Development of recycled polypropylene-based sustainable composites with recycled carbon fibre/ Kenaf fibre hybrid reinforcements

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Abstract: Recycled carbon fibre (RCF) and Kenaf fibre (KF) have been used as reinforcement materials in combination with recycled polypropylene (RPP) matrix to manufacture a sustainable composite. Maleic anhydride grafted polypropylene (MAPP) has also been used as a compatibilizer to modify the interface between fibres and matrix composites, resulting in improved composite strength and thermal resistance. After modified with MAPP, the recycled carbon fibre was combined with KF fiber to improve the KF/RPP composite properties such as mechanical and thermal stability. The results were indicated that the mechanical properties of RCF/RPP composite was improved with increasing of MAPP when MAPP added 8 Wt. %, these reached a Maximum of 77.6 MPa and 271.4 MPa, respectively. When the RCF combined with the KF hybrid composite, the mechanical strength of the hybrid composite was improved with the amount of RCF. The DSC results showed that the MAPP could reduce the Tc of RPP and increase the crystallization degree. The hybrid composite presented that the crystallization degree was increased with the increment of RCF content. The DMA results showed that the RCF can influence the β translation of RPP.

Key words: Recycled PP; MAPP; Recycled Carbon Fibre; Kenaf Fibre; Mechanical Properties; Thermal Properties

1. Introduction

Green composites have been attracting considerable attention in recent years with increased interest in reducing environmental pollution and manufacturing sustainable parts [1]. Green composites usually use plant-based fiber or recycled fibre reinforcement materials as an alternative to conventional reinforcement materials. Due to its low-cost and abundance, natural Kenaf Fibre (KF) is now becoming popular in industry and academic research [2-3]. Alternatively, recycled carbon fibre is also commonly studied as a high value and high-performance recycled reinforcement [4]. These recycled fibres can reclaimed via thermal pyrolysis, chemical, fluidized bed, or other recycling methods [4-6].

A range of recycled carbon fibre and nature fibre reinforced thermoplastic composites have been previously investigated. The methods of recycled carbon fibre reinforced thermoplastic composites have been processed by injection moulding, hybrid nonwoven mat, tape, and hybrid yarn [6], while KF reinforced thermoplastic composites have been manufactured by injection moulding and compression moulding [2,7]. Much of the previous research has focused on improving the fibre/matrix interface. For example, surface treatments, including alkali treatment, chemical treatment, and combination treatment, have all been investigated for KF [2, 8]. The surface of KF treated with NaOH was demonstrated to help...
remove the impurities from the fibre surface and improve the surface area, leading to an obvious improvement in the Tensile properties of composites [2,8-9]. Treatments using silane coupling agents also showed some capability to improve the bonding strength between fibre and matrix to improve the composite’s mechanical properties [9]. Alternatively, chemical surface treatment has also shown some capability to improve the thermal performance of KF composites, as reported by Mohammad N et al. [10]. To find the best treatment method, some combination treatment methods have also been studied. For example, an alkali combined silane coupling agent has been used to treat the surface of KF, which improved the mechanical properties of their composites efficiently [11].

Similarly, recycled carbon fibre has also undergone considerable studies with various surface treatment methods, such as sizing and plasma treatment. Wong et al. [12] reported that the molecular and anhydride groups of Maleic anhydrides grafted polypropylene (MAPP) could influence RCF/PP composite strength, the composite with the MAPP treated had the higher strength than the composite without treatment. Compared to the number of anhydride groups MAPP, the molecular weight of MAPP showed more importance.

One of the significant challenges for KF is that they can have poor compatibility with polypropylene [13]. To resolve this difficulty, several studies have tried to hybridize KF with a more compatible fibre such as glass or carbon for thermoset or thermoplastic composites. KF and carbon fibre hybrid woven mat reinforcements have been combined with an epoxy matrix to form a composite showing improved thermal stability with the increasing carbon fibre content [13]. Similar research from Md Ashraful Alam et al. reported that the mechanical strength of hybrid composites was influenced by the amount of KF content, reducing with greater KF content [14].

To improve the strength and compatibility of sustainably hybrid composite, the high stiffness fibre of recycled carbon fibre cooperated with KF was applied as reinforcement to enhance the recycled PP material. To the author’s knowledge, some research on KF and Carbon fibre hybrid composite was reported. The fully sustainably composite with the KF and RCF hybrid fibres reinforced RPP have not been previously investigated. This study firstly investigated the influence of MAPP on recycled carbon fibre composite and then added it into the KF composite and finally found the influence of RCF content on the mechanical strength and thermal stability of the hybrid composite.

### 2. Materials

The recycled PP (RPP) was purchased from Fengli polymer, Yuyao China, and all the RPP was recycled from the plastic frame. The maleic anhydride grafted polypropylene (MAPP) of ST-G-PP-10CW was supplied by Star Better (Beijing) China, with a density of 0.91g/cm3. A melt index of 20-50 g/10min was measured for the MAPP at the temperature of 170°C. The recycled carbon fibre (T300) was obtained from Nantong Fuyuan new material Co., Ltd., China, with a 7 μm diameter, 1.75 g/cm3 density and 3 mm length specified by the provider. Kenaf fibre (KF) of 10mm length was sourced from Tianjin Tech University.

| Table 1. The composites manufacture formulation. |
|-------------------------|-------------|----------------|-------------|----------------|----------------|----------------|----------------|----------------|
| 0MAPP  | 2MAPP  | 5MAPP  | 8MAPP  | 5KF  | 10KF  | 15KF  | 20KF  |
| 80    | 78    | 75    | 72    | 72   | 72    | 72    | 72    |
| 20    | 20    | 20    | 20    | 15   | 10    | 5     | 0     |
| /     | /     | /     | /     | 5    | 10    | 15    | 20    |
| 0     | 2     | 5     | 8     | 8    | 8     | 8     | 8     |

### 3. Preparation of composites

An initial group of composite samples was prepared with different amounts of MAPP (0 wt.%, 2wt.%, 5wt.%, and 8 wt.%) blended into RPP and RCF to determine to evaluate the most appropriate composition. Subsequently, the best performing MAPP blend was combined with different ratios of
RCF/KF to create the hybrid composites. All composites were first mixed by the internal mixer at 190°C at 40 rpm for 30 min. After blending, the composites were directly put in the press at 200°C for 1 minute under 5 MPa pressure and then cooled. The detailed formulation of all composite samples is summarized in Table 1.

4. Characterization

4.1. Mechanical properties
The Tensile and Bending properties were measured by a universal testing machine (MTS E42 MTS Co., Ltd., China) according to the standard ISO 527 and 178, with sample dimensions 160 mm and 80 mm x 10 mm x 4 mm respectively.

4.2. Scanning electron microscopy (SEM)
After mechanical testing, SEM images of fracture the composite fracture surfaces were obtained from Zeiss Supra 55 scanning electron microscopes.

4.3. Differential scanning calorimetry (DSC)
The thermal performance of different composites was analyzed using DSC Q20 (TA instruments China) with a temperature of -20°C-300°C. All samples were studied under nitrogen gas with 50 ml/min, with a sample weight of 5-10 mg and a heating rate of 20°C/min.

4.4. Dynamic mechanical analysis (DMA)
Dynamic mechanical analysis (DMA 8000, PerkinElmer) of single cantilever samples was conducted in this study to measure the storage modulus, loss modulus, and tan δ of composites; with a heating rate of 5°C/min and a frequency of 1HZ.

![Figure 1](image.png)

**Figure 1.** Mechanical strength of MAPP treated RCF/RPP composites.

5. Discussion

5.1. Mechanical properties
The Figure 1 Summarizes the Tensile and Bending results for MAPP modified samples. When 8 wt.% MAPP was added into the RCF/RPP composite, the Bending strength of RCF/RPP composite was improved from 182.1 (±18.9) MPa (without MAPP) to the maximum of 274.1 (±15.4) MPa, and the increment reached 50.5%. Simultaneously, the Bending modulus was improved from 23.5 (±2.9) GPa to 38.6 (±3.4) GPa. It also has a near 64.3% increment. The Tensile strength and modulus also presented a similar increasing tendency, the Tensile strength improved from 52.9 (±3.8) MPa to 77.8 (±5.2) MPa and the modulus increased from 3.5 (±0.4) GPa to 6.6 (±0.8) GPa, it near about 47.0% and 88.6% increment respectively. The reason for the Bending and Tensile properties improvement was that the RCF surface has –COOH and –OH functional groups, as a result of the recycling process, which can
react with the anhydride and maleic acid group of the MAPP, at last forming a hydrogen bonding and ester linkage (see Figure 2). [15]

Figure 2. The mechanism of MAPP reacts with RPP.

For the KF/RCF hybrid composites, the Bending strength was seen to increase from 114.3 (±8.2) MPa to 205.2 MPa (±7.3) (increased of 44.3%) with increasing RCF content at 15 wt. %, as seen in Figure 3. And the Tensile strength and modulus were found to be increased from 28.4 (±1.9) MPa to 48.1 (±2.5) MPa, near increased 69.4%. It matched the investigation reported by Mimi Azlina Abu Bakar et al. described that the strength of nature fibre hybrid composite was dependent on individual fibre and orientation [16]. According to the literature review, the strength of KF near about 980MPa, and the strength of recycled carbon fibre under pyrolysis recycling technology can reach at least of 86% compared to virgin carbon fibre [6, 2]; it means that the recycled carbon fibre in this study can reach near about 3035MPa. It was conducted that the amount of recycled carbon fibre that influenced the strength of the hybrid composite.

Figure 3. Mechanical strength of MAPP treated RCF/KF/RPP Hybrid composites.

5.2. DSC analysis

Figure 4 and Table 2 show the thermal analysis results of different samples. All of the crystallite temperature (Tc), melting temperature (Tm) and the melting heat of the composite (ΔHm) can be obtained from DSC curves directly. While Xc responded crystallite degree of composites and can be calculated from the below equation:
\[ X_c = \frac{\Delta H_m}{\Delta H \times (1 - W\%)} \times 100\% \]

Figure 4. DSC curves of the different sample (a) MAPP modified composites (b) Hybrid composites.

Where \( \Delta H \) is PP crystallite at 100% degree, taken from the literature to be 209 J/g [10, 17-18], and W represents the amount of reinforcement. From Table 2, it can be seen that increasing MAPP in the CF/RPP composite resulted in a reduction of Tc from 128.66°C to 128.12°C, but the crystallization degree was improved from 33.9% to 35.4%. This indicated that MAPP can reduce the Tc temperature of PP material and improve the crystallinity of the PP matrix. This change was that MAPP produced high bonding strength between fibre and matrix, which resulted in a higher crystallization degree of RPP and fibre [17,19].

Table 2. DSC analysis of different composites.

| Sample code | Tc (°C) | Tm(°C) | \( \Delta H_m \) | \( X_c \) |
|-------------|---------|--------|-----------------|---------|
| 0MAPP       | 128.66  | 164.17 | 56.76           | 33.9%   |
| 2MAPP       | 128.33  | 164.12 | 54.37           | 32.5%   |
| 5MAPP       | 128.15  | 163.14 | 57.38           | 34.3%   |
| 8MAPP(0KF)  | 128.12  | 163.17 | 59.19           | 35.4%   |
| 5KF         | 128.40  | 162.81 | 57.78           | 34.6%   |
| 10KF        | 128.78  | 163.02 | 57.57           | 34.4%   |
| 15KF        | 128.50  | 162.56 | 57.31           | 34.3%   |
| 20KF        | 127.89  | 162.16 | 56.42           | 33.7%   |

Conversely, the Tc temperature and crystallization degree of RCF/KF hybrid composites were both reduced with the addition of KF. The Tc temperature was reduced from 128.12°C to 127.89 °C, and the crystal degree reduced from 35.4% to 33.7%. Even though, the fibre and MAPP can be realized as nuclear agent and it help the RPP to reduce the Tc and increased the crystallization degree. In this study, the KF/RCF hybrid composites treated by MAPP was showed the different tendency. It suggests that compared to KF, the RCF has a greater benefit to composite crystallization. Since KF has lower stiffness
and longer length than the RCF, this is likely affecting the crystal formation [18]. Research has reported that the size of the filler could influence the PP crystallization, and the crystal degree was increment with filler size-reduction [17,20]. This reduction in crystallinity with increasing KF content may also be contributing to the reduction in mechanical properties.

5.3. DMA analysis
The storage modulus of the MAPP treated composites is shown in Figure 5(a), increasing with increasing MAPP concentration. This suggests that the group of anhydride and maleic acid in MAPP resulted in more complicated effects at the composite interface, supporting the trends observed in the mechanical performance [17].

![Graphs](image)

(a) Storage modules of RCF/RPP
(b) Loss modulus of RCF/KF/RPP
(C) tan D of RCF/KF/RPP

Figure 5. The DMA curves of different samples.

For the KF hybrid composite, the loss modulus was seen to be lowest at 0 wt. % KF and 20 wt. % KF (0wt% RCF) but highest at 5 Wt. % KF. It suggests that little KF benefits on molecular mobility of RPP. The loss modulus results also show that the RPP had α and β transitions, where the α transition relates to the glass transition temperature. It can be seen from Figure 5(a) that when there is no KF in the composite material, it showed a high Tg. When KF is added to the composite material, the Tg shows a downward trend; only KF in the composite material as reinforcement. The β transition cannot be found.
from DMA testing result, which indicated that the fibre type and fibre amount would influence the matrix of amorphous RPP forming and at last, influence the transition forming [17, 21].

The fracture surfaces of the composite, as observed by SEM, are presented in Figure 6. These results show an abundance of pull-out fracture for samples without MAPP modification (Figure 6 (a)), but after MAPP modification, the amount of fibre pull-out was reduced (Figure 6 (b)). It indicates that MAPP can improve the bond between fibre and matrix, again reflected by the improvement of mechanical strength.

Figure 6 (c) shows the fracture surface of the composite without RCF, which showed that MAPP provided a good chemical bond between KF and PP material. For the hybrid composite, the KF and RCF displayed good blending and less of the pull-out phenomenon. This further indicates that MAPP can enhance the surface contact strength of recycled carbon fiber while increasing the interfacial strength of KF; similar results have been demonstrated by other researchers [21].

6. Conclusion
The fibres reinforced RPP composite materials were manufactured via internal mixer and compression molding technology. The Bending strength of a recycled carbon fibre RCF and recycled polypropylene RPP composite blended with increasing MAPP content (up to 8%wt) was improved from 182.1 MPa to 274.1 MPa. However, the hybridization of this composite, replacing RCF with increasing natural Kenaf fibre (KF) content, was found to reduce the Bending strength from 274.1 MPa to 114.3 MPa. Tensile strength testing revealed similar trends for the RCF/RPP with increasing MAPP content (from 52.9 MPa to 77.8 MPa) and after hybridization with KF (reducing the strength to 28.3 MPa). DSC revealed a small improvement in the degree of crystallization (from 32.5% to 35.4%), increasing MAPP content, which again was improved slightly when replacing RCF with KF (33.7 to 35.4%). Overall, this work demonstrates how MAPP may help improve the thermal and mechanical performance of these materials.

Figure 6. The SEM images of different samples.
(A) RCF/RPP without MAPP treatment; (b) RCF/RPP with 8Wt.%; (C) RCF/KF/RPP composite
composites. However, hybridization or the complete replacement of recycled carbon fibres with natural Kenaf fibres will significantly reduce composite performance.

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