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Polymer and Composite Recycle and Upcycling

October 2019

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Summary

The work reported herein is focused on increasing the value of polymer and fiber-reinforced polymer composite waste by chemical deconstruction and subsequent modification, and incorporation into value-added products. This project comprises two distinct and independent tasks.

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1.0 Introduction

The production of polyethylene terephthalate (PET) worldwide in 2014 was approximately 41.56 million metric tons, and it is forecasted to be approximately 73.39 million metric tons by 2020. Likewise, it is estimated that by 2020 there will be 62,000 tons of end-of-life waste carbon fiber reinforced polymer generated. Additionally, the high cost of carbon fiber and the energy intensity required to produce virgin fiber, which is between 198-595 MJ/kg, fuels the need to recover the value of carbon fiber composites. The ability to chemically recycle PET and carbon fiber reinforced epoxy will enable the production of other value-added materials that can be utilized as additives into other products. Not only does the chemical recycling of such end-of-life products remove them from the landfill, but it recovers the petrochemical-based carbon imbedded within. The objective of the work is to demonstrate pathways to increase the value of waste PET and carbon fiber reinforced epoxy by chemical deconstruction or modification. The aims are to: 1. Synthesize a library of phthalimide additives from PET and evaluate them as asphalt additives; and 2. Recycle fiber reinforced vitrimers. The additives formed from PET were added to asphalt binder and the mechanical properties of the resulting composites were evaluated to demonstrate a feasible application for the intermediates. Fiber reinforced vitrimers were recast as new high value materials.

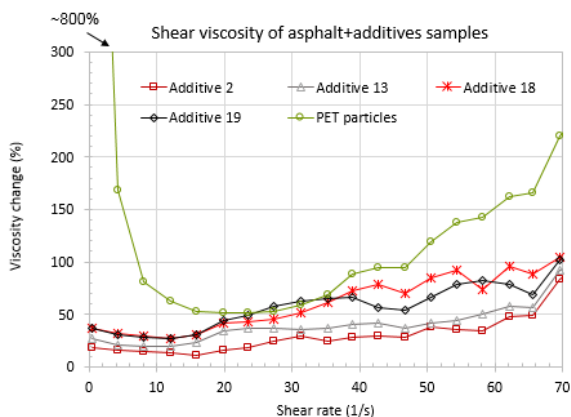
2.0 Results and Accomplishments

Task 1. A series of phthalimides were synthesized via PET aminolysis with various amines, with complete conversion of PET. The amines were selected to provide a variety of final products of differing chain lengths (Additives 18, 19) and polarity (Additives 2 and 13). In addition, one of the analogs was prepared from mixed waste PET, to demonstrate the feasibility of the chemical process for use with mixed waste (90 wt% PET, and 10 wt% labels, adhesives, cap rings). The phthalimides were added to asphalt binder at 5 wt% loading and their performance was evaluated against neat asphalt binder. We also included PET (~840 μm particle size) as a benchmark, as it has been reported to provide certain advantages in asphalt. All data is reported relative to the neat asphalt, which is free of *our* additives, however it may have additives included by the manufacturer.

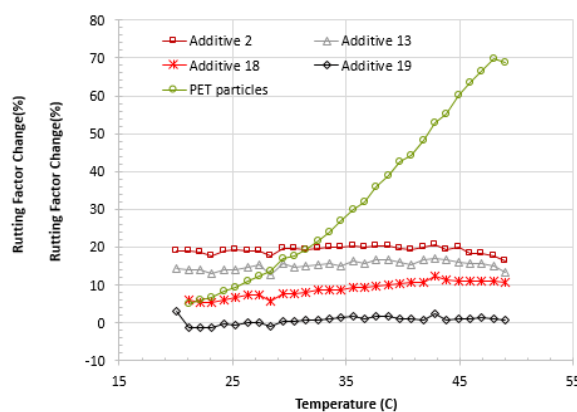
At melt processing temperatures, all additives in asphalts showed higher viscosity compared to neat asphalt. However, the formulation containing 5 wt% PET particles was significantly greater than all other compositions at all shear rates except the 20 to 35 1/s shear rate range. Additives improved the 'rutting factor' over neat asphalt by up to 20%, indicating improved resistance to rutting at temperatures above 20 °C. Additives 2, 13, and 18 improved 'fatigue factor' over neat asphalt by 5 to 19% indicating improved resistance to fatigue cracking. Improvements in rutting and fatigue factor of additive asphalts were temperature-independent in the range tested, while improvements due to PET particles diminished as temperature decreased.

DMA (dynamic mechanical analysis) temperature sweep tests showed significant improvement in storage modulus particularly for additives 2 and 18. DMA creep tests indicated improved resistance to creep under application of external load as well as improved deformation recovery after removal of the load. Notably, the additive samples showed quicker strain recovery with higher recovery ratios at -20 °C (as high as 90% versus neat asphalt at 45%). The improvement in creep resistance became more pronounced as temperature increased.

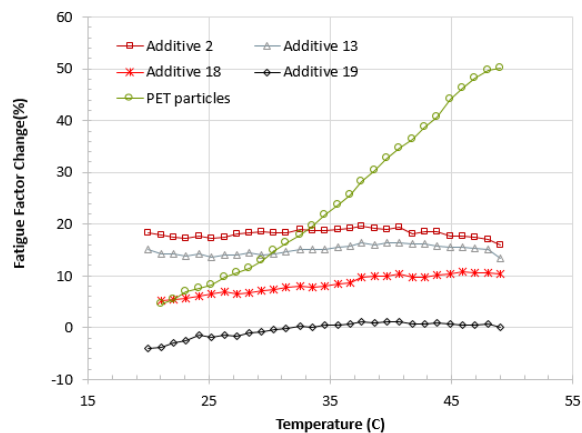
In conclusion, the rheology, creep, fatigue and rutting factors, demonstrate the performance advantages of the additives, not only over the neat asphalt, but also unmodified PET, which validates our chemical approach towards PET deconstruction.



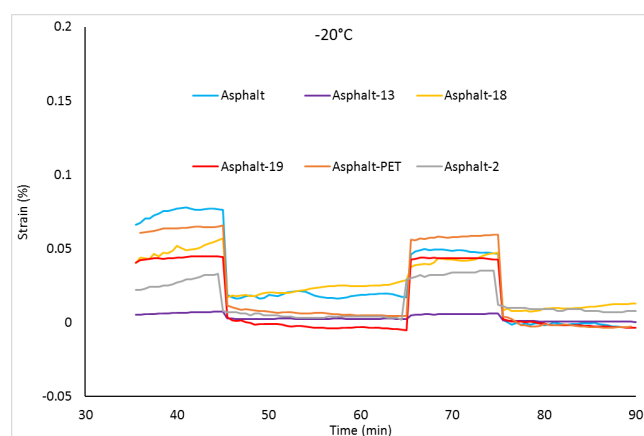
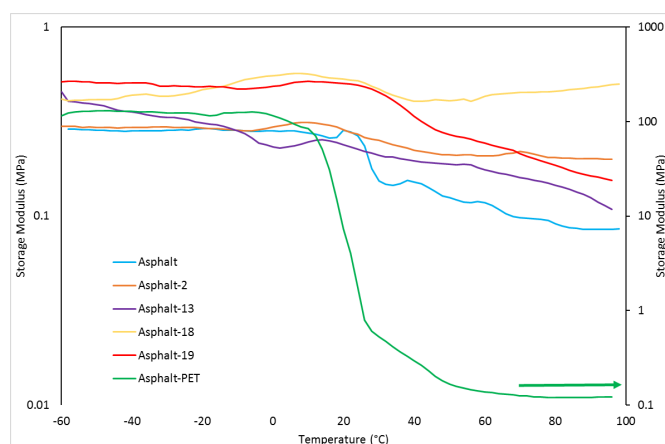
Percent increase in shear viscosity at 60°C



Percent increase in rutting factor



Percent Increase in fatigue factor



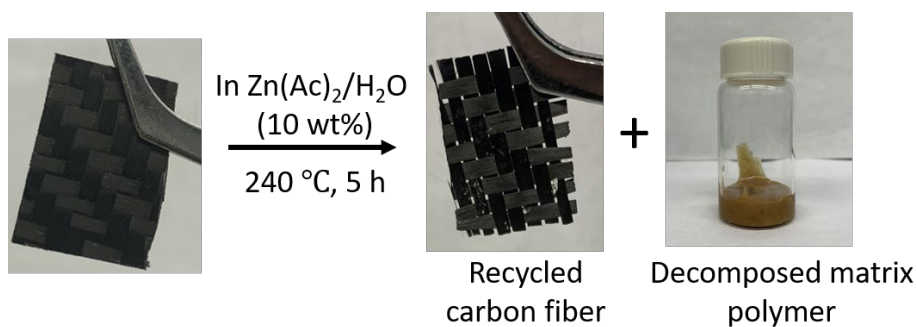
DMA Creep Results at -20 °C

Task 2. This task is divided into two parts. The first part of work is the chemical degradation of carbon fiber reinforced polymer (CFRP) containing 60wt% carbon fiber and 40wt% aliphatic amine-cured epoxy. The degradation reaction was performed in a pressure reactor. Zinc acetate ($Zn(ac)_2$) aqueous solution was used as catalytic solution, and the reaction time was fixed at 5 hours. 240 °C with a $Zn(ac)_2$ concentration of 10wt% was found to be the optimum condition for the complete dissolution of the cured epoxy in CFRP. Because both CFRP and decomposed matrix polymer (DMP) are hydrophobic, they were easily separated from the catalytic solution via filtration. The recycled catalytic solution was reused in new degradation reaction and was still effective for the degradation of the same CFRP material.

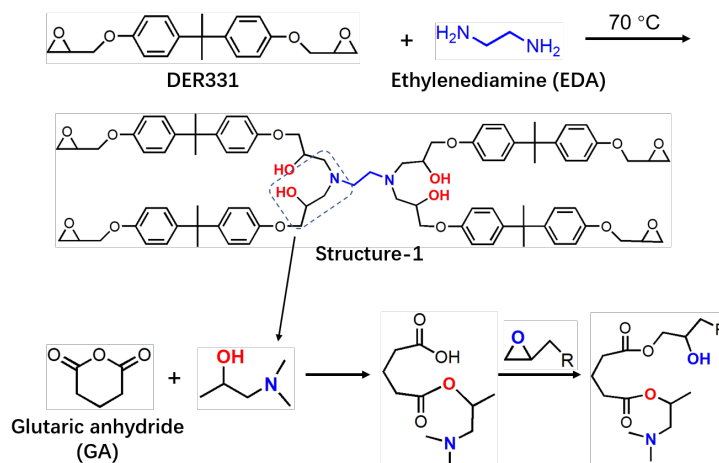
The surface of the recycled carbon fiber was clean and smooth. The DMP was soluble in common solvents, such as acetone and tetrahydrofuran. From the gel permeation chromatography (GPC) result, the DMP was found to be a polydisperse oligomer rather than a monomer. From the Fourier transform infrared (FTIR) spectra, peaks attributed to amine groups were noted in DMP, indicating that the C-N bonds were cleaved to form amine groups during reaction. In addition, the viscosity test result indicates the DMP was a viscous liquid at room temperature, but its viscosity dropped quickly as the temperature increased. This part of work set up a mild chemical degradation technology for the recycling of CFRP, which is environmentally and ecofriendly.

We reasoned that using vitrimer polymer as matrix to replace conventional cured epoxy would provide reparability and recyclability to the CFRP. In the second part of work, we designed a self-catalyzing epoxy prepolymer and reacted it with an anhydride monomer to produce a catalyst-free high-performance epoxy vitrimer. The self-catalyzing epoxy prepolymer is synthesized via the reaction of a diamine

(ethylenediamine) with an excess amount of bisphenol epoxy resin. The -OHs and tertiary amines from the epoxy prepolymer efficiently catalyzed both curing reaction and the dynamic exchange reaction, so no catalyst was needed. The prepared vitrimer exhibited excellent crack repairing, shape changing and shape memory properties, and its mechanical properties (tensile strength = 61.9 MPa, elongation at break = 10.4 %) were comparable to that of conventional epoxy polymers. This simple approach is readily integrated into current epoxy material manufacturing for CFRP preparation.



Schematic route of chemical recycling of CFRP



Preparation of self-catalyzing epoxy prepolymer and crosslinking reaction to prepare epoxy vitrimer

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