

Correlation of Mechanical and Structural Properties of Fly ash Filled–*isotactic* polypropylene composites

Dilip Chandra Deb Nath¹, Sri Bandyopadhyay¹, Aibing Yu¹, Darryl Blackburn² and Chris White²

¹ School of Material Science and Engineering, UNSW, Kensington, NSW 2052, Australia

² Research and Ash Development, Cement Australia, QLD 4076, Australia

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ABSTRACT:

The mixtures of Fly ash (FA) and *iso*-Polypropylene (PP) were used to make composite by injection molding at 210°C incorporating 20, 45 and 60 wt% of FA. The composites showed the decreased-tensile strength sequentially addition of FA at room temperature testing, whereas the tendency showed changed by gaining 15% tensile strength at elevated testing temperature, e.g. 50 and 70 °C in the case of 20wt% FA composite. The analyzed thermal behavior of composites by DSC (Differential Scanning Calorimetry) showed the functional nucleation role of FA in the formation of β - crystalline phase of PP chain and 11% level of β form crystalline has been achieved by 45wt% FA addition.

INTRODUCTION:

The naturally abundant layer-silicate clay was discovered as filler in combination with polymers. The composite materials showed high modulus, strength and heat resistance, and low the gas permeability and flammability compared to neat polymer.¹ The mechanical properties of composites generally depend on the filler's nature, size and distribution profile, aspect ratio, volume fraction, and the intrinsic adhesion between the surfaces of filler and polymer.² High aspect ratio (fiber type) fillers generally increase the yield strength because the filler is capable of attaining high local stress transferred from the polymer matrix.³

Coal-burning power stations generate the huge amount of fine powder by-product, known as FA. The storage and handling of FA are challenging tasks that affect the cost effectiveness of the relevant industry. The landfill method is mainly used to dispose FA in ash dams and lagoons. FA chemically is a mixtures of alkali and transition metal oxides mainly of silicon, aluminum and iron, and small percentage of oxides of calcium, magnesium, potassium, sodium, titanium depending on the processing and coal composition.⁴ Research on recycling and reuse of FA has become an interesting field of

study in the emerging markets for green and eco-friendly manufacturing processes and products.⁵ Recent research has used FA as filler/reinforcing material in metal⁶ and polymer matrix such as polyester⁷ epoxy² and PP⁸. Whilst PP is a very attractive thermoplastic with moderately high strength and stable at elevated temperature. The tensile strength of composite materials of PP decreased with the addition of FA⁸ which generally, happens with lower aspect ratio fillers such as FA. The reduced tensile strength in particulate fillers such as fly ash may arise from poor adhesion at the interface of the filler and the polymer that system is not in favorable in transferring the local stress from PP. The generated local stress may grow cracks followed by propagation and ends by fracture failure of the composites.^{3,9,10}

The main objectives of the current research topic were to

- a) make PP-FA composites and evaluate mechanical properties as a function of FA content at testing temperatures leading to 70°C.
- b) undertake a mechanistic study of the mechanical properties in terms of i) the microstructure and morphology and ii) calculation of interfacial interaction parameter between surfaces of FA and PP.

EXPERIMENTAL:

The tensile samples of composites (ASTM-638) were fabricated by injection molding in equipment Boy 15 S at 210°C from a 72 hour ball mill pre-mixed mixture of PP with FA concentrations of a) 20, b) 45 and c) 60 wt%. Pure PP tensile sample was also prepared injection molding under similar conditions. The details analysis of FA and composite materials were reported.¹⁰

RESULTS AND DISCUSSION:

The stress–strain diagrams of PP and PP-FA composites at 25, 50 and 70°C, and the calculated values of tensile strength, strain to failure, and percentage change in modulus of the materials were reported in recently.¹⁰ The percentage changes of tensile strength of the composite materials at different temperatures are shown in Figure 1. The tensile strength of the composites are lower than neat PP and the drop increased with increase of FA content, as reported in the literature⁹ and Figure 1 show the same behavior at 25°C.

The drop in failure strength is linear at 25°C which implies the absence of a chemical bonding between FA and PP. In higher concentration of FA additions, the larger defects are created which increase in the material linear elastic fracture mechanics type of failure.⁹ At 50 and 70°C, similar linear negative change in strength is observed between 20 to 60% FA. However, between 0 and 20% FA, there is noticeable positive increase in the strength which could be attributed to the enhanced free volume of the thermoplastic polymer at the elevated temperature. The enhanced free volume is being filled up by the fly ash apparently causing preferable wetting between PP and FA, thereby increasing

the strength. The system of talc and PP composite showed the similar behavior. The embedment of talc in void sites in PP enhanced the adhesion exceptionally with PP and gave the high performance of mechanical strength.¹¹ In the reduction of free volume environment, the segmental chain of PP gets restriction strongly, reflecting higher T_g values. The secondary binding forces -OH groups on the surface of FA may have a role in the formation of weak interfacial interactions in PP

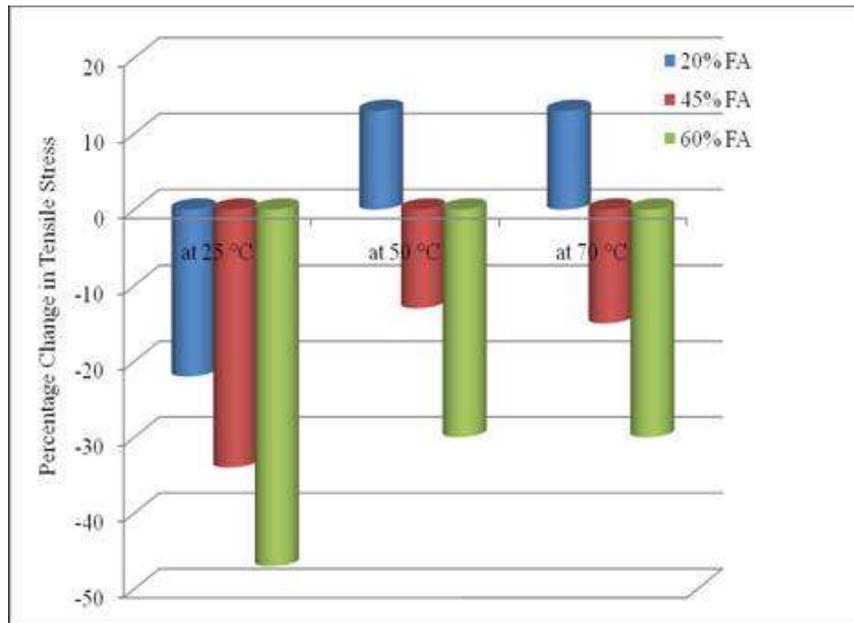


Figure 1. The percentage loss and gain in tensile stress of the PP-FA composites at different temperatures.

chain^{12,13} which is supported by further by the calculation of interfacial parameter by conventional equation later. However, 20% FA seems to be the limiting amount that can be absorbed in the free volume expansion, and any further increase in FA content results in increased linear elastic fracture. Exceeding 20% FA addition may reduce the intimate contact between the surface of FA and PP lessening the interfacial interaction.¹⁴ The mechanical properties of PP as a function of its three crystalline forms α -monoclinic, β -hexagonal and γ -triclinic phase are also reported in the literature.¹⁵

Figure 2 represents an as-expected improvement in modulus of elasticity of the composites as a function of FA%, following the rules of mixture.¹⁶

The representative SEM images of fracture surfaces of neat PP and composite of 20% FA tested at 70°C are shown in Figure 3. At 25°C, a portion of the fly ash particles are occupying heterogeneous nucleus sites consequently giving PP-FA binding interaction which led to a increase in strength to failure. In the case of 45 and 60% FA composites, the excess FA is obviously occupying sites within the spherulites and interspherulitic boundaries. In the absence of any chemical bonding agent as in this case, FA particles were separated cleanly from the PP surface.¹⁰ At 50 and 70°C, there is evidence of fragmentation, voids and more feeble flow of the polymer chains as shown Figure 3a. In 20% FA composites (Figure 3b), the PP fibrils appear to fully cover FA particles that

are within the spherulites. The phenomenon supports the presence of physical interaction between FA and PP chain and formation of interfacial interaction. The formation and development of interfacial interactions between filler and polymer in composites are critical in engineering application of composite materials. Composites that are more rigid have superior interfacial interaction due to superior transfer load from matrix to filler. Although the measurement of interfacial adhesion is an important task in the development of composites, the absolute quantification of interfacial interaction is really complicated task. Pukanszky *et al.*¹¹ have reported an empirical equation in relation with tensile strength to calculate the interfacial interaction, B_y between the filler and matrix by numerical values.

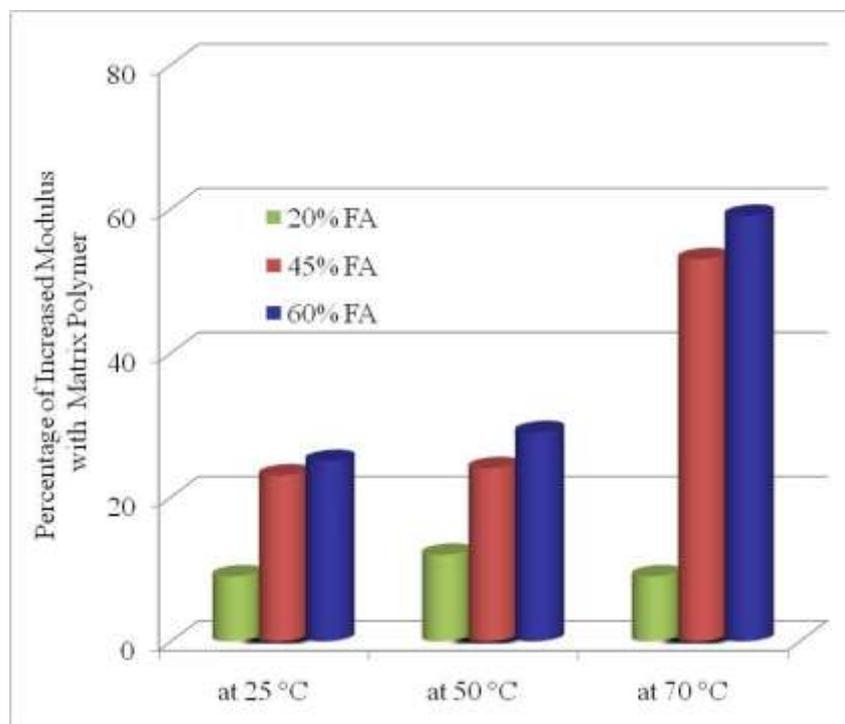


Figure 2. The percentage gains in modulus composites compared to neat PP at different test temperatures.

Higher values of B_y imply higher yield strength whilst lower values indicate materials having comparatively weaker strength composites.¹¹ Pukanszky parameter B_y , has been calculated and showed higher at elevated temperatures than room temperature, which are similar to those reported by Rong *et al.*¹⁷ and Leong *et al.*¹¹ in their composite systems using reinforcement such as calcium carbonate, talc and kaolin. The calculated values have consistence agreement with SEM images. Under atmospheric condition, a common functional hydroxyl (-OH) group or ion in general covers the surfaces of metal and metalloid oxides, which has significant role in the formation of physical bonding to the surfaces of substrates. The presence of -OH in fully hydroxyl ted silica powder has been identified elsewhere.^{12,13}

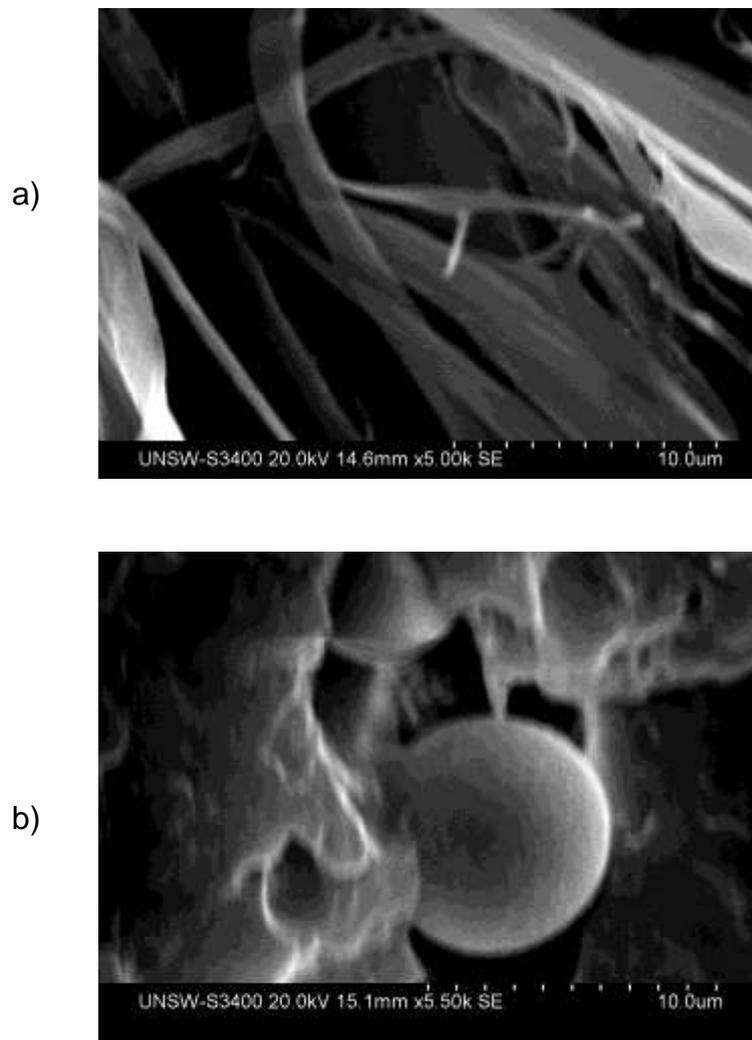


Figure 3. SEM images of fracture surfaces of tensile test at 70°C, a) neat PP and b) composite with 20% FA.

As the major ingredients of FA are oxides of silicon, aluminum – mullite and α – quartz, therefore we have made an attempt to examine the presence level of -OH group on the FA surface by XPS method in the range of binding energy 95-110 eV.¹⁰ Clearly combined peaks of -OH and -O- attached to α -quartz SiO_2 and mullite are present at the binding energy 103.7 eV. The -OH group on the surface of FA is considered in the formation of interfacial interactions with PP chain, as also is evident in Figure 3b.

CONCLUSIONS

The tensile strength decreases with fly ash content at 25°C, whereas at 50 and 70°C there is initial increase in strength up to 20% FA. The exceeding the 20% FA addition, the strength goes down and a linear drop in strength is observed between 20 to 60% FA. The drop in strength with addition of fly ash is believed to be due to stress concentration effect or formation of weak interface. The fracture surfaces of neat PP show α -spherulite fragments, voids, and bundles of drawn fibrils in neat PP. With FA addition, a portion of the fly ash particles acts as heterogeneous nucleation sites giving PP-FA interactive physical bonding, the remainder of the FA occupying sites within the spherulites and interspherulitic boundaries.

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