

DENDRITIC-BASED ADDITIVES FOR POLYMER MATRIX COMPOSITES

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SUMMARY: Functionalised dendritic hyperbranched polymers (HBP) are used as additives for both thermoset and thermoplastic polymer matrix composites. The main benefits of the HBP modifiers are a toughness increase in thermoset composites and improved fibre/matrix adhesive properties in thermoplastic composites. Moreover, for thermoset composites these additives allow to increase the mechanical performance while fully maintaining the composite processability. For thermoplastic composites, they can also be used to improve processability by achieving a better filler dispersion and mould filling capacity. These property improvements can be attained by exploiting the intrinsically high reactivity and low viscosity of the HBP modifiers and by tailoring their physical and chemical interactions with the other composite constituent materials.

KEYWORDS: Dendrimers, processability, internal stress, interfacial properties, toughening, fatigue properties, thermoset matrix, thermoplastic matrix

INTRODUCTION

Dendrimers and hyperbranched polymers (HBP) have a tree-like structure, as opposed to a linear architecture for conventional polymers, and belong to a group which is generally referred to as dendritic polymers. They are obtained by polymerising multifunctional repeating units onto a multifunctional core. A sequence of layers, or "generations", of repeating units, is thus formed around the core. For higher generation dendritic polymers, the molecular structure adopts a spherical shape, with a multitude of chain ends situated at the periphery. These chain ends can be functionalised with tailored groups to ensure compatibility and reactivity with a surrounding matrix. Due to the specific structural characteristics, dendritic polymers have a low viscosity, a high reactivity and unique visco-elastic properties. Intense research activity has been devoted to the synthesis of such molecules pioneered by Flory [1]. On the other hand, limited effort has been devoted to their application, for which the high cost of the step-wise syntheses used has been a handicap. Only recently, in 1992, has the development of a cost-effective synthesis of polyester-based hyperbranched dendritic polymers [2], allowed the use of this new type of polymers to be considered in engineering materials.

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Fig. 1 shows a schematic of such a three-generation hyperbranched dendritic polymer based on a tetra-functional core and tri-functional repeating units. The hyperbranched polymer molecule contains some branching defects compared to perfect dendrimers, but has shown reactivity and

rheological properties characteristic of dendrimers. The three-generation HBP shown in Fig. 1 possesses 32 chain ends which can be functionalised with, for example, reactive epoxy groups. Functionalisation of the chain ends, which constitute the shell of this spherical molecule, is used to tailor physical and chemical interactions with the other constituent materials so as to obtain the desired properties.

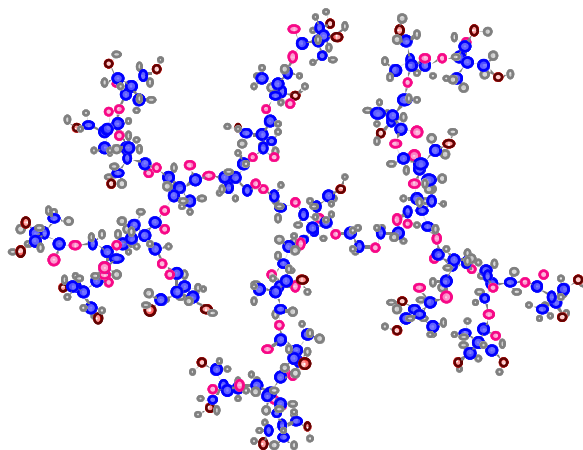


Fig. 1: A 3-generation hyperbranched dendritic structure with 32 chain ends which can be functionalised.

It has been chosen here to illustrate the versatility of the HBP modifiers by presenting applications both within thermoset as well as thermoplastic matrix composites.

Thermoset matrix composites have been used in a wide variety of applications due to their good processability and thermo-mechanical properties. However, they generally suffer from drawbacks such as an intrinsic brittleness, high processing costs and high levels of internal stress. Ideally, a modifier should thus be able to toughen the system without adversely affecting its processability and thermo-mechanical properties. This has proven to be difficult with existing modifiers such as reactive elastomers or thermoplastic modifiers, since both strongly affect the resin viscosity and generally lead to a reduction in its glass transition temperature. Functionalised reactive HBPs, on the other hand, are low viscous liquids and can as a result be used in processes such as resin transfer moulding (RTM). Furthermore, they can be functionalised with different reactive groups which can be tailored according to the nature of the thermoset resin. Thus, HBPs are suitable performance additives for not only epoxy composites but also unsaturated polyesters, acrylates, cyanate esters and phenolics.

Of the various thermoplastic resins used as composite matrices, polypropylene (PP) is the most widespread and its market is continuously expanding. It offers the advantages of a low cost and the possibility for recycling. A variety of reinforcement materials such as glass fibres and chalk particles are generally used. A PP matrix, however, has in general a weak interfacial bond strength with the reinforcing agent due to its low polarity and inert nature of the matrix. This can also lead to a poor dispersion of the filler and, together with a high matrix viscosity, can lead to mould filling problems and surface defects during rapid injection moulding processes. The unique features of dendritic polymers can be exploited to design more efficient additives for reducing these drawbacks and allowing the applicability of thermoplastic composites to be expanded.

EXPERIMENTAL

The modifiers used were based on two commercial polyester hyperbranched dendritic polymers, *Boltorn*[™]-H20 and *Boltorn*[™]-H30 supplied by Perstorp AB, which have a theoretical molecular weight of 1800 and 3600 g/mol respectively. Due to their dendritic structure, these molecules have a small radius of gyration of 2 and 2.5nm respectively. The HBPs were functionalised with different reactive groups in order to ensure a good stress transfer with the other constituent materials of the composites.

Two epoxy functional HBPs, *Boltorn*[™]-E1, with an epoxy equivalent weight (EEW) of 870g/eq and a theoretical epoxy-functionality of 11, and *Boltorn*[™]-E2 functionalised with a more reactive epoxy unit, with an EEW of 390g/eq and a theoretical epoxy-functionality of 30, were evaluated as modifiers in two amine cured epoxy matrix composites, a DGEBA based epoxy *LY5082/83* and a highly cross-linked system based on a TGMDA epoxy *LY1802/HY2954*, both from Ciba. An allyl-ether functional HBP, with a theoretical molecular weight of 4500g/mol and an allylether-functionality of 14, was used as a modifier in composites with a peroxide cured vinylester matrix, *Derakane*[™] 411-C50 from Dow Chemicals. Unidirectional and plain weave glass and carbon fibre reinforced composites with 45vol% of fibres were processed using resin transfer moulding. To increase the reactivity with the epoxy matrices, glass fibres were surface treated with an amino-silane, *A-1100* supplied by Witco.

In polypropylene composites, the *Boltorn*[™]-E2 epoxy functional HBP and a hydroxy-functional HBP, *Boltorn*[™]-H30, which was partly functionalised with fatty acids, were used as an adhesion promoter and processing aid respectively. To compatibilise and ensure a good stress transfer with the polypropylene matrix, the epoxy functional HBP was pre-reacted in a twin-screw extruder (PRISM TSE-16-TC) with a maleic anhydride grafted polypropylene (PP-MAH), *Orevac*[™] CA50, supplied by Elf-Atochem, generating a PP grafted epoxy functional HBP (PP-HBP). The modifiers were pre-blended at 1wt% within a polypropylene matrix, *Appryl*[™] 3050MN1 supplied by Elf-Atochem, using the twin screw extruder before adding the reinforcing phase. Short glass fibre and chalk particle reinforced PP composites were processed using the twin screw extruder and an injection moulder (Arburg 270S).

Mechanical testing was performed on a *UTS-100* screw driven load-frame. Composite critical strain energy release rates, G_{Ic} , were determined by double cantilever beam tests (DCB) following the ASTM-5528 testing standard. Tensile tests were performed following the ASTM-3039 testing standard. Damage evolution in cross-ply thermoset composites was followed using acoustic emission. The interfacial shear strength was measured using a microbond pull-through test in which a polymer droplet deposited on a fibre is sheared along the interface.

Optical microscopy (Olympus-BH1) and scanning electron microscopy (Philips XL-30) were performed to evaluate surface aspects, filler dispersion and fracture surface characteristics of the samples.

RESULTS AND DISCUSSION

Thermoset Matrix Composites

For thermoset matrix composites, the HBPs are functionalised with reactive groups. These ensure good stress transfer capacity between the modifier and the matrix. The functionality can also be tailored to induce phase separation upon resin cure by a chemically induced phase separation (CIPS) in order to increase the toughening efficiency. Using 5phr of a phase

separating BoltornTM-E1 in a DGEBA based amine cured epoxy resin, a five-fold increase in the K_{Ic} fracture toughness of the epoxy was obtained without any reduction in glass transition temperature and Young's modulus [3]. This was attributed to the specific properties of the phase separated particles and the strong chemical bonding between the modifier and resin [4]. This low viscosity and initially compatible modifier can be used in cost effective processing techniques such as resin transfer moulding (RTM), avoiding modifier particle filtering effects and the need to modify the processing conditions. RTM processed epoxy-glass fibre laminates and epoxy-carbon fibre laminates have shown more than a doubling in the G_{Ic} interlaminar strain energy release rate using 5phr of BoltornTM-E1 additives in the DGEBA epoxy composites, as shown in Fig.2. However, with a phase separating system, the fibre surface energetics must be controlled to avoid particle nucleation of the toughener at the interface. This has been observed with some glass fibres, which had a low surface coverage density of functional units, and has led to a reduction of the interfacial shear strength limiting the effect of resin toughening by inducing a partially adhesive failure [5]. These effects are avoided when no CIPS occurs, as is the case with the BoltornTM-E2 modifier in the resins studied here. The toughening effect of this fully soluble modifier was slightly less pronounced. This was attributed to the fact that it is only the deformability of the HBP molecule which induces toughening and no synergetic effects exist with failure mechanisms occurring only with larger particles [6]. With 10phr of the BoltornTM-E2, however, similar toughening properties were obtained as with 5phr of the BoltornTM-E1 modifier and again with no loss in the thermo-mechanical properties. For highly cross-linked systems such as TGMDA based epoxies, the modifier content had to be further increased to 15phr to obtain comparable effects.

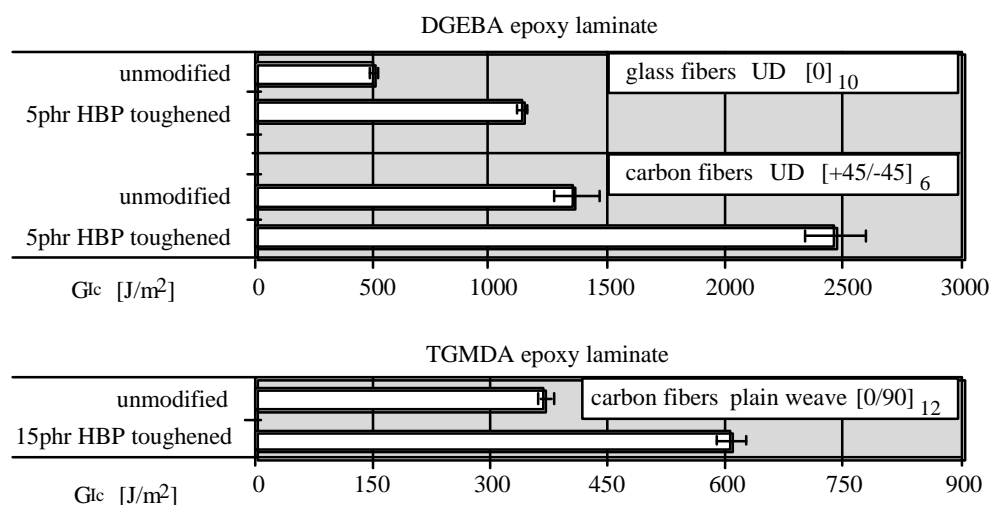


Fig. 2: G_{Ic} critical interlaminar strain energy release rate comparing unmodified and HBP toughened DGEBA and TGMDA epoxy resin composites.

The toughening properties were also accompanied by an increase in elongation to break and fatigue resistance. In vinylester-glass fibre composites, the strain at damage initiation and the strain damage evolution rate determined by acoustic emission during tensile tests were both improved by a factor of two when using 10phr of the allylether functionalised HBP modifiers. In this way, the thermoset resin systems can be upgraded to the properties of a competing system, as is illustrated in Fig. 3. The modified vinylester composites showed similar properties to the unmodified epoxy composites. The damage evolution behaviour of the latter was, however, further improved using 5phr of the epoxy functional HBP.

Finally, the HBP additives were also shown to reduce the internal stress levels in thermoset composite laminates due to a lowering of the cure-induced resin shrinkage. Stress localisations

around the particles and a reduction of the stress relaxation times due to the presence of HBP also contributed to lowering the internal stress levels. This reduced the number of cure induced defects such as resin voiding and cracks which can appear in highly cross-linked resin composite systems. It improved the dimensional stability of composites and in some cases allowed to reduce excessively long curing cycle times which would otherwise be required for limiting cure-induced internal stress effects.

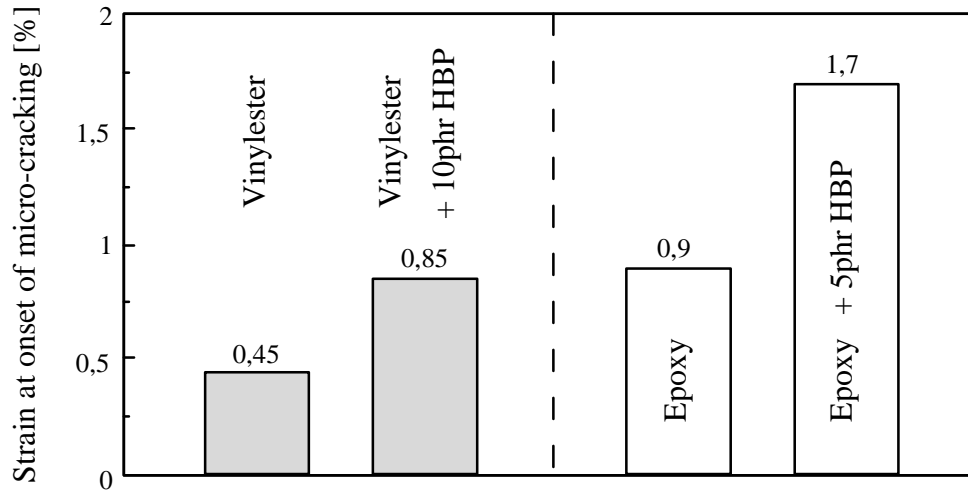


Fig. 3: Material upgrading using HBP additives. The strain at onset of micro-cracking for both glass fibre reinforced resin systems is almost doubled. The modified vinylester composite reaches the performance of the unmodified epoxy laminate.

Thermoplastic Matrix Composites

In thermoplastic resin composites, low viscosity HBPs can be used as processing aids and have been shown to efficiently reduce surface defects and increase the mould filling capacity. In order to avoid particle coalescence and ensure a good reinforcing agent dispersion, the chemical nature of the HBP shells has been designed to reduce the surface tension between the polymer matrix and the filler. This has allowed processing of particle filled PP composites which do not suffer from a loss of strength due to particle coalescence.

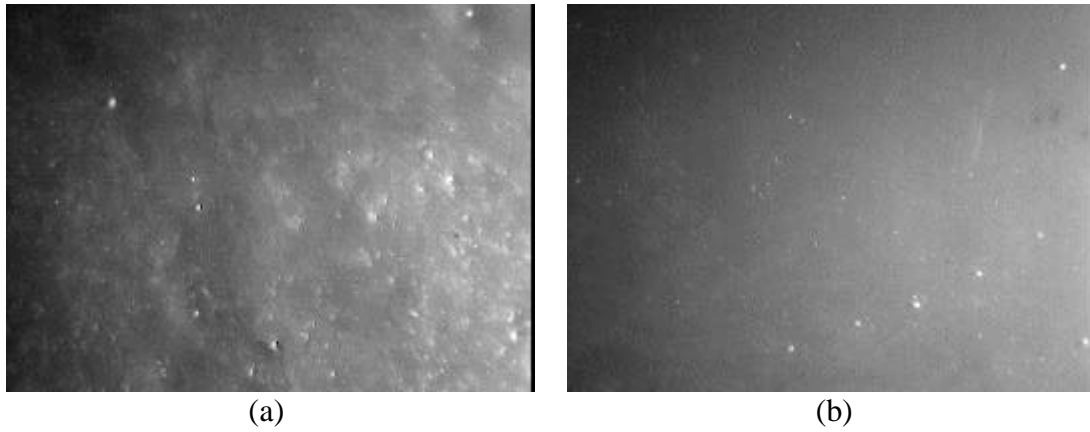


Fig. 4: Surface aspect of an injection moulded particle filled PP. (a) without additive, (b) with the partly fatty acid functionalised HBP additive. It can be seen that a smooth surface is obtained with the HBP processing aid.

To increase the interfacial strength in PP composites, the high reactivity of epoxy functional HBPs has been exploited. The PP-HBP modified PP-glass fibre composite performances have been compared to a PP-MAH (CA50) modified system. A previous study [7] showed that a PP-HBP modifier is more reactive and diffuses faster than a PP-MAH modifier. In other words, the chemical bonding potential is stronger and occurs faster during processing. The PP compatibilised HBP additives have shown unique interfacial properties with low modifier contents which were not obtained using conventional additives such as MAH. Fig. 4 illustrates the drastic effect of epoxy-functional HBPs on the interfacial properties in PP-glass fibre composites. The fracture surfaces exhibit debonding with an unmodified matrix and a cohesive failure when using HBP modifiers, as illustrated by the residual polymer material on the fibres. With the HBP modifiers, the interfacial shear strength reached the PP bulk shear strength. As a result, the cohesive strength of the glass fibre reinforced PP is increased, as shown in Fig. 5.

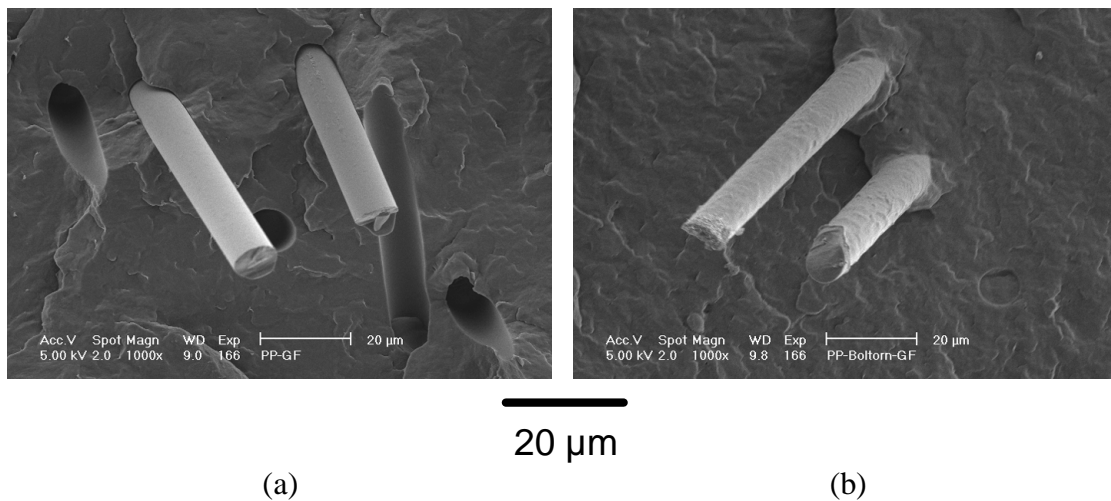


Fig. 5: Fracture surfaces of (a) an unmodified and (b) a HBP modified PP-glass fibre composite. A cohesive failure is observed with a layer of the PP matrix remaining on the fibre when using the HBP modifier.

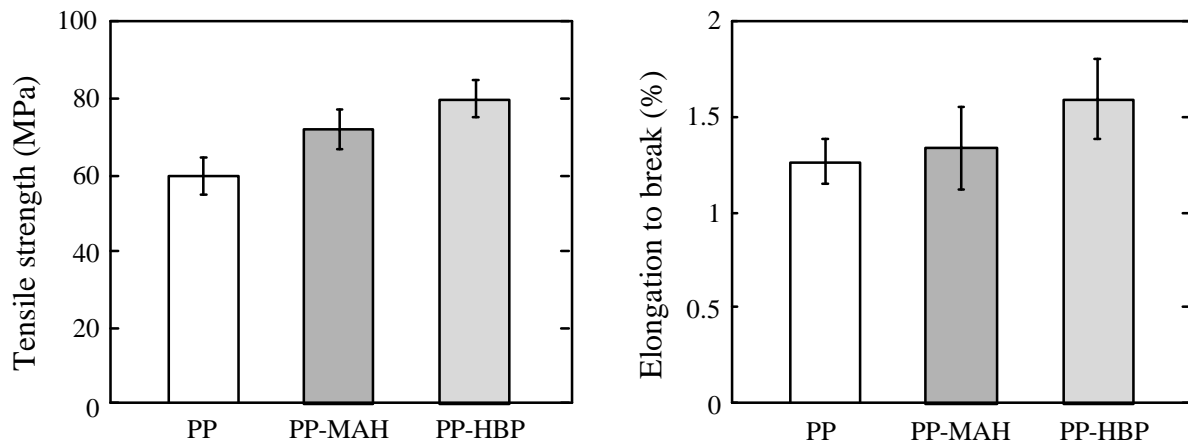


Fig. 6: Tensile strength and elongation to break of PP-glass fibre composites comparing the performances of an unmodified system, a PP-MAH modified system and a PP-HBP modified system.

CONCLUSIONS

Functionalised HBP modifiers can advantageously be used as processing aids and performance additives in both thermoset and thermoplastic resin composites.

In thermoset resin composites, the good resin processability of the low viscous resins is fully maintained using HBP modifiers. They also reduce the internal stress levels developed during cure, thus limiting process-induced defects and increasing the dimensional stability of laminates. A high toughness increase was obtained with both phase separated and soluble modifiers without reducing the modulus or glass transition temperature. Using properly functionalised HBPs, the properties of vinylester resin composites were upgraded to the properties of epoxy resin composites with as little as 10phr of modifier.

In thermoplastic resin composites, the mould filling capacity during injection moulding can be improved using HBP as a processing aid. In polypropylene matrix composites, the surface roughness of injection moulded or extruded parts was also reduced and the filler dispersion was improved when using partly fatty acid functionalised HBPs. This lead to improved aesthetic and mechanical performances. The latter were also improved using a reactive PPgrafted-HBP. This modifier ensured a good stress transfer capacity from the matrix to the fibre. Reactive PP-HBP modifiers have been shown to be more effective than other commercial modifiers such as PP-MAH. This was attributed to the higher reactivity and diffusivity of the PP-HBP modifier.

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REFERENCES

1. Flory, P.J., *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, 1953.
2. Hult, A., Johansson, M., Malmström, E. and Sörensen, K., "Dendritic Macromolecule, Process and Use", *Swedish Patent No 9200564-4*, 1992.
3. Boogh, L., Pettersson, B., Japon, S. and Månson, J.-A.E., "A Novel Toughening System for Thermoset Resins and its Composites", *Proceedings of the Tenth International Conference on Composite Materials*, Whistler, British Columbia, Canada, August 14-18, 1995, Vol. VI: Microstructure, Degradation and Design, Poursartip, A. and Street, K.N., Eds, pp. 389-396
4. Boogh, L., Pettersson, B. and Månson, J.-A.E., "Dendritic Hyperbranched Polymers as Tougheners for Epoxy Resins", *Polymer*, Vol. 40, 1999, pp. 2249-2261.
5. Boogh, L., Pettersson, B. and Månson, J.-A.E., "The Influence of Fibre Surface Properties in Hyperbranched Dendritic Polymers Toughened Composites", *EPS-97*, Lausanne, Switzerland, June 1-6, 1997, pp. 39-40
6. Pearson, R. A., Yee, A.F., "Toughening Mechanisms in Thermoplastic-Modified Epoxies", *Polymer*, Vol. 34, 1993, pp. 3658-3670.
7. Jannerfeldt, G., Boogh, L., and Månson, J.-A.E., "The Influence of Hyperbranched Polymers on the Interfacial Tension of Polypropylene/Polyamide 6 Blends", *accepted in J. of Pol. Sci. Part B*