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THERMOPLASTIC COMPOSITES BASED ON FLAX FIBRES AND POLYPROPYLENE: INFLUENCE OF FIBRE LENGTH AND FIBRE VOLUME FRACTION ON MECHANICAL PROPERTIES

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Abstract: Natural-fibre-mat-reinforced thermoplastic (NMT) composites based on flax fibre mats and a Polypropylene (PP) matrix were manufactured using (i) a film-stacking method and (ii) a paper making process. The influence of fibre length and fibre content on stiffness and strength is reported and compared with data for glass-mat-reinforced thermoplastic (GMT) composites, including the influence of using maleic-anhydride grafted PP. The data is also compared with existing micromechanical models like Kelly-Tyson and Cox-Krenchel for strength and stiffness, respectively. A good agreement was found between theory and experiment in case of stiffness while in case of strength the experimental values fall well below the theoretical predictions. Results indicated that NMTs are of interest for low-cost engineering applications and can compete with commercial GMTs, especially when a high stiffness per unit weight is desirable. Results also indicated that the key area for future development lies not only in improved adhesion but mainly in improving the fibre strength.

INTRODUCTION

In the last decade, research activities in the area of thermoplastic composites have shifted towards the development of 'cost-performance' engineering materials. Especially, glass-mat-reinforced thermoplastic (GMT) materials [1], being stampable sheet products based on commodity resins such as polypropylene (PP) and moderate loadings of relatively long glass fibres in random array have proven to be very successful in high volume markets such as the automotive industry. Because of their excellent price-performance ratio, E-glass fibres are by far the most important fibres for these type of composites. However, these fibres do have some disadvantages regarding

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(thermal) recycling issues and abrasive wear of processing equipment. Moreover, glass fibres are non-renewable and can cause skin irritations during processing and assembly of fibre-reinforced parts.

Nowadays, ecological concern has resulted in a renewed interest in natural materials and issues such as recyclability and environmental safety are becoming increasingly important for the introduction of new materials and products. An interesting alternative for the use of glass fibres as reinforcement in engineering materials are natural fibres based on lignocellulose such as flax, sisal and jute [2]. These vegetable fibres are renewable, nonabrasive, can be thermally recycled, and show less concern with safety and health. In addition, they exhibit excellent mechanical properties, especially when their low density and price in comparison to E-glass fibres is taken into account. Although these fibres are abundantly available, especially in developing countries such as Bangladesh and India, the applications are still rather conventional, i.e. ropes, matting, carpet backing and packaging materials. Moreover, in the last few decades the use of natural fibres for these type of applications has been declined due to the introduction of synthetic fibres, such as nylon and polypropylene. Hence, also in the economic interests of developing countries, there is an urgent need for new application areas for these natural fibres.

The first natural-fibre-reinforced composites were based on thermoset matrices, such as unsaturated polyester or phenolic resins, together with sisal and jute [3,4]. More recently, developments shifted to thermoplastic matrix composites [5-7]. This research focuses on the development of natural-fibre-mat-reinforced thermoplastic (NMT) composites, being GMT-like materials based on natural fibres [8]. In this development study flax fibres are used as reinforcements, mainly because of their excellent mechanical properties when compared with other natural fibres and also because of availability in different forms in Western-Europe. PP is used for a number of reasons. First, it is easy to process and one of the cheapest polymers on the market. Secondly, it has a low processing temperature, which is essential because of the relatively low thermal stability of natural fibres (200-250°C). Finally, it has the perfect ability to protect the hydrophilic natural fibre because of its strong hydrophobic and apolar character. A clear disadvantage of this apolar character for composite applications is its limited wettability as well as poor interfacial bonding with reinforcing fibres. This disadvantage can, however, be overcome by functionalization of the polymer, which has proven to be very effective in enhancing fibre/matrix adhesion in composite systems based on polyolefins [9,10]. For the optimisation of the mechanical performance of the flax/PP composites it is expected that both flax content and the flax fibre length should be as high as possible. However, high fibre volume fractions and large fibre lengths will limit the processability of such composites. Therefore, a balance between mechanical performance and processability should be found.

In this research the influence of fibre length and volume fraction is investigated on random flax-mat-reinforced PP composites, which were manufactured using the film-stacking method and the suspension impregnation method, respectively. The latter method allows for a systematic variation of the fibre length, since no fibre break-up occurs during processing. The use of conventional melt-processing methods for the production of short fibre reinforced compounds such as extruders will degrade the fibre length and are therefore not suitable for such a systematic study. In addition, the influence of maleic anhydride PP (MA-PP) on the mechanical performance of flax/PP composites was also studied. Flax fibres, as well as glass fibres, contain functional OH-groups that are able to interact chemically with the maleic anhydride grafted polypropylene. From this an improved interfacial bond strength between the flax fibre and the modified PP is expected. In order to get a better insight in the importance of all these different parameters, the experimental results were compared with model predictions using micromechanical models for random short-fibre-reinforced composites [11-15].

EXPERIMENTAL

Materials

In this study random flax fibre mats of Eco Fibre Products BV (The Netherlands) in combination with an isotactic polypropylene (PP) matrix of Shell (XY6500T) with a melt flow index of 35 were used. In order to study the effect of improved fibre/matrix adhesion on composite performance, 5 wt.% of a maleic anhydride-modified polypropylene (MA-PP) (Polybond® 3002, BP Chemicals Ltd.) was added to the homopolymer. NMT composite plates with different fibre contents were manufactured using the film-stacking method. In this film-stacking method, pre-dried flax fibre mats and PP film were stacked alternately. PP as well as films based on a blend of PP and MA-PP were made using film-blowing equipment. Impregnation was achieved by applying heat and pressure in a hot-press (200°C, 25 bar for 15 min.). The obtained composite plate was cut into tensile specimens according to ASTM-D 638 specifications. The Young's modulus of the PP matrix was approximately 1.6 GPa and the yield stress was about 32 MPa. Random MA-PP/flax composites were manufactured in a similar way. The modification of PP with a commercially available MA-PP (Polybond 3002, BP Chemicals Ltd.) was performed in a twin-screw extruder (Werner & Pfleiderer ZSK25).

For the suspension impregnation process a dispersion of flax fibres and PP-fibres (Young's modulus = 1.6 GPa and yield stress = 29 MPa) was made in an ethanol/water (1:1) mixture. In separate production runs, three different flax fibre lengths were used (3, 6 and 25 mm). Significantly differing fibre lengths were removed before use. After drying of the materials at room temperature for 24 hours and at 60°C for one hour, this lofted mixture of flax fibres and PP fibres was consolidated in a hot-press. For the suspension impregnation process random flax/MA-PP composites were made by treating the fibres with MA-PP (Hostaprime® HC5, Hoechst). Degreasing of the flax fibres was executed via extraction of the flax fibres with an ethanol/toluene (2:1) mixture, refluxed for three hours. The extraction fluid was replaced by a new, fresh fluid after which it was refluxed for one hour. The fibres were subsequently washed for approximately 30 minutes with cold ethanol, followed by 6 litres of cold water over a büchner-funnel. The extracted fibres were dried at 60°C in an oven with circulating air for 24 hours. Afterwards they were immersed in a solution of MA-PP copolymer in hot toluene (100°C) for 10 minutes. The concentration of copolymer in solution was approximately 2 wt.% on the fibres. After treatment, the fibres were extracted with toluene for one and a half hour to remove all components not chemically bonded to the flax fibres. Finally, the fibres were dried at 60°C for 24 hours. These treated flax fibres were used in the suspension impregnation process, yielding a composite plate using the compression moulding method described above.

Test methods

Uniaxial tensile tests on random flax mat composites were performed on a Frank tensile machine, type 81565, according to ASTM standards (D638M). The specimens were cut in a dog-bone shape with dimensions 200mm x 20mm x 1.8mm. An extensometer was used to monitor the elongation of the tested specimen. The uniaxial tests on random flax/PP composites, made by the paper making process, were performed on a Zwick tensile testing machine, type Z010. The specimens were rectangular cross-sections having dimensions of 100mm x 20mm x 2mm. Again, an extensometer was used to monitor the elongation of the tested specimen.

RESULTS AND DISCUSSION

Influence of fibre length

Composite stiffness

The results of the tensile tests on the manufactured flax-fibre-reinforced composites, with varying fibre lengths, are given in Figure 1 and 2. Figure 1 shows the Young's modulus for the systems based on PP and MA-PP together with the Cox-Krenchel model predictions. Cox [11] introduced a fibre length efficiency factor into the 'rule-of-mixtures' equation for the composite stiffness E_c, to account for the 'ineffective' loading of fibres over their stress transfer length. Since the fibre is only partly utilised in the case of a short fibre composite, these effects have to be taken into account when modelling the mechanical performance of such composites. The expression used by Cox yields:

$$E_c = \eta_{LE}\, V_f E_f + (1 - V_f) E_m \tag{1}$$

In the case of stiffness related problems Cox's 'shear lag' model is used for the calculation of the fibre efficiency factor η_{LE} [16-21] the assumption of elastic fibres in an elastic matrix, leading to:

$$\eta_{LE} = [1 - \frac{\tanh(\beta\ L/2)}{\beta\ L/2}] \tag{2}$$

where $\beta = \frac{2}{D}[\frac{2G_m}{E_f \ln(R/r)}]^{1/2}$ (3)

The R/r factor can be related to the fibre volume fraction V_f by:

$$\ln(R/r) = \ln(\sqrt{\pi / \chi_i V_f}) \quad (4)$$

so that Equation 3 can be rewritten as

$$\beta = \frac{2}{D}[\frac{2G_m}{E_f \ln(\sqrt{\pi / \chi_i V_f})}]^{1/2} \quad (5)$$

where c_i depends on the geometrical packing arrangement of the fibres, r is the fibre radius and R is related to the mean spacing of the fibres. In this study a square packed fibre arrangement is assumed, following Thomason *et. al* [20], where similar equations were used for the modelling of glass/PP composites. The inter-fibre spacing in the composite is $2R$ and c_i equals 4. Besides the ineffective fibre length, another reason why the fibre can only be partially utilised is the fibre orientation. In order to take this into account, the theory of Cox was extended by Krenchel [12], who took fibre orientation into account by adding a fibre orientation factor η_o into the 'rule-of-mixtures' equation.

$$E_c = \eta_o \eta_{LE} V_f E_f + (1 - V_f) E_m \quad (6)$$

The Krenchel orientation factor η_o allows for the introduction of a fibre orientation distribution. If transverse deformations are neglected, η_o is given by:

$$\eta_o = \sum_n a_n cos^4 \phi_n \quad (7)$$

where a_n is the fraction of fibres with orientation angle ϕ_n with respect to the reference axis. For a two-dimensional (in-plane) random orientation of the fibres it can be shown that η_o = 3/8. In a three-dimensional random fibre orientation the fibre orientation factor yields the value of 1/5. For thin section laminates with fibre lengths greater than the thickness of the sample, fibres are expected to be oriented mainly in two directions. However, deviations are expected to occur due to out-of-plane oriented fibres or bend fibres. In the model a modulus of 45 GPa for the flax fibre and a modulus of 1.6 GPa for the PP matrix is used. An effective fibre length of 25 mm for the random flax mat material, together with a distribution function for the fibre diameter is used. A rather good agreement is found between the model predictions and experimental data. No effect of improved adhesion on the modulus of flax/PP composites is observed indicating good wetting of the fibres. Only the data for a fibre length of 3 mm shows a somewhat increased composite stiffness with the use of MA-PP. Presumably, the higher interfacial bond strength in case of flax/MA-PP leads to a slight decrease of the critical fibre length (from ~3.5 mm to ~2.5 mm) and consequently a small improvement in composite stiffness might occur. At fibre lengths of 6 and 25 mm this improvement is not observed since in both cases the fibre length is well above the critical fibre length. No fibre length dependence is observed for the developed flax/MA-PP as the fibre lengths are higher than critical lengths thus showing the curve in the plateau zone.

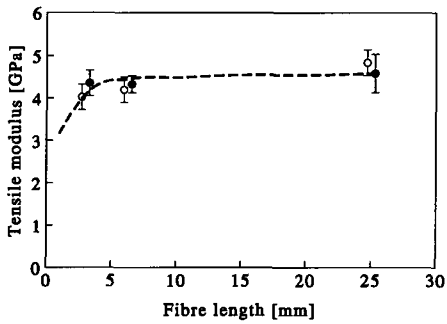

Figure 1: *Tensile modulus of the flax/PP composites* (o) *and the flax/MA-PP composites* (•) *as a function of the flax fibre length. The dashed line represents the Cox-Krenchel' prediction.*

Composite strength

In Figure 2 both the results of the tensile strength measurements as well as the model predictions for flax/PP and flax/MA-PP, as a function of the fibre length, are plotted. In the case of tensile strength modelling of discontinuous fibre composites, Kelly and Tyson [14] extended the 'rule-of-mixtures' equation for composite strength in a way similar to Cox's 'rule-of-mixtures' for composite stiffness:

$$\sigma_{uc} = \eta_O \eta_{LS} V_f \sigma_f + (1 - V_f)\,\sigma_m \tag{8}$$

where η_{LS} is the fibre length efficiency factor and η_o is the fibre orientation factor, similar to the Cox-Krenchel model, in order to take off-axis fibre orientation into account. For the fibre length efficiency factor, Kelly and Tyson used [14] :

$$\eta_{LS} = \frac{1}{V_f}\left(\sum_i \left[\frac{L_i V_i}{2L_c}\right] + \sum_j \left[V_j\left(1 - \frac{L_c}{2L_j}\right)\right]\right) \tag{9}$$

The first summation term in Equation 9 accounts for the contribution of all fibres of sub-critical length ($L<L_c$). The second summation term incorporates the strength contribution from fibres whose lengths are super-critical ($L>L_c$). A combination of Equation 8 and 9 results in the Kelly-

Tyson model [14,15] for the prediction of the strength (σ_{uc}) of a polymer composite reinforced with short off-axis fibres:

$$\sigma_{uc} = \eta_o \left(\sum_i \left[\frac{\tau L_i V_i}{D} \right] + \sum_j \left[\sigma_j V_j \left(1 - \frac{L_c}{2L_j} \right) \right] \right) + (1 - V_f)\,\sigma_m \qquad (10)$$

In the case of stiffness, the related Cox-Krenchel model, including a theoretical orientation parameter for in-plane random fibre orientations (η_o = 3/8), can be used quite effectively for the prediction of the stiffness of random fibre composites. However, previous studies have shown that the Kelly-Tyson model for strength yields far too high values for the strength of random fibre composites. In general this discrepancy is accounted for by adopting the fibre orientation efficiency parameter η_o and as a result no unambiguous value for η_o is found in the literature for the prediction of random composite strength. In this paper we used a value of 0.2 for the fibre orientation efficiency parameter η_o of our random flax/PP composites. This value, having no physical meaning, was reported by Thomason *et al.* [20] and was obtained by fitting η_o to the experimental strength data of a similar type of composite based on glass/PP. Moreover, a fibre strength of 750 MPa is used together with an interfacial bond strength (τ) of 10 MPa for flax/PP and 16 MPa for flax/MA-PP. The interfacial shear strength value of 16 MPa for the flax/MA-PP system is taken similar to the shear yield stress of the pure PP matrix as calculated from the Von Mises yield criterion (29/√3 MPa), which means that for this composite system perfect adhesion, or a matrix dominated rather than interface dominated shear failure mode, is assumed. First of all, when looking at Figure 2, it becomes clear that the experimental results at high fibre lengths (6 and 25 mm) of the flax/PP as well as the flax/MA-PP composites are significantly lower than the Kelly-Tyson predictions for tensile strength. With respect to the effect of improved interfacial bonding the model predicts only a small increase in strength in the case of improved adhesion. Similar to the stiffness there appears to be no significant influence of the flax fibre length on the measured composite strength. Only the experimental results of the 3 mm flax/(MA-)PP composites are more or less comparable with the model prediction. Due to the easier way of mixing and consequently better impregnation, the composite with 3 mm long fibres is of a higher quality in comparison to the 6 and 25 mm ones. Moreover, during the chopping of the fibres into the desired length the weak internal interaction between the elementary fibres results in extensive fibrillation of the fibres and a decrease of the flax fibre diameter and consequently, an increase in fibre aspect ratio. As a result, the stress transfer becomes more effective, yielding a composite with relatively better properties.

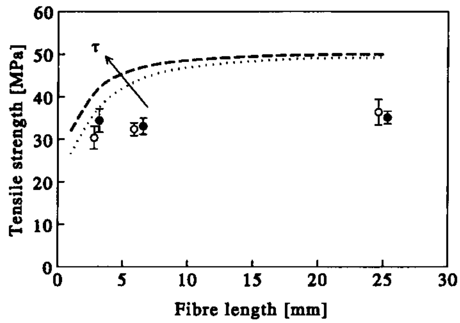

Figure 2: *Tensile strength of the flax/PP composites (o) and the flax/MA-PP composites (•) as a function of the flax fibre length. The dotted line and the dashed line represent the Kelly-Tyson prediction for the flax/PP and the flax/MA-PP ccomposites, respectively.*

Influence of fibre volume fraction

Composite stiffness

Figure 3 shows the tensile modulus of the flax/(MA-)PP composites together with the Cox-Krenchel prediction and the commercially known glass-mat-reinforced thermoplastic (GMT) materials, as a function of fibre volume fraction. Based on the data obtained, it can be concluded that the stiffness of flax-fibre-reinforced PP is comparable to E-glass fibre composites. Especially, when the relatively low density of the flax fibre is taken into account, the stiffness per unit weight approaches or even surpasses that of GMT materials. Moreover, as a result of the relatively low price of flax fibres compared to E-glass fibres these materials are particularly of interest from a cost-performance point of view. From this it can be concluded that flax/PP composites can compete with glass fibre based GMT materials in stiffness critical applications.

A rather good agreement is found between the experimental data and the predictions using the Cox-Krenchel model. In the model a modulus of 45 GPa for the flax fibre and a modulus of 1.6 GPa for the PP matrix is used, together with an effective fibre length of 25 mm for the random flax mat material and a distribution function for the fibre diameter.

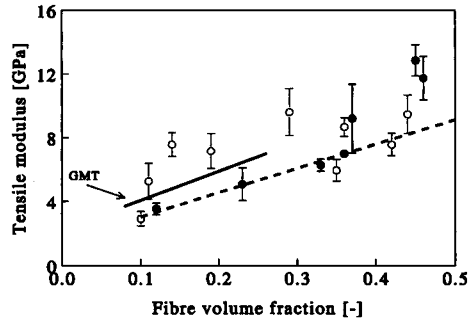

Figure 3: *Tensile modulus of the flax/PP composites* (o) *and the flax/MA-PP composites* (•) *as a function of* V_f. *The dashed line represents the Cox-Krenchel prediction. The solid line represents the commercially available GMT.*

Composite strength

Figure 4 shows the tensile strength of the manufactured flax/PP and flax/MA-PP composites, together with the Kelly-Tyson predictions for flax/PP and flax/MA-PP as well as the commercially glass fibre based GMT materials, as a function of the fibre volume fraction. In the model the same material parameters are used as in the Cox-Krenchel model for the prediction of composite stiffness. Again, a fibre strength of 750 MPa is used. These micromechanical calculations also indicate that the difference in interfacial bond strength in the case of flax/PP (τ = 10 MPa) and flax/MA-PP (τ = 16 MPa) has no significant influence on the predicted composite strength (see Figure 4).

Clearly, GMT materials show superior strengths compared to flax-fibre-reinforced PP composites for all volume fractions. With respect to the effect of improved interfacial bonding in the case of flax/MA-PP composites no significant difference in tensile strength was found. Moreover, based on micromechanical calculations no significant improvements can be expected since already an 'upper limit' matrix dominated shear strength value is used for the calculation of the theoretical strength of flax/MA-PP. Obviously, the strength of the flax based composites is intrinsically limited by the relatively low strength of the technical flax fibres (~750 MPa). Therefore the present study shows that the key area for the improvement of the tensile strength of the flax/PP composites lies not only in the interphase modifications for improved adhesion but mainly in fibre modifications for improved fibre strength.

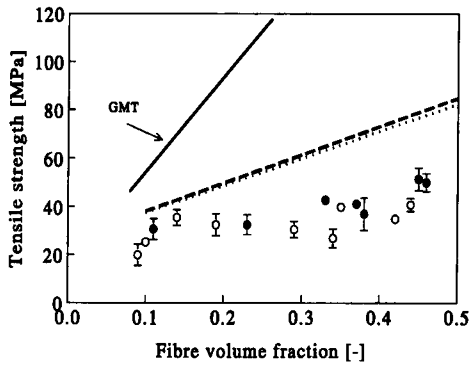

Figure 4: *Tensile strength of the flax/PP composites (o) and the flax/MA-PP composites (•) as a function of V_f. The dotted line and the dashed line represents the Kelly-Tyson predictions for flax/PP and flax/MA-PP composites, respectively. The solid line represents the commercially available GMT.*

CONCLUSIONS

For the production of flax/PP random composites two production methods similar to the commercially known methods for glass/PP composites were used. First, the so-called film-stacking method based on flax non-woven fibre mats and secondly, a suspension impregnation process using chopped short flax fibres were used. Material parameters that were studied for the optimisation of the mechanical performance of such composites were (i) fibre volume fraction, (ii) fibre length and (iii) fibre matrix adhesion. In order to get a better insight in the importance of these different parameters for the optimisation of composites, the experimental results were compared with model predictions using micromechanical models for random short-fibre-reinforced composites. As expected, there is a significant effect of fibre volume fraction on mechanical properties, whereas, no real experimental evidence for the anticipated increase in mechanical performance with increasing fibre length was found.

Based on the experimental results it can be concluded that the tensile modulus of the flax-fibre-reinforced composites is comparable to E-glass-fibre-reinforced composites. Especially, when focusing on the specific properties as a result of the low density of flax, the stiffness per unit weight of flax-fibre-reinforced composites approaches that of glass-fibre-reinforced materials. Moreover, as a result of the relatively low price of flax fibre compared to E-glass fibres these materials might be of interest from a 'cost-performance' point of view. However, due to the relatively low tensile strength of flax fibres compared to E-glass fibres, the tensile strength of technical flax-fibre-reinforced composites is significantly lower than that of their glass fibre counterparts. In short, it can be concluded that thermoplastic NMT composites based on a PP matrix and flax fibres can compete with E-glass reinforced GMT materials in stiffness critical structures, whereas for strength critical applications these materials still need to be optimised.

REFERENCES

1. Berglund, L.A. and Ericson, M.L. in: *Polypropylene: Structure, blends and composites, Vol. 3,* Ed. J. Karger-Kocsis, Chapman & Hall, London (1995) 202.
2. Morton, W.E. and Hearle, J.W.S., *Physical Properties of Textile Fibres*, 2nd ed., John Wiley & Sons, Inc., New York (1975).
3. Satyanarayana, K.G. et al. in: *Composite Structures*, Vol. 1, Ed. I.H. Marshall, Elsevier Appl. Sci.., London (1981) 618.
4. Chawla, K.K. and Bastos, A.C. in: *Proc. 3rd. Int. Conf. Mech. Behaviour of Materials*, Vol. 3, Pergamon Press, Toronto (1979) 191.
5. Kuruvila, J., Thomas, S., Pavithran, C. and Brahmakumar, M., *J. Appl. Polymer Sci.*, 47 (1993) 1731.
6. Selzer, R., *Advanced Composite Letters*, 4 (3) (1995) 87.
7. Sanadi, A.R., Caulfield, D.F., Jacobson, R.E. amd Rowell, R.M., *Ind. Eng. Chem. Res.*, 34 (1995) 1889.
8. Heijenrath, R. and Peijs, T., *Advanced Composite Letters*, 5 (3) (1996) 81.
9. Rijsdijk, H.A., Contant, M. and Peijs, T., *Composites Science & Technology*, 48 (1993) 161.
10. Felix, J., Ph.D Thesis, "Enhancing Interactions Between Cellulose Fibres and Synthetic Polymers", Chalmers University of Technology, Goteborg, Sweden (1993).
11. Cox, H.L., *Brit. J. Appl. Phys.*, 3 (1952) 72.
12. Krenchel, H. in: *Fibre reinforcement*, Akademisk Forlag, Copenhagen (1964).
13. Folkes, M.J. in: *Short fibre reinforced thermoplastics*, Research Studies Press, Chichester (1985) 16.
14. Kelly, A. and Tyson, W.R., *J. Mech. Phys. Solids*, 13 (1965) 329.
15. Kelly, A. and Macmillan, N.H. in: *Strong Solids*, Clarendon Press, Oxford (1986) 269.
16. Ericson, M. and Berglund, L., *Composite Science and Technology*, 43 (1992) 269.
17. Ericson, M. and Berglund, L., *Composite Science and Technology*, 49 (1993) 121.
18. Thomason, J.L. and Vlug, M.A., *Composites, Part A*, 27A (1996) 477.
19. Rosenthal, J., *Polymer Composites*, 13 (1992) 462.
20. Thomason, J.L.,Vlug, M.A., Schipper, G., Krikor, H.G.L.T, *Composites, Part A*, 27 (1996) 1075.
21. Pan, N., *Polymer Composites*, 14 (1993) 85.

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