DSC). Short-cut pristine BFs, KBFs, and LBFs were blended with BADCy monomer and ground to obtain homogeneous mixtures with BF, KBF, or LBF loadings of 10 wt%. The non-isothermal curing of BADCy, BF/BADCy, LBF/BADCy, and KBF/BADCy systems was studied in the temperature range of ~25 to 800 °C in a nitrogen atmosphere at heating rates of 5, 10, 15, and 20 °C min$^{-1}$ using a synchronous thermal analyzer (TGA/DSC3+, METTLER, Switzerland), and the acquired data were used to calculate kinetic parameters.

2.4.5. Flexural properties. Room-temperature flexural properties were probed using a universal electronic testing machine (CMT 5304-30 kN, Shenzhen, China) according to GB/T1449-2005 (Chinese Standard) at a test rate of 10 mm min$^{-1}$.

3. Results and discussion

3.1. FT-IR spectroscopy

![FTIR spectra of pristine BF, KBF and LBF.](image)

The chemical structures of modified BFs were probed by FT-IR spectroscopy (Figure 2). The bands at 3400–3500 and 1630 cm$^{-1}$ in the spectrum of pristine BFs were assigned to the O–H stretching of Si-bonded hydroxyl groups [6]. Compared to that of pristine BFs, the spectrum of KBFs featured two new absorption peaks assigned to the vibrations of C–H (1386 cm$^{-1}$) and C–N bonds (1570 cm$^{-1}$) in $-\text{CH}_2\text{NH}_2$ moieties. The observation of bands at 2886 and 2978 cm$^{-1}$ (attributed to methyl and methylene groups, respectively) implied that the hydroxyl groups of BFs had reacted with KH-550 [21, 34].

The FT-IR spectrum of LBFs featured bands at 565, 1386, and 1640 cm$^{-1}$, which were ascribed to La–O [26], C–H, and C=O stretching vibrations [28], while the N–H stretching vibration peak at 3057 cm$^{-1}$ originated from CO(NH$_2$)$_2$ [35]. The strong band at 3400–3500 cm$^{-1}$ was ascribed to the $-\text{OH}$ groups of EDTA and BFs [29]. Thus, the above results indicated that the hydroxyl groups of BFs had successfully reacted with La-EDTA.
Although the obtained findings demonstrated that both La-EDTA and KH-550 successfully reacted with the surface hydroxyl groups of BFs, they also highlighted the differences between the modified fibers, which could also be manifested in surface structure variations. To prove/disprove this assumption, pristine and modified BFs were characterized by XRD.

3.2. XRD

![Figure 3. Comparison of XRD spectra of pristine BF, LBF and KBF.](image)

The investigation of modified BF microstructure is particularly important in view of the fact that BF crystallization and flaws can affect the mechanical properties of these fibers [21] and those of the corresponding composites. Herein, the effects of modification on BF structure were probed by XRD (Figure 3). The patterns of BFs and KBFs featured a very broad band (halo band) at 30° (indicative of the presence of an amorphous phase) and did not contain any crystalline phase peaks, whereas the pattern of LBFs featured three characteristic peaks (at 22°, 33°, and 43°) ascribed to lanthanum hydroxyethyl ethylenediaminetriacetic acid dihydrate (La-HEDTA). On the other hand, the amorphous band was shifted to lower angles, which, according to the Scherrer equation, indicated a decrease of short-distance-order structure size and was expected to be reflected in an increase of tensile strength [36]. Thus, in contrast to KH-550 modification, La-EDTA modification was concluded to change the surface structure of BFs.

3.3. SEM

![Figure 4. Comparison of SEM images and the possible surface reaction product of BF (a), (b), LBF (c), (d) and KBF (e), (f).](image)
SEM imaging of pristine and modified BFs was carried out to compare the effects of modification on BF surface morphology. Figure 4(a) shows an SEM image of pristine BFs, revealing that their surface was smooth and featured only few pits and grooves [37], while Figure 4(b) shows the surface chemical structure of pristine BFs elucidated based on the combined results of SEM imaging and FT-IR spectroscopy.

Figure 4(c) shows that the surface of LBFs was covered with crystalline particles and exhibited a decreased amount of pits and grooves, confirming the formation of La-HEDTA on the BF surface and indicating that La-EDTA treatment resulted in a significant decrease of surface roughness. Figure 4(d) shows the schematic surface chemical structure of LBFs.

Compared to that of LBFs, the surface of KBFs was coated by an amorphous phase (Figure 4(e)), with the corresponding chemical structure presented in Figure 4(f). The surface of KBFs was evidently rougher than that of LBFs, which was ascribed to the non-uniformity of the KH-550-fiber surface interaction [21].

3.4. Curing behavior of BF/BADCy systems

BF/BADCy, KBF/BADCy, and LBF/BADCy systems were subjected to DSC characterization to compare the effect of BF surface chemical groups on curing behavior. Figure 5(a–d) show the non-isothermal DSC curves of BADCy, BF/BADCy, KBF/BADCy, and LBF/BADCy systems, respectively, recorded at different heating rates (β), revealing that the exothermic peak temperature (Tp) of all systems increased with increasing β. The highest Tp (at constant β) was observed for the BADCy prepolymer, shifting to lower values upon the incorporation of 10 wt% pristine BFs and exhibiting an even greater decrease when modified BFs were used, which was attributed to the reaction of cyanate groups with active hydrogen-containing groups on the BF surface. In particular, the Tp of LBFs/BADCy was lower
than that of KBFs/BADCy, i.e., La-EDTA modification was better suited for lowering the curing temperature of BADCy.

To further analyze the cause of this phenomenon, each system was characterized by DSC, which is commonly used to study the curing reaction kinetics of thermosetting resin systems and can reveal the chemical changes of the resin system during curing. Moreover, analysis of DSC curves allows one to extract the basic kinetic parameters of the curing reaction (e.g., apparent activation energy (Ea), reaction order (n), and pre-exponential factor (A)) that are of great significance for understanding the above reaction.

Ea and A can be obtained by the Kissinger method [38] (Equation (2)) under the assumption that the maximum reaction rate is observed at Tp [36]:

\[
\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_p},
\]

Where \(\beta\) is the heating rate (°C min\(^{-1}\)), Tp is the DSC curing peak temperature (K), R is the ideal gas constant (8.314 J mol\(^{-1}\) °C\(^{-1}\)), Ea is the reaction activation energy (J mol\(^{-1}\)), and A is the pre-exponential factor.

The Kissinger equation implies that the plot of \(\ln(\beta/T_p^2)\) vs. 1/Tp should be a straight line with a slope of \(-E_a/R\) and an intercept of \(\ln(AR/E_a)\), exactly as observed in Figure 6(a). The reaction order n can be determined using the Crane equation (Equation (3)) [40]:

\[
\frac{d(\ln\beta)}{d(1/T_p)} = \frac{E_a}{nR} + 2T_p.
\]

Since \(\frac{E_a}{nR}\) is generally much larger than 2Tp, the latter term can be ignored, which affords the simplified Crane equation (Equation (4)):

\[
\frac{d(\ln\beta)}{d(1/T_p)} = \frac{E_a}{nR}.
\]

Based on Equation (4), a plot of \(\ln\beta\) vs. 1/Tp should be a straight line (as shown in Figure 6b) with a slope of \(-E_a/nR\), and the reaction order n can therefore be obtained from this slope if Ea is known.

**Table 1.** Kinetic parameters calculated using the Kissinger and Crane methods

| System       | Ea (kJ/mol) | A (s\(^{-1}\)) | n   |
|--------------|-------------|----------------|-----|
| BADCy       | 72.76       | 9.47×105       | 0.88|
| BF/BADCy    | 79.35       | 5.17×106       | 0.89|
| KBF/BADCy   | 89.47       | 4.24×107       | 0.90|
| LBF/BADCy   | 85.39       | 5.85×107       | 0.90|
Table 1 lists the kinetic parameters calculated using the Kissinger and Crane methods, showing that all systems featured \( n \approx 1 \), i.e., close-to-first-order reactions were observed. The \( E_a \) is of the investigated systems decreased in the order of \( \text{KBFs/BADCy} > \text{LBFs/BADCy} > \text{BFs/BADCy} > \text{BADCy} \), which was believed to reflect the concomitantly decreasing number of functional groups on the BF surface, i.e., the formation of polymers with higher extents of cross-linking in the presence of larger amounts of surface functional groups restricted the reaction of BF active hydrogens with BADCy. Additionally, \( \text{BF/BADCy} \), \( \text{KBF/BADCy} \), and \( \text{LBF/BADCy} \) systems exhibited higher pre-exponential factors than that of the BADCy system, i.e., molecules in BF-containing systems were more likely to react with each other than those in the BADCy system. Thus, the \( \text{LBF/BADCy} \) system could be cured at a lower temperature than \( \text{BF/BADCy} \) and \( \text{KBF/BADCy} \) systems in view of its moderate activation energy and high pre-exponential factor [41]. Additionally, LBFs contained more reactive surface groups than KBFs and were therefore expected to be better suited for catalyzing the polymerization of BADCy [42].

### 3.5 Flexural properties

In view of the fact that flexural load contains multiple stress patterns, the flexural strength of a given material is a comprehensive index of its mechanical properties [34,43]. To compare the effects of BF modification on the mechanical properties of BF/BADCy composites, we determined the flexural strengths and moduli of BF/BADCy composites with different BF loadings (Figure 7).

![Figure 7](image.png)

**Figure 7.** Flexural strength (a) and flexural modulus (b) of BADCy, BF/BADCy, KBF/BADCy and LBF/BADCy composites.

As shown in Figure 7(a), the flexural strengths of all composites exceeded that of the BADCy resin, which was explained by the enhancement of interfacial adherence upon the reaction of BF surface hydroxyl groups with the BADCy matrix. It is worth noting that composites reinforced with modified BFs exhibited higher flexural strengths than those reinforced with pristine BFs, since the reactive groups introduced onto the BF surface by modification catalyzed the curing of the BADCy resin. Moreover, the
Flexural strengths of LBF/BADCy composites were lower than those of KBF/BADCy composites at BF loadings below 10 wt%. Numerous investigations have revealed that the reinforcing effect of fibers is determined by fiber strength, fiber-matrix interfacial adhesion, and polymeric matrix nature [44], whereas interfacial adhesion is, in turn, influenced by surface roughness and chemical bonding [45]. At low fiber content, the extent of reinforcement was determined by the resin matrix and interfacial adhesion, i.e., was largely influenced by interfacial adhesion and fiber strength, since the same resin was used in all cases. The results of FT-IR spectroscopy and SEM imaging illustrated that the extent of functionalization and surface roughness of BFs increased after modification, with a particularly high surface roughness observed for KBFs. Therefore, it was understandable that the KBF-matrix interfacial adhesion was stronger than that observed for LBFs. However, LBF/BADCy composites featured higher flexural strengths than KBF/BADCy ones at modified BF contents of ≥10 wt%. For example, the flexural strength of 12 wt% LBFs/BADCy was as high as 128 MPa, which was ascribed to the fact that the load was largely sustained by BFs at high fiber contents. According to the results of XRD analysis, LBFs featured a short-range-ordered structure with a grain size smaller than that of BFs, which resulted in increased fiber strength. Nevertheless, no strength improvement was observed as a result of BF modification with KH-550. Thus, LBF/BADCy composites exhibited higher flexural strengths than KBF/BADCy ones at BF contents of ≥10 wt%.

Flexural modulus is commonly used as a measure of material rigidity [43]. As shown in Figure 7(b), the flexural moduli of BF/BADCy, KBF/BADCy, and LBF/BADCy composites increased with increasing fiber content, in agreement with the results of previous studies [46, 47]. Notably, composites reinforced with modified BFs exhibited higher flexural moduli than BADCy and BF/BADCy systems, with the highest flexural modulus at different mass fractions observed for LBFs/BADCy. The extent of modulus increase and its relationship with filler loading mainly depended on the chemical structures introduced by the addition of fillers. Thus, rigid triazine rings formed during the curing process [42] restricted the movement of chain segments, i.e., composite rigidity was mainly affected by the degree of BADCy curing. DSC results showed that LBFs promoted curing more effectively than KBFs and BFs, and the rigidity of LBFs/BADCy was therefore larger than those of BFs/BADCy and KBFs/BADCy. At a fiber content of 12 wt%, the flexural modulus of the LBF/BADCy composite was 0.6 GPa higher than that of the KBF/BADCy composite.

In summary, flexural tests demonstrated that La-EDTA modification improved the flexural properties of BF/BADCy composites to a greater extent than KH-550 modification.

3.6 Microstructure and fractography of composites

![Figure 8](image)

**Figure 8.** SEM images of the flexural fracture surfaces of the different composites containing 10 wt % of fiber at two different magnifications (a), (d) BF/BADCy (b), (e) KBF/BADCy (c), (f) LBF/BADCy composites.
To further confirm the effect of BF modification on the mechanical properties of composites with 10 wt% fiber content, the fracture surfaces of composites subjected to flexural tests were characterized by SEM imaging (Figure 8). Figures 8(a, d) show the fracture surfaces of BFs/BADCy, revealing the presence of holes caused by fiber pull-out, which means that the reinforcement of BF/BADCy composites could be influenced by both fiber pull-out and fiber breakage [44]. Moreover, BFs were more prone to exhibit fracture failure than being pulled out, i.e., the reinforcing effect of pristine BFs was poor.

Compared to the case of KBFs/BADCy (Figure 8(b, e)), fiber pull-out on the fracture surfaces of LBFs/BADCy (Figures 8(c, f)) was more pronounced, which was ascribed to the fact that the surface of KBFs was more rough than that of LBFs (Figure 4). Obviously, the force required to pull out a fiber from the resin matrix is positively correlated with fiber roughness, and the KBF-resin matrix interfacial adherence thus exceeded that of the LBF system. The above viewpoint was supported by analyzing the amounts of resin remaining on extracted fibers and fiber-resin matrix gaps.

On the other hand, the results of XRD analysis (Figure 3) indicated that LBFs exhibited better mechanical properties than KBFs. Therefore, under the same bending load, the probability of being pulled out instead of being broken was higher for LBFs than for KBFs. Thus, although the fiber-matrix interfacial adhesion was higher for KBFs than for LBFs, the latter fibers exhibited higher mechanical strength and could therefore absorb more energy during extraction, which ultimately resulted in improved bending properties of the corresponding composites.

4. Conclusions

Herein, we successfully modified BFs by KH-550 and La-EDTA treatments and characterized modified fibers by a range of instrumental techniques, showing that KBFs were different from LBFs in terms of both surface chemical groups and microstructure. Further, we compared the curing behavior and flexural properties of BF/BADCy, KBF/BADCy, and LBF/BADCy composites. DSC results showed that the introduction of functional groups onto the BF surface during modification resulted in a curing temperature decrease, and kinetic analysis of the curing reaction revealed that compared to the KBF/BADCy system, the LBF/BADCy system exhibited a higher A and lower Ea, and hence a lower Tp. At a fiber loading of 12 wt%, the flexural strength and modulus of the LBF/BADCy composite exceeded those of the KBF/BADCy composite by 15 MPa and 0.6 GPa, respectively. Morphological characterization confirmed that LBF/BADCy composites featured better flexural properties than their KBF/BADCy counterparts because of the moderate interfacial adherence and improved fiber mechanical properties in the former case. Thus, we concluded that La-EDTA modification can potentially outperform KH-550 modification as a method of improving the curing behavior and flexural properties of BF-reinforced BADCy composites without harming fiber tensile strength.

Acknowledgements

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