WHY ARE NATURAL FIBRES FAILING TO DELIVER ON COMPOSITE PERFORMANCE?

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SUMMARY

The poor performance of natural fibres as composite reinforcements where the focus on chemical aspects has not yet delivered the "holy grail" of glass fibre replacement in volume applications is discussed. An explanation is proposed based on the anisotropic structure of these fibres and its influence the composite interphase.

Keywords: natural fibres, interphase, adhesion, residual stress, thermal expansion.

INTRODUCTION

Glass fibres currently still represent more than 95% of the reinforcement fibres used globally in the composites industry. However, the increasing pressure on natural resources and the large amounts of energy required in glass fibre production has led to an upsurge in interest in the reinforcement potential of natural fibres [1-14]. Part of the justification often used for the current intense level of research of natural fibres is their apparent potential to replace high carbon footprint glass fibres with a more environmentally friendly reinforcement [1-4]. However, commercial considerations require a certain level of reinforcement performance from such fibres and many researchers refer to the respectable and sometimes equivalent level of axial stiffness exhibited by some natural fibres, which can be made to look even more attractive by comparing stiffness/density ratios [1-11]. If one severely limits the range of performance requirements on a reinforcement fibre to only its specific stiffness, it may be possible to make a case for direct replacement of glass fibre with some forms of natural fibres. However, material choice in any engineering application depends on the balance of price-processibility-performance, and one should carefully evaluate this balance for any material system. A further important point which is often passed over when presenting the case for glass fibre replacement by natural fibres is the anisotropic nature of natural fibres which means that their transverse modulus may be orders of magnitude lower than the axial values [14]. Nevertheless, it is a relatively simple exercise to use these axial data in typical rule-of-mixtures models for predicting composite performance to make a case for the possibility that some natural fibres have the potential to replace glass fibres. There has been an upsurge in research activity on natural fibre reinforced composites over the past decade based to some degree on these arguments. However, many researchers have reported disappointing levels of performance from their natural fibre composites which are significantly less than the level implied from such fibre property comparisons [1-13].

This disappointing level of reinforcement performance exhibited by many natural fibres is often discussed in terms of the challenges of obtaining good compatibility and adhesion between such fibres and polymer matrices. One of the generally accepted manifestations of 'adhesion' is in the mechanically measured value of interfacial shear strength (IFSS). The frequent inability of natural fibres to deliver an acceptable level of reinforcement is often explained by a poor level of IFSS. Particularly in thermoplastic matrix composites, reference is often made to the low level of chemical compatibility between polyolefin matrices and the polar materials found in natural fibres [1-12]. The early history of the development of composite materials is dominated by the use of chemically reactive thermosetting polymers. A natural consequence of this fact is that much of the published work relating to adhesion and stress transfer at the fibre-matrix interphase has been grounded in the assumption that chemical bonds play a key role. Consequently there are many ongoing research activities investigating chemical modification of either natural fibre surfaces or the polymer matrix or both. In the field of natural fibre reinforced polyolefins the chemical modification approach has typically followed the routes already identified as successful in improving the performance of glass fibre reinforced composites. Thus chemical modification of fibre surfaces and the use of maleic anhydride modified polyolefins (MAP) as matrix additives have been investigated by many groups [1-12]. This work can also be summarised by saying that chemical modification of the interphase has been significantly less successful with natural fibres in comparison with glass fibres. The use of MAPs has had better results but in general these additives must be used in much greater concentrations than is typical in glass fibre reinforced systems and also show significantly less effect. Moreover, many researchers in this area do not fully take into account the cost of such large scale chemical modifications on the overall financial picture for these composite materials. The relative cost advantage of natural fibre can be rapidly diminished by the necessity of using expensive chemical methods to improve composite performance.

To date the influence of the anisotropic physical structure of natural fibres, although often commented on, has received little attention. Characterisation of fibre mechanical performance is an exacting task with many potential pitfalls; however it is intuitively obvious that most fibre testing will be least challenging experimentally when characterising axial properties. The characterisation of the transverse properties of a reinforcement fibre [13] is a much greater challenge. Cichocki and Thomason have studied [14] jute reinforced composites where a full thermo-mechanical characterisation of the fibre was carried out and they quantified very high levels of anisotropy in these fibres. This paper will present data on the performance of injection moulded jute reinforced polypropylene and give a balanced comparison with equivalent glass reinforced composites. Data will be presented on the effects of chemical modification of the interphase in the jute-polypropylene composites. Both chemical modification of the PP matrix and mercerisation and silane treatment of the fibres will also be shown to have little significant effects on the level of natural fibre reinforcement of polypropylene in comparison to glass fibres. Finally, a hypothesis based on the fibre anisotropy is proposed which can explain the poor performance, in comparison to expectation and to glass fibre performance, of natural fibres in many composite systems.

EXPERIMENTAL

The long natural fibre polypropylene (LNFPP) compounds used in this investigation have been produced using a combination of a crosshead extrusion wire coating process in combination with a proprietary sizing technology as previously described[15,16]. Jute yarn, linear density 2.9 g/m, (Lehigh Company) was used, as received or after surface treatment, with polypropylene homopolymer (Huntsman) P4C6Z-059 polypropylene, MFI=35 g/10min, to produce LNFPP composites. The yarn was pulled through the crosshead coating device which was fed with PP melt at 225°C from the attached single screw extruder. When required, the level of fibre-matrix interaction in some systems was changed by the addition of the desired amount of Polybond 3200 MAP coupling agent dry blended with the PP pellets fed to the extruder. On exit from the die the coated yarn was cooled in a water bath and chopped into pellets of 12.5 mm length. When required a sizing was applied to the Jute yarn via an inline continuous applicator positioned before the entry to the crosshead coating die [15]. The compounds were dried at 90°C for 6 hours prior to injection moulding using a 200-ton Cincinnati Milacron moulding machine with an 225 g barrel capacity. The temperature profile from the hopper to the mould varied as follows: rear 143°C, centre 199°C, front 188°C, nozzle 188°C, mould 54°C. Mechanical testing was performed at 23°C and at a relative humidity of 50%. Tensile properties were measured according to ASTM D-638, flexural properties were measured according to ASTM D-790. The preparation of the glass fibre PP composites referenced in this work has been described previously [17,18]. These glass fibre PP materials were, in general, prepared using the same conditions described above.

RESULTS AND DISCUSSION

Figure 1 presents results for the modulus of LNFPP as a function of fibre content and the level of MAP added to the system. This figure also includes values of modulus calculated using the modified rule-of-mixtures [14,17] $E_c = \eta_0 \eta_l V_f E_f + (1 - V_f) E_m$

where E_f=40 GPa, E_m=1.3 GPa, η_o=0.65 [17], η_l calculated using a fibre length of 3.5 mm, and V_f calculated using densities ρ_{nf}=1.4 g/cc and ρ_{gf}=2.6 g/cc. It can be seen that the modulus of the system increases significantly with increasing natural fibre content. At 30% weight NF there is an approximate 200% increase in tensile modulus above that of unreinforced PP. However, it is also clear that the measured value of modulus of the LNFPP system is significantly lower that the levels predicted by using the longitudinal fibre modulus E_f=40 GPa. Furthermore, at the 30% weight reinforcement level the LNFPP modulus is only approximately 60% of the 6-7 GPa modulus typical of an injection moulded 30% GF-PP material [17, 18]. The addition of MAP does not appear to have any significant effect on the modulus of LNFPP. Similarly Figure 2 presents results for the strength of LNFPP as a function of fibre content and the level of MAP added to the system. It can be seen that addition of natural fibre to PP actually reduced the tensile strength of the system, with a greater reduction in strength with increasing fibre content. The tensile strength is increased with increasing fibre content when 2% MAP is present in the PP matrix. It can also be seen that the flexural strength of the system is higher than the tensile strength on average by a factor of approximately 1.6. This ratio of flexural to tensile strength has been observed in a number of composite systems [19,20]. In general it can be seen that the flexural strength is little improved by

addition of natural fibre unless MAP is present in the PP matrix. It can be commented that the addition of NF to PP does increase the strength performance by up to 30% when MAP is used as a coupling agent. However, the data for GFPP puts this statement into some perspective. It can be seen that the addition of short glass fibre to PP leads to significant improvements in strength performance even in the absence of MAP coupling agent. When 2% MAP is added to the PP matrix, increases in strength greater than 200% can be achieved over the base PP matrix. This Figure makes clear the difference in the reinforcement performance of glass and natural fibre and emphasises the challenge still before natural fibre materials development to fulfil the idea of glass fibre replacement. Figure 3 compares the influence of the MAP matrix concentration on the strength performance in LNFPP and SGFPP. The data in this Figure again confirms the large difference in reinforcement performance level of glass fibres versus natural fibres in PP. Without MAP added to the matrix there is already a significant difference between the strength levels in these materials. The LNFPP system responds very weakly to the addition of MAP and appears to reach a maximum at around 4% added MAP. The SGFPP system responds more rapidly to the addition of MAP and reaches a plateau level already at 0.5% addition. At this low concentration of MAP the SGFPP system shows a 50% increase in strength compared to the LNFPP increase of only 25% requiring an eight times higher concentration. This requirement for high MAP levels will have significant negative implications for the cost of the LNFPP system.

Figure 4 summaries the effects of various chemical modifications made to the interphase in the LNFPP composite (20% wt jute fibre) in this investigation. It can be observed that addition of 20% water treated Jute fibres has no significant effect on the tensile strength of PP whether or not MAP is present. Mercerisation (NaOH pre-treatment) of the fibres also has no significant effect on composite tensile strength. Only the combination of NaOH fibre pretreatment and added MAP resulted in a small, but significant, increase in tensile strength. In the case of the composite flexural strength the addition of 20% Jute fibres either the control water treated or NaOH treated led to only a minor increase over the PP resin alone. Once again the combination of NaOH fibre treatment and added MAP lead to the greatest effect on flexural strength. As previously discussed it has often been suggested that the use of silane coupling agents may also improve the interphase in natural fibre composites. These multifunctional molecules have been extremely important to the growth in the use of glass fibres for composite reinforcement. It is thought that hydrolysed silane molecules have the ability to react by condensation reaction with the many hydroxyl groups which are present in the chemical components of natural fibres. Although a large number of silanes were screened in this investigation there were very few significant effects measured on the resultant performance of the LNFPP composites. Figure 4 also reviews some results obtained with aminopropyltriethoxysilane (APS), one of the more effective silane coupling agents in this study. It can be seen that the surface treatment of Jute fibre with silane alone has little significant effect on the tensile strength of 20% LNFPP composites and also brings little improvement in comparison with the PP alone. Finally, when the jute fibres were pretreated with NaOH and then APS and the PP matrix contained 2% MAP a significant increase (+30%) in the composite tensile strength is obtained over the performance of unreinforced PP. Furthermore, an increase in flexural strength of a similar level was observed. However, the results on composite strength obtained in

these experiments, cannot be said to be a likely *cost effective* route to improving natural fibre composite performance. Moreover, to put these results into perspective, Figure 4 also contains data on glass fibre reinforcement of the same PP matrix. Data for LGFPP are presented at both equal fibre weight fraction (20%) and equal fibre volume fraction (≈0.135) as the LNFPP samples. These results emphasis the huge challenge facing natural fibres if they are to be used as a direct replacement for glass fibres.

It would appear from the above results and discussion that, in general, natural fibres do not deliver the level of reinforcement of polypropylene that might be anticipated from the initial analysis of their longitudinal modulus combined with their low density. Furthermore extensive use of chemical methods to improve fibre-matrix interaction does not appear to deliver significant, cost effective, improvements in the performance of natural fibre reinforced PP in comparison to glass fibre reinforcement. It can be suggested that one of the principal reasons for this poor performance is the known anisotropic structure of these natural fibres. The level of thermo-mechanical othotropicity of jute fibres has recently been quantified [14] and it is of interest to note that the transverse and shear moduli of these fibres are an order of magnitude lower than the longitudinal modulus. This significantly lower level of transverse and shear modulus can explain the low moduli of natural fibre composites when a large fraction of the fibres are loaded off-axis, as is the case with most injection moulded thermoplastics. It seems likely that the othrotropic physical nature of natural fibres may also have an important influence on the stress transfer capability of the fibre-matrix interphase.

Despite the high level of focus on the chemical nature of 'adhesion' and interphase modification, a number of authors have also commented on the role of shrinkage stresses contributing to the stress transfer capability at the fibre-matrix interphase[18-27]. Thermoplastic composite materials are generally shaped at elevated temperature and then cooled. Since in most cases the thermal expansion coefficients of polymers are much greater than reinforcement fibres this cooling process results in compressive radial stress σ_r at the interphase [23]. Assuming that the static coefficient of friction (β) at the interphase is non-zero these compressive stresses will contribute a frictional component $\tau_f = \beta . \sigma_r$ to the apparent shear strength of the interphase. Thomason has examined the level of IFSS in a number of glass fibre reinforced thermoplastics and shown how the results can be well modelled by assuming that the main component of the IFSS is actually due to residual stress and static friction at the fibre-polymer interphase [17,18,24-27]. Thomason has further shown how an increase of the IFSS in SGFPP caused by the addition of 2% MAP could be explained by an increase in the fibre-matrix static coefficient of friction from 0.4 to 0.7. It was proposed that such an increase in β could be explained by an increased level of polymer-fibre contact area on a nanoscale due to an improved wetting of the fibre surface by the higher polarity MAP matrix [17,27]. Schoolenberg [28] has reported a value of $\beta=0.65$ in GF-PP.

Consequently, we can make a case for residual thermal stress contributing a significant amount to the apparent IFSS in thermoplastic composites. It is therefore of interest to compare the relative levels of residual compressive stress in polypropylene composites where different reinforcements are used. Unlike glass, many other reinforcement fibres are otrthotropic in their mechanical and thermal properties and this may have significant

influence on the residual stress state in any composite. This point is illustrated in Figure 5 which shows results of calculations of the residual radial compressive stress present at the fibre-matrix interphase in polypropylene containing various common reinforcing fibres. The relevant input parameters for the calculation are given in Table 1 [14,22-24]. As indicated above it can be seen that carbon, aramid and jute are highly anisotropic in comparison with glass. These fibres all have small but negative LCTE's in the fibre direction and much larger positive LCTE's in the transverse direction. The effect of this anisotropy is clearly illustrated in Figure 5. All these systems exhibit compressive residual radial stress at the interphase at room temperature and all show a mild dependence on the fibre content. However, the magnitude of these residual stresses is strongly dependent on the fibre properties. Glass fibres exhibit the highest levels of residual stress with carbon fibres lower but at a similar level. Aramid fibres show significantly lower levels and the natural fibres have a very low level of residual radial compressive stress at all fibre contents. These results are well in line with the generally accepted view on interphase adhesion in thermoplastic composites that glass and carbon are often well bonded, aramid fibres present some adhesion challenges, and that there are serious problems with IFSS levels in natural fibre composites. Although the remedies for these issues are often sought in the chemistry of the system, these results suggest that we also need to better understand the role of fibre structure, the residual stress, and interphase friction, on apparent IFSS in thermoplastic composites.

Table 1 Input data used for modelling interphase residual stress [27]

	Glass	Carbon	Aramid	Jute	PP
Longitudinal Modulus (GPa)	72	220	130	40	1.5
Transverse Modulus (GPa)	72	14	10	5.5	1.5
Longitudinal Poisson Ratio	0.22	0.08	0.3	0.11	0.35
Transverse Poisson Ratio	0.22	0.01	0.1	0.01	0.35
Longitudinal LCTE (mm/m.^{o}C)	5	-0.36	-3.6	-0.6	120
Transverse LCTE (mm/m.^{o}C)	5	18	50	77	120

This analysis can be carried further by noting the average level of residual compressive stress at the interphase in the Jute-PP system in Figure 5 is approximately 3 MPa. In the absence of values for β in this system we can approximate the potential IFSS contribution in Jute-PP using the GF-PP values [27] of β=0.4 for unmodified PP matrix and β=0.7 for a 2% MAP modified matrix. By this means we obtain a value for the IFSS in the Jute-PP system with or without the use of MAP. This is one of the input values required in the Kelly-Tyson model for the prediction of composite strength which has been well validated for the GF-PP system [17,18,24,26]. Further required input parameters for this Jute-PP system have been published previously [14,29], average fibre diameter 42±0.9 mm, average fibre length 3.5±0.5 mm, average fibre strength 410±38 MPa. Using these input values, the predicted tensile strength for the composites shown in Figure 2 have been calculated using the Kelly-Tyson equation [26,30]. The results are shown in Figure 6 where the shaded areas represent the range of strengths predicted by using the 95% confidence limits on the input parameters given

above. In both cases the experimental data for the Jute-PP systems with and without MAP fall well within the range of predicted values. Consequently, it appears that it is possible to fully explain the tensile strength exhibited by injection moulded LNFPP using existing strength models and the assumption that an apparent IFSS for the system can be calculated directly from the residual compressive interfacial stress and appropriate values for the static coefficient of friction of the system. Moreover, this analysis is also able to match the experimentally observed trends for the effects of fibre content and matrix modification using MAP on the composite strength. Furthermore, the analysis relates the poor level of performance in this LNFPP system directly to the anisotropic nature of the fibre morphology. This hypothesis opens the possibility of novel routes towards the improvement of natural fibre reinforcement performance through manipulation of the internal structure of these highly anisotropic fibres.

CONCLUSIONS

One of the most commonly used justifications for research and development activity of natural fibres is that the some properties of some of these fibres can match the reinforcement level of glass fibres. However, an overwhelming number of the published results have failed to fulfil these expectations and most natural fibres show only moderate reinforcement in stiffness and little significant positive effect on composite strength in comparison to glass fibres. Such results are often explained in terms of the poor interfacial compatibility between many natural fibres and polymers. However, investigations based on this hypothesis and subsequently on surface and interfacial modification of natural fibres are also failing to show substantial (and economically acceptable) improvements in composite performance. The data on injection moulded long fibre jute reinforced polypropylene presented here support the above conclusion. Addition of jute fibre to PP led to some increase in modulus, although much less than expected from a rule-of-mixtures analysis. The strength of PP was significantly reduced by the addition of untreated natural fibres. Furthermore, in comparison to the magnitude of the effects in glass fibre reinforced PP, chemical modification of the matrix using MAP, and surface modification of the natural fibres using mercerisation and silane treatments resulted in little significant improvement in strength.

It is concluded that one of the principal reasons for this poor reinforcement performance is the internal anisotropic structure of these natural fibres. The level of thermo-mechanical othotropicity of most natural fibres results in transverse and shear moduli of these fibres an order of magnitude lower than the longitudinal modulus which consequently delivers significantly lower than expected moduli for natural fibre composites. Furthermore, the othrotropic physical nature of natural fibres also has an important influence on the stress transfer capability of the fibre-matrix interphase. It is shown possible to predict a value of the stress transfer capability of a natural fibre – polypropylene interphase purely from the level of static friction at the interphase and the residual compressive interfacial stress as determined by the orthotropic thermo-mechanical characteristics of the natural fibres. Using this value of IFSS it is then possible to predict the strength of these NF composites close to the experimentally observed values. This analysis is also able to match the observed trends for the effects of fibre content and matrix modification using MAP of the composite strength.
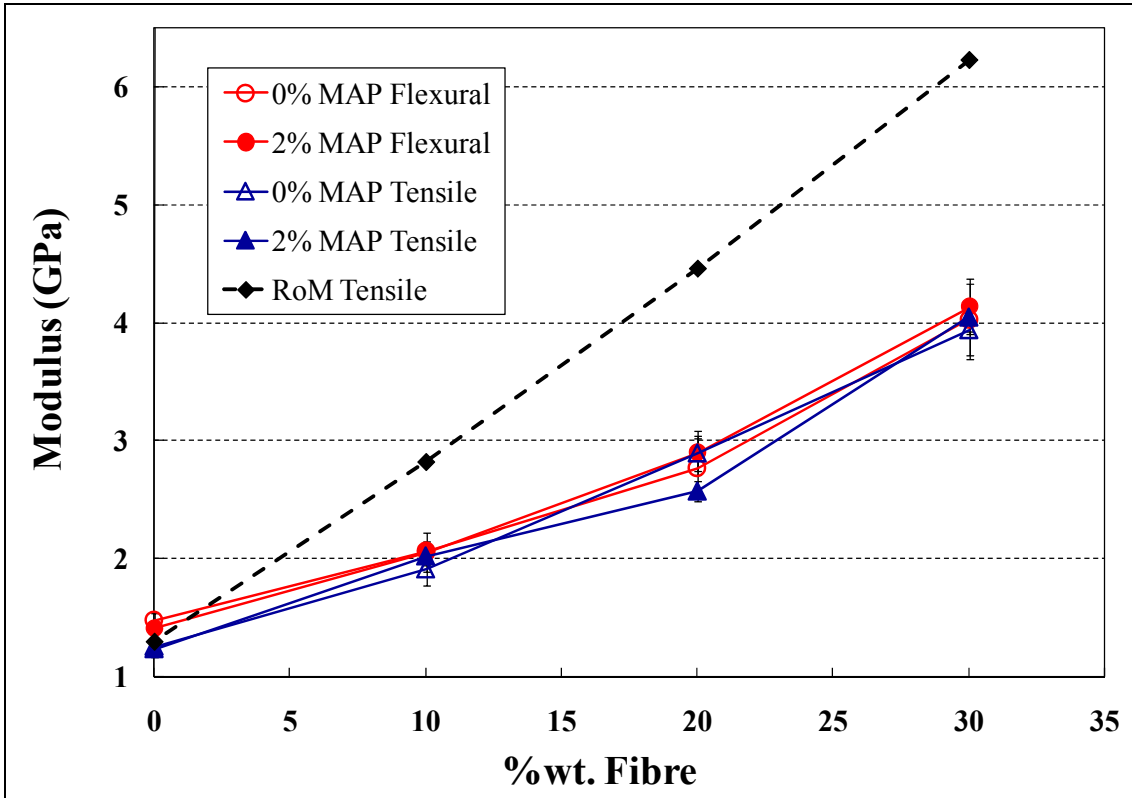
Figure 1 Influence of fibre content and MAP content on the modulus of LNFPP
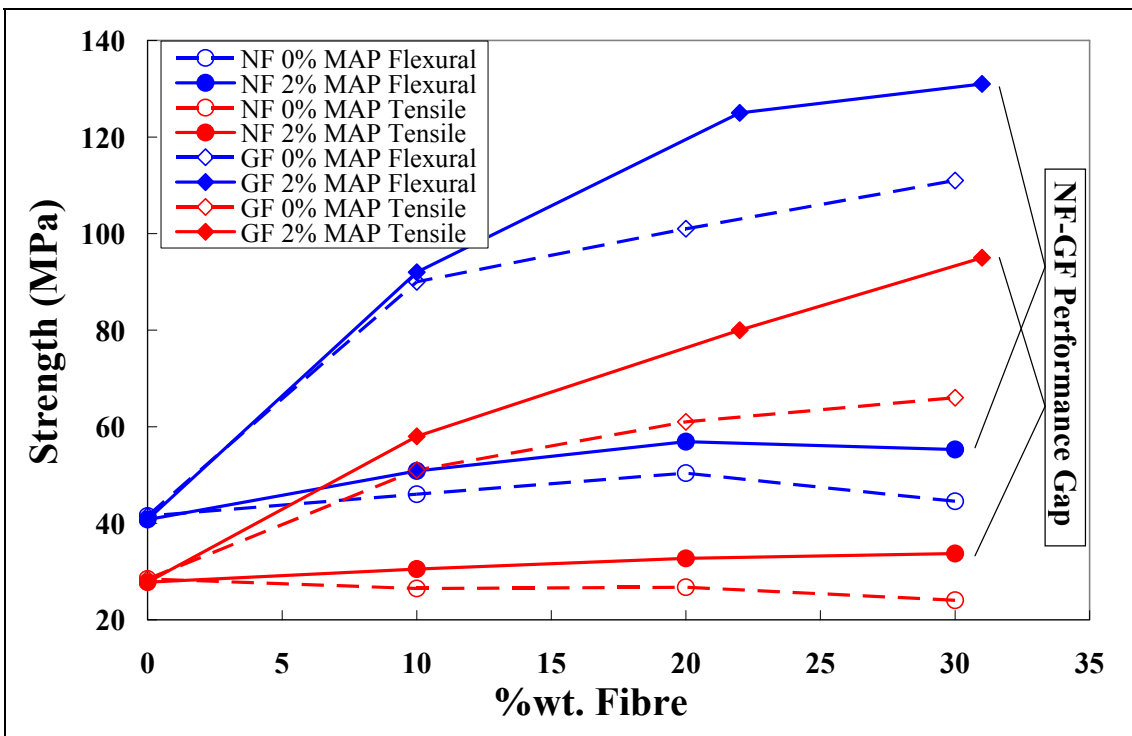

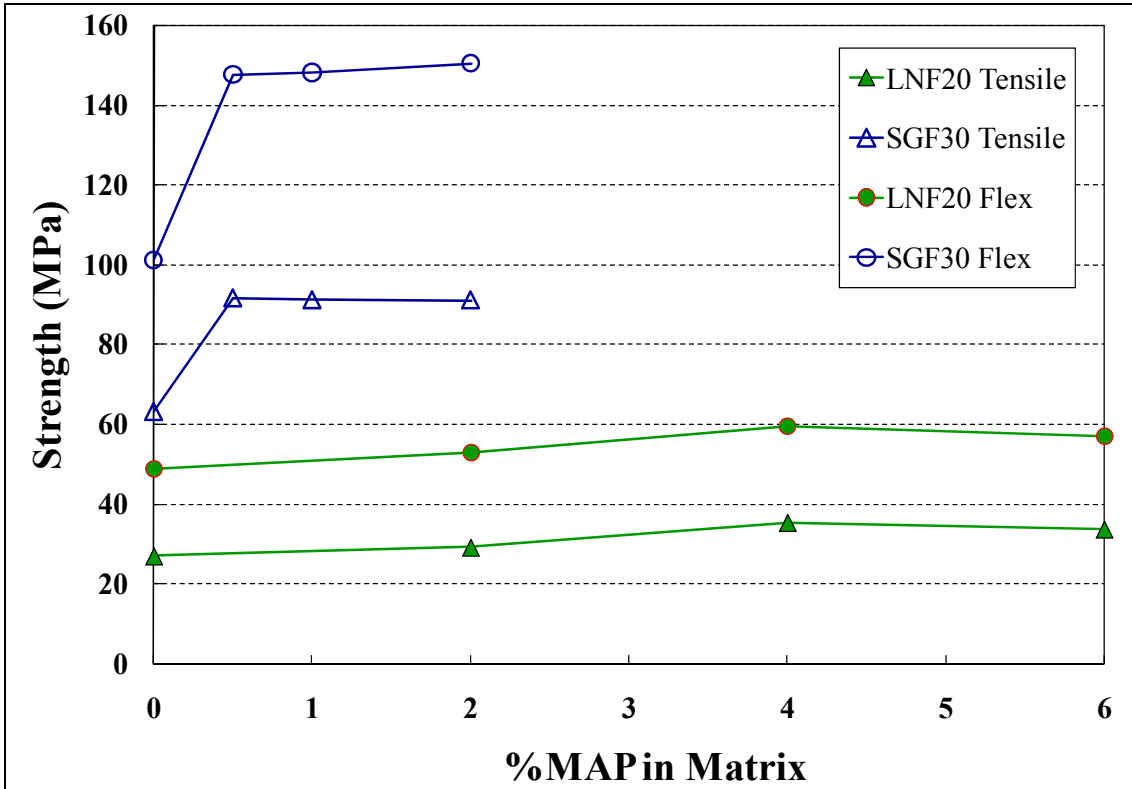Figure 2 Strength of Injection Moulded NFPP and GFPP Composites.

Figure 3 Influence matrix MAP content on the composite strength with 30%GF and 20%NF (approximately equal volume fractions of 0.135)
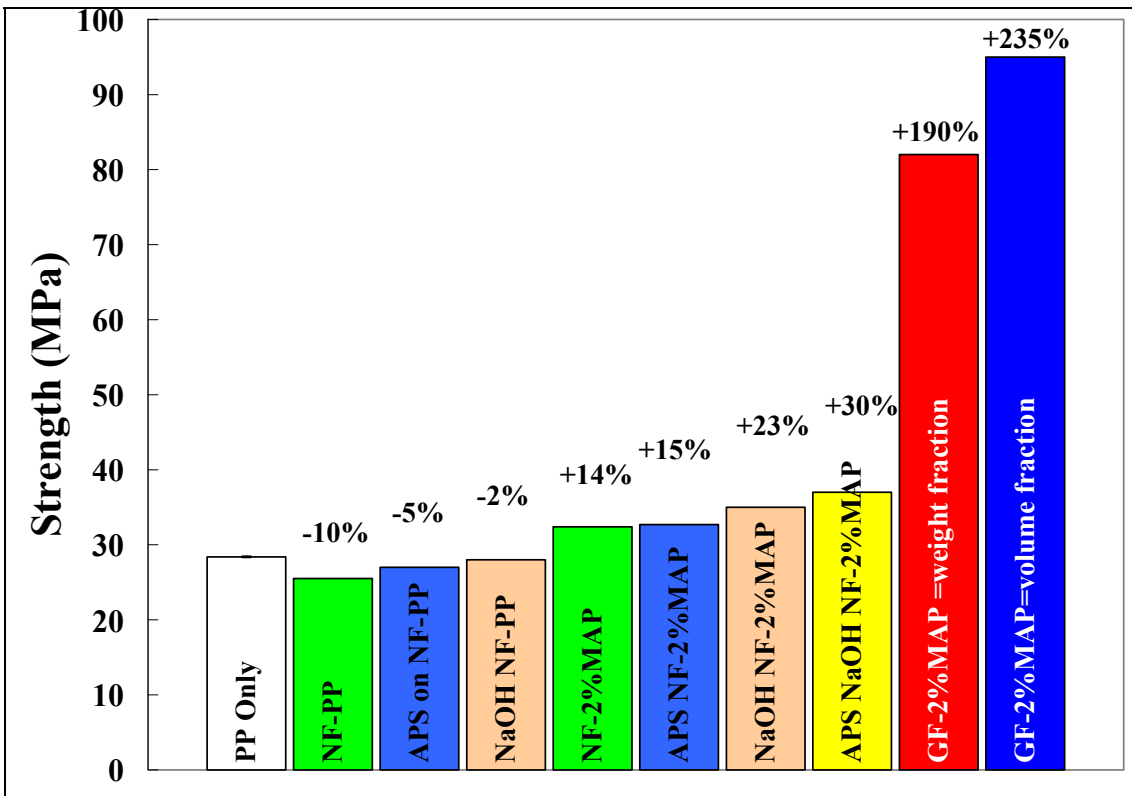

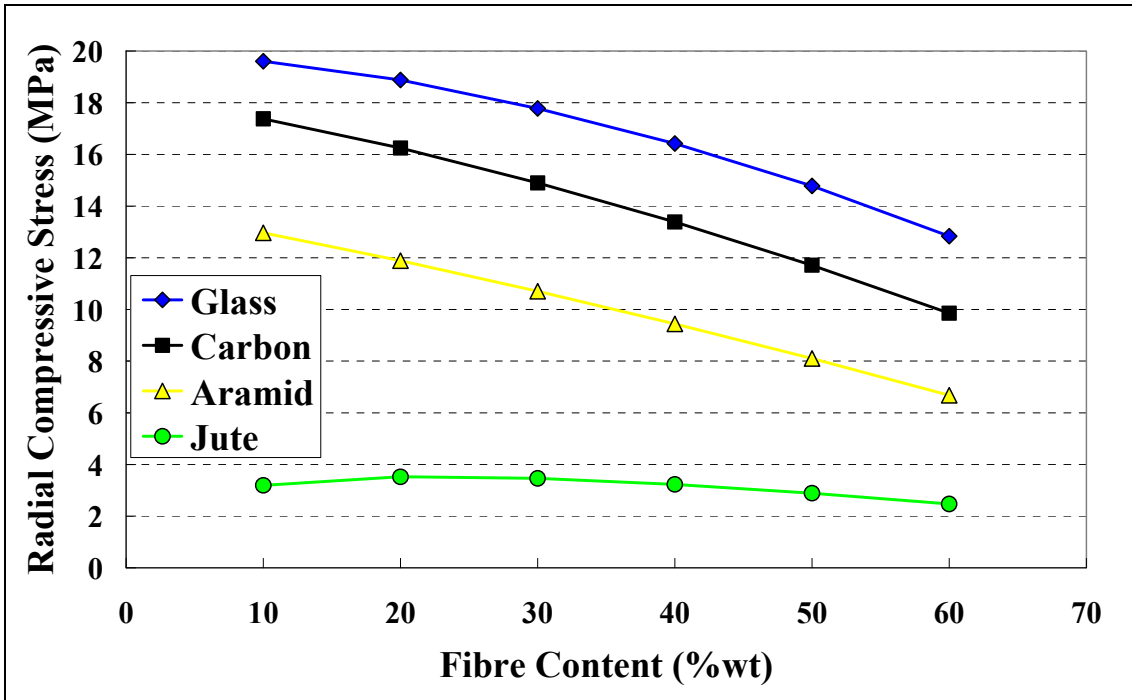Figure 4 Influence of chemical modifications on the tensile strength of 20% LNFPP

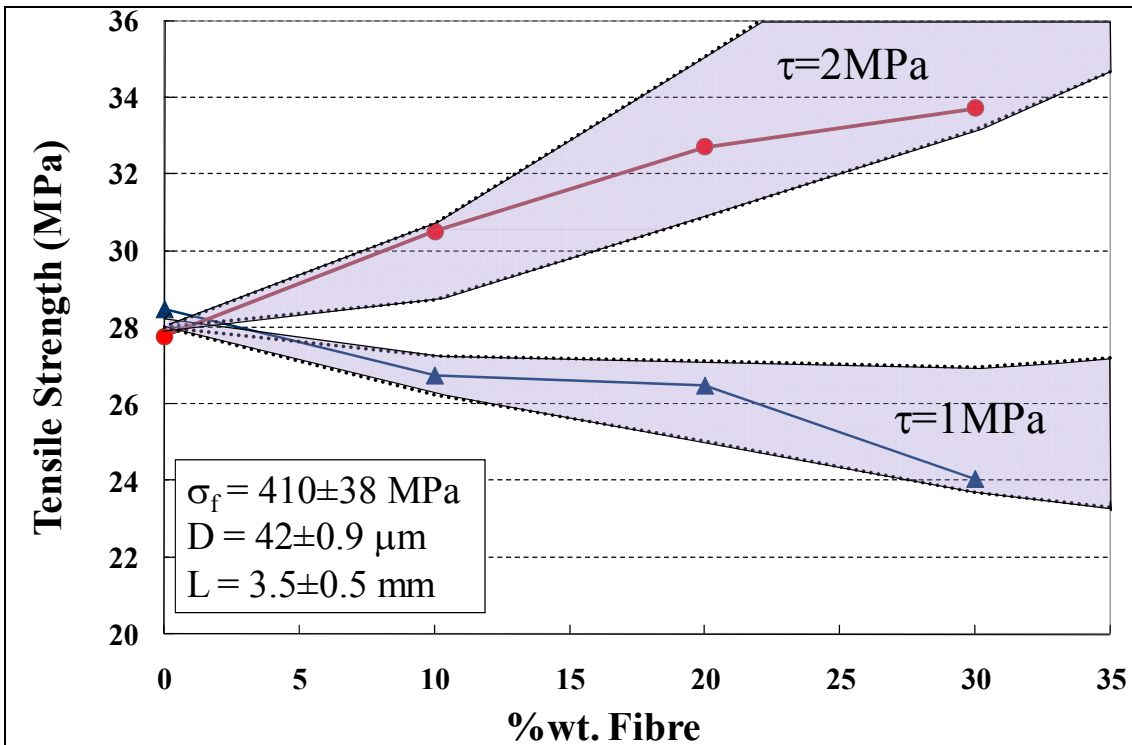Figure 5 Modelling of interphase residual radial compressive stress in reinforced PP

Figure 6 Comparison of experimental strength of LNFPP with Kelly-Tyson modelling using IFSS calculated from interfacial residual radial compressive stress

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