Impact and dynamic mechanical thermal properties of textile silk reinforced epoxy resin composites

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Abstract. Silk fabric reinforced epoxy resin composites (SFRPs) were prepared using simple techniques of hand lay-up, hot-press and vacuum treatment, and a series of volume fractions of silk reinforcements were achieved. The impact properties and dynamic mechanical properties of SFRPs were investigated using a pendulum impact testing method and dynamic mechanical thermal analysis (DMTA). The results suggest that silk reinforcement could greatly enhance the mechanical performances of SFRPs. The impact strength reached a maximum of 71 kJ/m² for 60%-silk SFRP, which demonstrated a potential of silk composites for defence and impact-resistant materials.

1. Introduction

Recently, natural fibre reinforced composites have been investigated with considerable interest owing to their advantages such as high specific strength, low density, promising biodegradability and environmental friendliness [1-6]. Generally, plant fibres (e.g. flax, hemp and jute) and basalt fibre reinforced composites have been the focus of natural fibres, whereas animal-sourced fibres (such as silk and wool) have seldom found to be utilised as composite reinforcements. Silk from domestic silkworm *Bombyx mori* (*B. mori*) is highly crystalline in the molecular structure and stands as the only continuous filament of natural fibrous fibre[7]. Mei-po Ho *et al.* [8] prepared short silk fibres reinforced poly (lactic acid) (PLA) composites via twin-screw micro-extruder, and they found the Young's modulus and flexural modulus were enhanced by 27% and 2% compared to the pure PLA. Zhao[9] studied the dynamic thermal mechanical properties of silk-PLA composites, and the storage modulus was shown to be improved at higher temperatures (from 70 to 160°C). Another biocompatible polymer, poly(ε-caprolactone) (PCL) was also widely used as the matrix of composites for biomedical applications. Li *et al.* [10] prepared silk fibre reinforced PCL and the 35 wt.%-silk showed the highest tensile strength while the 45 wt.%-silk showed the highest flexural strength. It is until very recently that Shah *et al.* [11] point out the unique properties of silk fibres could provide new opportunities for high-performance composites [12,13]. Despite the above mentioned specific studies on silk reinforced composites, the general effect of silk as reinforcements to improve the mechanical properties of plastics and composites has not been studied.

Epoxy resin is widely used with credentials such as easy processibility, low cost, balanced mechanical properties, good adhesive properties, good corrosion resistance and great high-temperature tolerance [14-19]. However, due to the high degree of crosslinking, many materials of epoxy resin are inherently brittle, and the impact properties are poor, often shown as catastrophic failure. These disadvantages limit the engineering applications of epoxy resin, which also drive the research on modifications of epoxy resin materials to improve their toughness [20-24].

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This study intended to prepare silk fibre reinforced epoxy resin plastics/composites (SFRPs) via easily accessible hot-press technique, aiming to investigate the effect of silk reinforcements on improving the mechanical properties of the pure epoxy resin, especially toughness. The prepared SFRPs were tested for impact performances and dynamic mechanical thermal properties. The aim of the work was also to validate a hypothesis that silk fabric can greatly improve the toughness of the brittle epoxy resin, which may widen the engineering applications of these thermosets materials.

2. Materials and methods

2.1. Materials

Epoxy resin E-51 with curing agent DS-300G was supplied by Dasen Material Science & Technology Inc. (Tianjin, China) which would be used as the matrix material. According to the product company, the cured density of this E-51 resin product was 1200 kg·m⁻³. Tensile strength the impact strength was tested to be about 72-78 MPa and 12.5-13.1 kJ·m⁻².

A plain woven fabric with an areal density of 90±5 g·m⁻² was provided by Huzhou Yongrui Textile Co. Ltd. (Zhejiang Province, China). The fibre yarn includes nearly 80 threads of silk fibre of each strand. The density of the neat silk fibre was assumed to be 1300 kg·m⁻³[25].

2.2. Fabrication of composites

SFRPs were fabricated by hand lay-up followed by a hot-press process. The specimens with size of 20 cm × 10 cm were cured at 120°C for 2 hrs with a 300 kPa pressure. The silk fabric reinforced composites (SFRPs) with silk fabrics of different volume fractions \( v_f \) from about 30% to 70% were prepared, and specimens were noted as 30%, 40%, 50%, 60% and 70%-silk for property analysis. \( v_f \) is calculated from the density and the weight of the silk, epoxy resin and the final prepared composites. The density of all specimens were tested by drainage method with Electronic Density Balance (FA1104J). Besides, a vacuum treatment (100 Pa for 1 hr at 40°C) was added after hand lay-up and prior to the hot-press process to facilitate the infiltration of epoxy resin and the removal of air bubbles.

2.3. Impact testing

The impact properties testing was conducted according to ISO 179:1997 with a Pendulum Impact Testing Machine (MTS ZBC 1000). The specimens (without notch) were loaded with a 2 J hammer.

2.4. Dynamic mechanical thermal analysis

Dynamic Mechanical Thermal Analysis (DMTA) for SFRPs of different \( v_f \) was conducted on a dynamic mechanical analyser (TA Instruments, Waters Ltd., DMA Q800) under 3-point bending mode at a dynamic strain of 0.2% and a fixed frequency of 1 Hz and a heating rate of 3 °C·min⁻¹ from 25 to 170 °C. The testing specimens were cut with rectangular shape: 20mm × 10 mm × 2 mm.

3. Results and discussion

3.1. Impact properties

A major limitation of the applications of epoxy resin composites is the low toughness and weak impact properties. The impact strength (IS) have therefore become a most important measure of our work that aimed to convert brittle epoxy resin into a tough material.

From Figure 1(a), we found that when \( v_f \) of silk reached 60%, the impact properties of the SFRPs surged to 70.70 kJ·m⁻² from about 12.80 kJ·m⁻², whereas the trend of increasing was mild when \( v_f \) was below 60%. The results suggest there may be a critical \( v_f \) effect on the impact properties of silk reinforced composites. Shah’s study[11] showed when \( v_f \) of woven silk fabric reached 58% a great improvement in quasi-static mechanical properties could be achieved. The hot-press technique allowed us to apply a higher pressure to achieve even higher \( v_f \) of silk. Thus we successfully prepared SFRPs with \( v_f \) as high as 70%. According to classical fibre reinforced composites fracture mechanics,
when the reinforcement fibre’s $v_f$ reaches a critical value, e.g. 50%, the reinforcements could carry more than 10 times of the load carried by the matrix resin. This is because upon a critical $v_f$, the effect of crack inhabitation could be maximised and the fracture behaviour of the composites could switch to a totally different mode [26,27]. The large number of fibres could firstly inhibit the initiation of micro-cracks and secondly act as crack stoppers or deflect the crack path during crack growth. In this work, the critical $v_f$ of silk reinforcement is between 50% and 60%, where the fracture mode of SFRPs transformed from brittle to tough.

**Figure 1.** Impact properties of different composites (a) Comparing of different fibre $v_f$ of SFRPs and (b) Comparing of 60%-silk and plant reinforced composites.

### 3.2. Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical thermal analysis (DMTA) is widely used to research the thermomechanical properties and viscoelastic behaviour of polymers and polymer composites such as epoxy-based composites[28-30]. Thermosetting resin used as matrix of composites would undergo a softening process which is called glass transition from glassy phase to rubbery phase, so the thermomechanical properties need to be estimated for reliable engineering applications.

Storage modulus $E'$ and loss tangent $\tan\delta$ are the two most important properties measured in DMTA. Figure 2 (a) showed $E'$ of pure epoxy resin and SFRPs with different $v_f$ in a temperature range from 25 to 170 °C; and Figure 2 (b) compared $E'$ of each specimen at room temperature 25 °C before the glass transition and at 140 °C after the glass transition. $E'$ was greatly enhanced after introducing silk fibres and it showed a linear increasing trend with increasing $v_f$. For 70%-silk SFRP at room temperature 25 °C, $E'$ (8800 MPa) was three times of that for pure epoxy resin (2970 MPa). More importantly, $E'$ could remain a high value of 1483 MPa for 70%-silk and 941 MPa for 60%-silk at 140 °C, while as it dropped to only 11 MPa for pure epoxy resin. This enhancement in $E'$ for SFRPs especially at high temperatures would certainly widen the application of epoxy resin especially at $T>T_g$.

Figure 2 (c) showed the $\tan\delta$ profiles of the pure epoxy resin and the SFRPs with different $v_f$. It was seen that the incorporation of silk fabric suppressed the $\tan\delta$ peak height with increasing $v_f$ of the fibre, as shown in figure 2 (d). The pure epoxy resin displayed the highest $\tan\delta$ peak temperature at about 128 °C, which is defined as the $T_g$ of this epoxy product. Interestingly, $T_g$ shifted lower for all the SFRPs. The low $\tan\delta$ values indicated better damping-resistant properties for SFRPs. Moreover, the good correlations between silk’s $v_f$ and the integrated $\tan\delta$ area could be used to back calculate $v_f$ of the silk reinforcement from property measurements for silk composite products. The enhanced post-$T_g$ modulus and the low damping factor through $T_g$ for the high $v_f$ SFRPs could be attractive to particular applications.
3.3. Comparing PFRPs and SFRPs

Compared to plant fibre reinforced plastics (PFRPs), SFRPs showed obvious advantages in impact performance. It can be found in the literature that the flax reinforced composites have an impact strength of 8-15 kJ m\(^{-2}\) for nonwoven flax and 23-36 kJ m\(^{-2}/[kg\ m^{-3}\] for woven flax, which were lower than that of SFRPs reported here. One important reason was that we managed to achieve high \(v_f\) for silk reinforcements. According to Shah’s study, the easy compressibility of silk fibres compared to plant fibres was owing to the irregular (almost-triangular) shape of the silk fibres and their concave and convex cross-sections. Moreover, it should also be noticed that the hexagonal shape of plant fibres could result in uneven packing and increased porous defects, which may become the controlling factor for impact resistance.

Considering the improved impact properties of SFRPs, crashworthy and impact-critical materials would be good choices for the use of SFRPs. Our new test record of IS for SFRPs indicates a good potential in the application of light-weight, defence and impact-resistance applications, such as wind turbine blades.

4. Conclusion

In our study, we have successfully prepared a series of silk fabric reinforced epoxy composites (SFRPs) by hand lay-up followed by hot-press techniques. The \(v_f\) of the SFRPs were achieved from 30% to a highest value of 70%. The impact properties were found to greatly enhance when \(v_f\) reached 60%. Moreover, dynamic mechanical thermal analysis showed the SFRPs with high \(v_f\) possessed high dynamic storage modulus (nearly 1.5 GPa at 140 °C) and a low loss factor (\(\tan\delta <0.3\)) through the
glass transition of the matrix epoxy. Our findings would shed light on improving the brittle and weak epoxy resin through incorporating tough and strong silk fibres.

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