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Utilizing composite recyclate as reinforcement in inverse-vulcanised polymers†

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A sustainable approach to prevent filler settling in vitrimeric polymers, using a mechanically recycled composite filler, is reported. The resulting composites demonstrate over 40% improvements in flexural strength and an over 70% improvement in material hardness while maintaining recyclability and mechanical performance after remanufacturing.

Carbon fibre-reinforced polymer composites (CFRPs) have grown in importance across an ever-expanding range of industries and applications, including the aerospace and automotive sectors, to sporting goods and other commercial items.[1] CFRPs have replaced materials like metals due to their high strength-to-weight ratio making them an attractive candidate for strong, lightweight components.[2] CFRP materials consist of reinforcing carbon fibres (CF) that are bound within a polymeric matrix that is responsible for stress transfer to the fibres. The overwhelming majority (up to >90%) of polymers used in CFRPs are thermoset or thermoplastic polymers.[3] Although composites offer advantages such as complex component manufacturing, tailorable matrices for various requirements and electromagnetic shielding, the majority of currently operational composites are not repairable, in contrast to their metallic counterparts. Additionally, they are not easily recycled due to their complex composition, leading to a growing stockpile of composite waste.[4]

The most popular methods for composite waste valorisation focus solely on CF reclamation. The fibre reclamation processes use chemical or thermal treatments to remove the polymeric component of the composite and extract the CF (referred to as reclaimed CF). Out of these methods, pyrolysis is the most developed and recognized method in industry for preventing disposal of composites into landfills.[5] The reclaimed CF is reprocessed into different forms including milled CF (mCF) (<1 mm), chopped CF (>1 cm) and can also be made into nonwoven recycled CF fabrics by carding the discontinuous chopped fibres into a felt-like mat.[6] It should be noted that CF reclamation typically disregards the polymer matrices that make up a large portion of a composite material. For this reason, it is criticized for not being a form of true recycling as only one component of the composite is salvaged and, the large energy expenditure required for pyrolysis undermines the value of second life applications.[7] However, mCF is an accessible commodity used in the manufacturing of composites and is often added to polymers for conductivity and some modest physical properties improvements. Alternatively, a method of "true" composite recycling is mechanical recycling.[8] This method involves grinding or milling of the composite; resulting in powdered recyclates consisting of reclaimed CFs with matrix material still adhered to the fibre. Even though mechanically recycled products are often regarded to be at a disadvantage due to the presence of the polymer phase in the final product and are occasionally removed *via* pyrolysis. In this work, we show how the judicious choice of second life polymer can make these reclaimed matrix-coated fibre particles an advantage using a complementary, functionally active polymer phase present within the recycled matter facilitating the exploration of a carbon-negative footprint material.[9]

The work presented in this paper first explores incorporating mCF into a sulfur-based polymer synthesised *via* inverse vulcanisation. This polymer, poly(*S-r*-DCPD), is derived from elemental sulfur, a by-product of oil refining, and dicyclopentadiene (DCPD). This polymer was first reported for its mercury sorption capabilities and was also shown to be an effective coating due to its resistance to harsh environments.[10,11] Previous work has shown the potential for this polymer to be reinforced with continuous and reclaimed non-woven fabrics of carbon fibre, though consistent 'wet-out' is difficult. Thus in this work, we explore mCF as a reinforcing agent to improve the mechanical properties of this material.[12,13] Moreover, the poly(S-*r*-DCPD) has been shown to be

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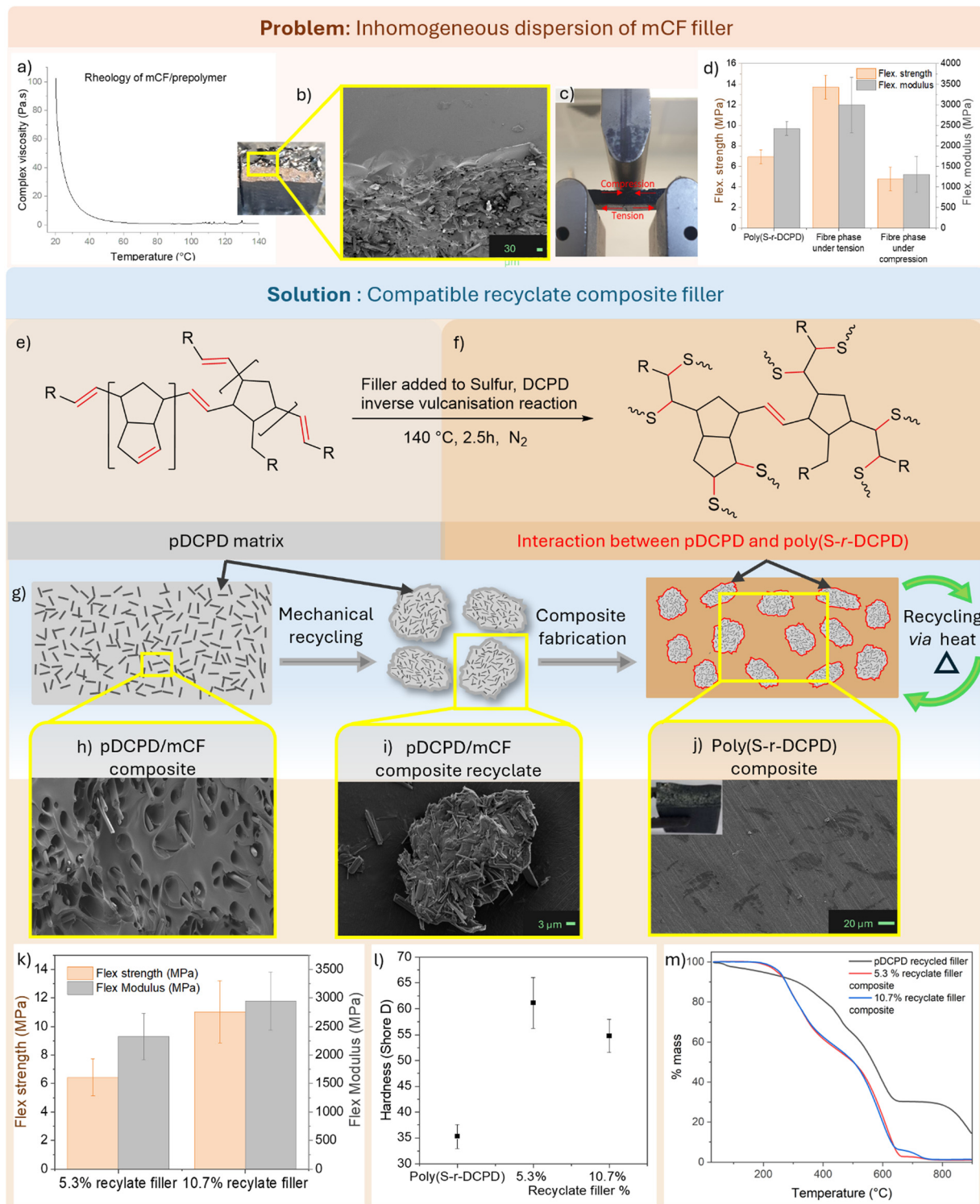
Fig. 1 (a) Rheology of mCF/prepolymer; (b) photograph and electron micrograph of cured mCF composite; (c) forces exerted on flexural sample specimen during testing; (d) flexural properties of biphasic cured composite; (e) pDCPD; (f) expected interactions between pDCPD and sulfur following reaction; (g) schematic demonstrating the approach to avoid filler settlement; scanning electron micrographs of; (h) pDCPD/mCF composite fracture surface; (i) pDCPD/mCF recyclate filler; (j) cross-sectional view of novel poly(S-*r*-DCPD)/recyclate filler composite.; (k) flexural properties of novel composite; (l) hardness of novel composites; (m) thermogravimetric analysis of composites.

vitrimeric in nature providing a potential avenue for in-service repair and recycling, reducing composite waste even further.

The polymer was synthesised by using equal weights of elemental sulfur and DCPD at 140 °C, resulting in poly(S-*r*-DCPD),

which requires a second heating cycle to fully cure.[11] To promote effective mixing, the fibres were incorporated during this synthesis before the second heating stage. Upon curing the mCF was seen to have settled to the bottom of the sample, giving a biphasic system with neat polymer on top and mCF reinforced polymer at the bottom (Fig. 1b). This result was found to be the result of the polymer undergoing a significant decrease in viscosity before finally cross-linking and curing (Fig. 1a), despite the fibres being added. Therefore, while the pre-polymer had a relatively high viscosity of ~100 Pa s and demonstrated even fibre distribution at room temperature, the loss of viscosity at the curing stage caused the fibres to sink and settle. Despite this inhomogeneity, when subjected to flexural testing, if the fibre-rich side of the composite is under tension (bottom layer) (Fig. 1c), the mCF is seen to provide a reinforcing effect, doubling the flexural strength of the neat polymer before failure. However, when the mCF-rich side undergoes compression, the material fails at much lower stress as is consistent with CFRPs. While this biphasic system might be of interest for certain applications, the manufacturing of homogenous composites with isotropic properties is preferred and the goal of this study.

To overcome the mCF settling, we explored the use of a mechanically recycled composite using a polymer able to undergo reaction with the inverse-vulcanised system.[7] Dicyclopentadiene polymers (pDCPD) are thermosetting materials used as a matrix in commercial carbon fibre composites, combining extreme toughness with resistance to chemicals and moisture.[14] The resulting polymer network possesses alkene groups along the backbone, making it an ideal copolymer with sulfur (Fig. 1e), as it is hypothesised that poly(S-r-DCPD) synthesis proceeds by addition of sulfur at the alkenes of the comonomer.[10,15]

Thus, mechanically reclaimed recyclate from those CF-pDCPD systems would provide mCF with a coating of alkene rich polymer on the external surface. Even though this polymeric presence is commonly regarded as a disadvantage, we viewed this functionality as an excellent opportunity for recycling or up-cycling of CF-pDCPD composites. A recyclate composite filler was made using pDCPD/mCF composites and then incorporated into poly(S-r-DCPD) system. This presence of pDCPD provides alkenes that can undergo reactions within the inverse-vulcanisation process, setting it in place and minimising fibre settling (Fig. 1e and f).[16]

To obtain the reclaimed carbon fibre-pDCPD powder, the samples were abraded, and the particulate matter was collected (as detailed in ESI†). This method of recycling can be considered more environmentally friendly than pyrolysis and gives small particles of composites observed via SEM (Fig. 1i). As described above, the filler material was incorporated into the sulfur-DCPD mix during the initial reaction and stirred to give a homogenous dispersion. It is important to note that the recyclate was derived from composites with an approximate fibre weight fraction of 40%. Thus, when the filler was added to a reaction vessel at 5.3 and 10.7% w/w, this equates to a 2 and 4% w/w mCF content with the remainder being the original

pDCPD polymer. Attempts to increase the effective fibre weight fraction were unsuccessful as, even when preparing samples based on 10.7% w/w recyclate, became viscous and difficult to process. Nevertheless, once placed into moulds and fully cured, a homogenous composite material incorporating the recycled composite filler was obtained (Fig. 1j). This recycled composite filler was visibly homogenous, unlike the virgin mCF specimens. The homogeneity was corroborated on the microscale via SEM, showing the filler material was distributed evenly through the polymer with distinguished settled filler or fibres present in the material (Fig. 1j). It was also noted that the filler was seen to be well adhered to the poly(S-r-DCPD) matrix without signs of de-bonding, supporting the hypothesis that the alkene rich residual pDCPD provided a means of reaction with the second life poly(S-r-DCPD).

With these samples in hand, the composites were then assessed for their mechanical properties. Firstly, flexural properties of the composite with 5.3% w/w and 10.7% w/w recycled fillers were determined (Fig. 1k). The flexural strength demonstrated a ~40% improvement when the recycled fillers amount was doubled (5.3% w/w to 10.7% w/w) in the composite. Notably, the flexural properties of the 10.7% w/w (effective mCF loading of only 4%) recycled filler composites demonstrated comparable results to the maximum flexural strength and moduli achievable through the addition of 10% w/w mCF. It was hypothesised that the efficient reinforcing effect induced by the recycled filler, compared to the mCF, allowing for the effective transfer of stress from the polymer to the fibres. Additional hardness measurements of recycled filler incorporated composites showed that both samples possessed significantly improved hardness for the 5.3% w/w and 10.7% w/w samples, at 61.14 ± 4.9 and 54.78 ± 3.2 Shore D, respectively, (Fig. 1l) and were statistically indistinguishable from each other. Thermal analysis, to determine T_g, of the control composite and the recyclate containing composite were 114.7 °C and 116.8 °C, respectively (thermograms in ESI†), showing no major change in glass transition when using the recyclate.

Now that the filler was shown to improve mechanical properties, composite repair was explored utilising the dynamic and repairable nature of sulfur backbone of the poly(S-r-DCPD). Thus, a suitable temperature that allows for the polymer to undergo S–S exchange reactions, but without degrading the material, was sought. Thermal analysis of the composites was conducted using thermogravimetric analysis (in air) to assess the thermal degradation and inform of a methodology to recycle spent composites. All composites showed similar thermal degradation temperatures of ~170 °C. Beyond this, the composites showed an almost total mass loss by 800 °C. Therefore, an appropriate temperature of 160 °C could be used to regenerate the composite.

The fractured composites from flexural testing, with the highest filler loading (10.7 w/w%), were crushed, placed in a mould and hot-pressed at 160 °C to reconsolidate specimens suitable for flexural testing (Fig. 2a and b).[7] SEM analysis of the recycled composites' fracture surface showed a consistent polymeric matrix, along with the presence of some CF still with
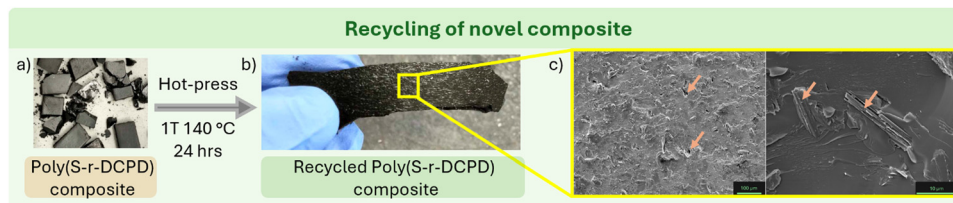
Fig. 2 (a) Process for composite recycling; (b) recycled composite specimen; (c) scanning electron micrographs of fracture surface of recycled composite.

good fibre-matrix adhesion and no settling or aggregation of the filler material was visually observed (Fig. 2b). However, small voids were observed, potentially because of air gaps within the crushed composite.

These specimens were then tested for their flexural properties. Interestingly, the recycled composites show no degradation in mechanical properties. Instead, an improvement in both flexural strength and modulus was observed. Composites composed of 10.7% w/w recyclate filler demonstrated a flexural strength and modulus of 11.03 ± 2.19 MPa and 2.95 ± 0.5 GPa, respectively. Once the material was recycled, the resulting material showed a flexural strength modulus of 18.11 ± 4.8 MPa and 4.78 ± 0.8 GPa, respectively. The authors expect at least 5 cycles of rehealing to be possible though some material degradation will occur due to oxidation of the sulfur in the matrix when exposed to multiple heating cycles.

In conclusion, this study presents a sustainable solution to the problematic settling of high-density fillers when combined within a vitrimeric polymer system. The solution explores the use of recycled composite matter that is usually disregarded as waste. Here, we demonstrate that by aligning the chemistries of a filler made from a mechanically processed CFRP with a new polymer matrix, a new composite material was produced with favourable matrix/filler interfacial interactions. Moreover, the ability to repair and remanufacture this green composite was demonstrated.

Data availability

The authors confirm that the data supporting the findings of this study are available within the article and its ESI.†

Conflicts of interest

The authors confirm that there is no conflict of interest.

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