RESEARCH ARTICLE

Preparation and characterization of composites using blends of divinylbenzene-based hyperbranched and linear functionalized polymers

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Abstract

In this study, hyperbranched polymers were explored as matrix modifiers to create E-glass fiber (GF) reinforced polymer composites with enhanced mechanical properties. Hyperbranched polymers have lower viscosities than their linear equivalents, potentially providing enhanced fiber wet out leading to improved stress transfer. Hyperbranched (HB), hydrogenated hyperbranched (H-HB), and linear functional (LF) divinyl benzene were blended with linear polystyrene (LP) to form a range of composite matrix formulations. Blends of the HB and LP polymers were used since the neat hyperbranched polymers alone proved to be highly brittle when formed into a film. A neat LP-GF composite was also prepared as control. Of the three matrix modifiers considered, only the H-HB provided an improvement in mechanical properties in comparison to LP-GF. With the addition of 10 and 20 wt% H-HB, respectively, the flexural modulus increased by 25% ($p < 0.05$) and 36% ($p < 0.05$) and flexural strength increased by 15% ($p < 0.05$) and 31% ($p < 0.005$). The enhanced mechanical properties were attributed to better fiber wetting along with crystallization observed with the addition of 20 wt% H-HB. The non-reactive ethyl ($—CH_2—CH_3$) chain end group of the macromolecular H-HB resulted in a plasticizing effect, which in turn improved its wettability. The LP:HB polymer blends, on the other hand, underwent crosslinking due to the presence of the vinyl ($—CH=CH_2$) chain ends leading to poor wettability in comparison to the LP:H-HB and LP:LF blended films and hence lower mechanical properties.

KEYWORDS
composite, crosslinking, hyperbranched, wettability

1 | INTRODUCTION

Hyperbranched (HB) polymers are highly branched polymers containing a large number of functional end groups, which possess monomer/organic solvent solubility and low melt viscosity, due to the "globular" nature of their structures, making these materials suitable matrix modifiers for polymer fiber composites.[1,2] Consequently there have been literature reports of their use as additives for both thermoset and thermoplastic polymer matrix composites.[3] For example, with thermoset materials, Mezzenga, et al.[3] used an epoxy functionalized

HB polymer to modify an epoxy matrix based composite and reported a 2.5 fold increase in fracture toughness (K_{IC}) with addition of 5 phr (parts per hundred rubber) of HB and also reported that this increase was obtained without affecting the viscosity, processability, and glass transition temperature of the epoxy resin. DeCarli et al.[4] also reported a 224% increase in fracture toughness for carbon fiber reinforced epoxy anhydride composite on addition of 10 wt% of epoxy terminated HB polymer (Boltorn E1) as a toughening agent.

In addition, HB polymers functionalized with vinyl reactive groups have been used as fiber/filler processing aids for thermoset epoxy composites.[1,3,5,6] For example, Li et al.[2] used epoxide terminated hyperbranched polymer grafted glass fibers (GF-HBPE) as the reinforcement to produce epoxy based composites. They reported that the addition of only 1 wt% GF-HBPE increased the tensile strength, percentage elongation at break, flexural strength, and impact strength of the epoxy composite by 23.6%, 125%, 26%, and 74.5% respectively.

In the field of thermoplastic composites, HB polymers were investigated to improve fiber/matrix adhesion and filler dispersion.[7] Sun et al.[8] used sisal fibers grafted with poly(amidoamine) dendrimer as reinforcement to produce sisal fiber-reinforced polypropylene composites. They studied the effects of dendrimer generations on the mechanical properties of composites. For generation 2.0 dendrimer, they found that the tensile, flexural, and impact strength of the composites (at 30 wt% fiber loading) increased by 29%, 13%, and 54%, respectively. Lu et al.[9] prepared sisal fiber/polypropylene/carboxyl terminated HB polymer composites and reported a 21.5% and 9.7% increase in impact and flexural strength, respectively, for the HB modified composites in comparison to unmodified polymer fiber composites. Wong et al.[10] reported improved brittleness of a polylactic acid matrix via addition of an HB polymer and also reported that with addition of 10% v/v HBP, the toughness of the composite doubled. They suggested that the improved wetting of the fibers by the matrix (when HB was present) had improved the toughness.

On the other hand, non-fiber, composites have also been prepared with HB polymers to exploit their unique properties. Zhou et al.[11] reported on the modification of multi-wall carbon nanotube (MWCNT) with an HB polymer containing UV reactive functional groups. The resin was cured under UV irradiation and revealed improved tensile strength and toughness values by 41% and 105%, respectively, with addition of only 0.1 wt% MWCNT.[11] Other studies also report on the use of HB containing composites due to their unique properties. For example, HB Polymers have facilitated a wide range of applications in inorganic–organic composite materials,[12] dental composites,[13] and ion conducting membranes.[14]

This study reports on the preparation and comparison of polymer composites containing E-glass fibers as reinforcement materials using matrices of; (a) pure (linear polystyrene) LP, (b) blends of LP with HB polymers containing reactive vinyl ($-CH=CH_2$) chain end group, (c) hydrogenated hyperbranched (H-HB) with non-reactive ethyl ($-CH_2-CH_3-$) functional groups, and (d) linear functional (LF) with vinyl ($-CH=CH_2$) chain end.[15] The temperatures utilized in this study for composite manufacture were determined from a previous

rheological study of pure LP and its blends. In that study it was observed that LP started to show flow behavior at around 190°C, whereas LP:HB 90–10 and 80–20 did not show any flow behavior from room temperature up to 200°C. Whereas, the LP:H-HB showed flow behavior at around 170°C while LP:LF 90–10 and 80–20 showed flow behavior around 135°C.

In this study, HB polymers were used in blends, with their linear analogs, in order to create the matrix materials used in the preparation of polymer E-Glass fiber composites. Furthermore, in the manufacture of these composites, the E-Glass fiber was used as received so that the study concentrated solely on the effects of matrices on the mechanical properties of the polymer fiber composites. The mechanical properties of the LP film and blends prepared at both room temperature (R.T) and heat treated (H.T) at elevated temperatures during composite manufacture were also evaluated. Furthermore, the flexural properties of the composites produced were evaluated and compared.

2 | EXPERIMENTAL METHODS

2.1 | Materials

Linear poly(styrene) (LP) (Grade 430,102) (M_w ~ 192 KiloDalton [kDa]) was purchased from Sigma Aldrich, UK. The hyperbranched poly(divinyl benzene) (HB) of (M_w 60 kDa, respectively) and hydrogenated hyperbranched poly(divinyl benzene) (H-HB) (M_w ~ 60 kDa) and the linear functional poly(divinyl benzene) (LF) (M_w ~ 10 kDa) were synthesized using the methods described in prior literature.[15] Woven E-glass fiber was purchased from Plastic Direct (UK), weave style: plain woven, thickness: 0.2 mm, overall weight: 200 g m^{-2}, sizing type: silane and chloroform (10% w/v) was purchased from Fisher Scientific (UK).

2.2 | Preparation of polymer blends

The films of LP and the blends (~0.3 mm thick) of linear poly(styrene) (LP) with hyperbranched (HB) (LP:HB), hydrogenated hyperbranched (H-HB) (LP:H-HB), and linear functional (LF) (LP:LF) poly(divinyl benzene) of two different compositions (90:10 and 80:20) were prepared using the methods described in our previous paper.[15] The LP film and the blends were prepared by dissolving specific amounts of the polymers in chloroform (4% w/v). The solution was stirred for 3 h using a magnetic stirrer for homogenization at room temperature (~25°C) and then poured into a PTFE mold. The solvent was then allowed to evaporate at room temperature (25°C). The films were further dried in an oven at 50°C for 3 days to remove any residual solvent.

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2.3 | Preparation of composites

The composite samples were prepared via a film stacking process. The polymer films were stacked alternately with woven E-glass fiber mats into a 1 mm thick mold cavity between two metallic plates. The width and length of the mold were 60×60 mm^2, respectively. For composites with matrices of LP, LP:HB, and LP:H-HB, the entire stack was then heated in the press for 10 min at 200°C and then pressed for another 10 min at 40 bar. However, for the composite with LP:LF matrices, the polymer fiber stack was heated at 140°C (rather than 200°C) for 10 min and then pressed for 10 min at 40 bar pressure. After pressing, the composites were cooled, while maintaining the same pressure, at a rate ~10 °C min^{-1} to below the T_g of LP (~101°C) for LP-GF, LP:HB-GF, and LP:H-HB-GF composites. Meanwhile, for LP:LF-GF composite, cooling was maintained at the same pressure at a rate ~10 °C min^{-1} to below the T_g of LF (~80°C). LP-GF composite was prepared to use as control.

The resulting laminated composites were cut into 25 mm length × 10 mm width coupons for flexural testing, using a Diamond cutter. The composites prepared in this study with their respective sample codes, polymer blends, and volume fractions of polymer blends and fibers are presented in Table 1.

2.4 | Characterization

2.4.1 | Dynamic viscosity measurement

The dynamic viscosity was determined using an Anton-Paar 302 rheometer. Measurements were performed using a 25 mm parallel plate gap, which was adjusted between 0.5 and 0.6 mm. All tests were performed with a logarithmically increasing shear rate range between 0.01 s^{-1} and 100 s^{-1}. Viscosity of LP, LP:HB, and LP:H-HB blends

were measured at 200°C and LP:LF was measured at 140°C to match the processing temperatures used during composite manufacture. All samples were tested in triplicate.

2.4.2 | Differential scanning calorimetry (DSC)

LP:H-HB 90–10 and 80–20 blends were investigated for thermal properties using a DSC (Q2000, TA instruments, UK). Samples (approximately 5 mg) were heated from 25°C to 200°C at a heating rate of 10°C min^{-1} under nitrogen gas flow (100 ml min^{-1}). After heating, the samples were subsequently cooled to room temperature (i.e., at a rate of approximately 20°C min^{-1}) before ramping again to 200°C at the same heating rate. The data were taken from the second cycle.

2.4.3 | Thermo-gravimetric analysis (TGA)

A SDT Q600 thermo-gravimetric analyzer from TA instruments (USA) was used to analyze the thermal degradation of pure LP and blends when used as matrices. Approximately 5 mg of each samples were heated from room temperature (25°C) to 200°C at a heating rate of 10°C min^{-1} under 100 ml min^{-1} air flow and kept at 200°C for 30 min. The same procedure was repeated for LP:LF 90–10 and 80–20 from room temperature (25°C) to 140°C at a heating rate of 10°C min^{-1}. A blank analysis was conducted for background correction. The mass loss (%) with respect to time was determined. Data acquisition and processing were performed using TA Universal analysis 2000 software.

2.4.4 | Burn off tests

The fiber volume fraction of the composites was determined via the standard test method (BS 2782–10: Method 1002:1977 EN 60) for ignition loss of cured reinforced resins. The mass of the metal sample tray was measured with and without the composite sample. Triplicate samples were then placed into a furnace at 500°C (below the glass T_g) for an hour, ensuring complete combustion of the polymer. The mass of the trays and residues were measured after removal from the

TABLE 1 Composite sample codes, polymer matrices, and volume fractions of polymer matrices and fibers (determined via burn-off test)

Composite code	Polymer films	E-Glass fiber (vol^m %)	Polymer films (vol^m %)
LP-GF	LP	40 ± 0.07	60 ± 0.05
LP:HB 90-10-GF	LP:HB 90–10	38.7 ± 0.2	61.21 ± 0.09
LP:HB 80-20-GF	LP:HB 80–20	38.1 ± 0.1	61.86 ± 0.1
LP:H-HB 90-10-GF	LP:H-HB 90–10	40.5 ± 0.09	59.45 ± 0.07
LP:H-HB 80-20-GF	LP:H-HB 80–20	40.3 ± 0.08	59.62 ± 0.08
LP:LF 90-10-GF	LP:LF 90–10	37.8 ± 0.3	62.11 ± 0.2
LP:LF 80-20-GF	LP:LF 80–20	37.8 ± 0.1	62.17 ± 0.1

furnace. Then the fiber volume fractions were calculated according to the following equation

$$P = \frac{m_2 - m_3}{m_2 - m_1} \times 100 \qquad (1)$$

where, P is the percentage loss on ignition.

m_1 is the mass of the container.

m_2 is the initial total mass of the container plus the specimen.

m_3 is the final total mass, after combustion, of the container and the residue.

2.5 | Mechanical testing

2.5.1 | Tensile tests

The polymer films of the different compositions were cut into dog bone shapes (width ~4 mm, thickness ~0.3 mm) using a dog bone cutter and the tensile properties were determined using an Instron tensile test machine 5969 (Software-QMAT) with a cross head speed of 0.5 mm min^{-1}, gauge length 25 mm, and a 1 kN load cell. Strain was captured using an Imetrum video gauge and values were collected from at least five repeat specimens. The tensile strength and modulus were calculated from experimental data according to the standard (ISO/DIS 527–1).

2.5.2 | Flexural testing

The flexural strength and modulus of the composite samples (10 × 25 mm^2) were evaluated by flexural (three-point bending) tests using an Instron 5969 testing machine (Software-QMAT). These measurements were done according to the standards BS EN ISO 14125:1998. A crosshead speed of 0.5 mm min^{-1} and a 5 kN load cell was used. Flexural studies were conducted using three repeat specimens.

2.5.3 | Scanning electron microscopy

Scanning electron microscope images were taken to examine the cross section of the freeze-fractured composite plates. The specimens were carbon coated prior to examination and viewed with a JEOL 6400 SEM scanning electron microscope operated at 10 kV in secondary electron mode (SE).

2.5.4 | Statistical analysis

Statistical analysis on a sample group (more than two specimens) was performed using Tukey's Multiple Comparison Test (95% confidence intervals) through a one-way analysis of variance (ANOVA), employing Graph Pad Prism software (version 5.01).

3 | RESULTS AND DISCUSSION

3.1 | Viscosity

The temperature of composite making and as well as viscosity study of LP and its blends were based on a previously performed rheological study. In that study, LP showed flow behavior (loss modulus became higher than storage modulus; $G'' > G'$) at ~190°C and LP:H-HB 90–10 and 80–20 ~ 170°C. Whereas LP:LF 90–10 and 80–20 at ~140°C and ~125°C, respectively. On the other hand, LP:HB 90–10 and 80–20 did not show any flow behavior ($G' > G''$) even at higher temperature until 200°C, which confirmed crosslinking of the HB polymer.

The viscosity of the LP and blends are presented as a function of shear rate in Figure 1. Both LP and the blends showed shear thinning behavior. It has been reported that HB polymers show Newtonian behavior due to the absence of chain entanglement.[16,17] The shear thinning behavior of LP and blends was, therefore, attributed to the contribution of polymer chain entanglements from LP.[18] The viscosity of LP: HB blends were found to be highest (5.9 × 10^4 Pa.s) at 200°C at low shear rate (0.01 s^{-1}). This behavior could be explained taking into account the crosslinking effect of the HB polymer at that temperature, which was confirmed from the previous rheological study performed as described in,[15] where both LP:HB 90–10 and 80–20 did not reach a flow state (storage modulus > loss modulus; $G'' > G'$) even at high temperature (~200°C). However, viscosity of LP:H-HB 90–10 and 80–20 blends were found to be slightly lower (3.8 × 10^3 Pa.s and 3.1 × 10^3 Pa.s, respectively) in comparison to LP (4.0 × 10^3 Pa.s) at shear rate of 0.01 s^{-1}. Lower viscosity of LP:H-HB blends compared to LP was expected as there are no reactive vinyl functional groups in the chain end of H-HB polymer and as a result no crosslinking should have occurred. Moreover, decrease of LP:H-HB blends viscosities in comparison to the LP in the lower strain rate region could also be attributed to the non-entanglement
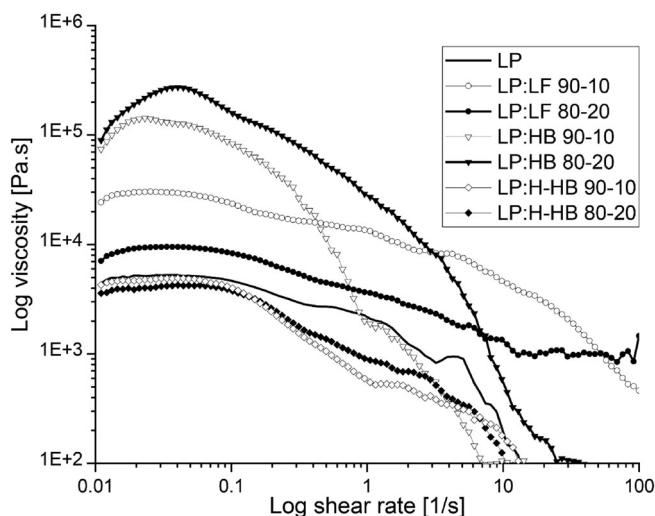
FIGURE 1 Dynamic viscosity of pure LP, LP:HB, and LP:H-HB polymer blends at 200°C and for LP:LF blends at 140°C

of H-HB polymer chains.[19] Nunez et al.[18] measured solution viscosity of blends of linear poly hydroxyl methacrylate and HB polyester and reported that reduction in viscosity from 40 Pa.s to 20 Pa.s for blends containing 5 wt% of HB polyester occurred due to the absence of physical entanglements in the HB polyester. LP:LF 90–10 and 80–20 at 140°C showed higher viscosity (1.9×10^4 Pa.s and at 5.3×10^3 Pa.s, respectively) than that of LP at 200°C (Figure 1) since the viscosity of the polymers decreased with increasing temperature.

3.2 | Thermogravimetric analysis

The thermal degradation (Figure S2) of LP, LP:HB, LP:H-HB blends at 200°C and for LP:LF blends at both 140°C and 200°C were investigated to explore potential degradation effects of the polymer blends during composite preparation stage.

The residual weight percentage (wt%) of pure LP, LP:HB, LP:H-HB blends at 200°C and LP:LF blends at 140°C showed almost similar thermal degradation profiles over the period of the study. However at 200°C after 28 min, the LP:LF blends underwent higher thermal degradation (residual wt% at ~89% and ~88% for 90–10 and 80–20, respectively) in comparison to LP (residual wt% ~96%) and the other polymer blends (LP:HB at 90–10 and 80–20 residual wt% ~95 and LP:H-HB 90–10 and 80–20 residual wt% ~93) tested. The higher thermal degradation of LP:LF blends at 200°C may have been due to the lower molecular weight of LF in comparison to LP, HB, and H-HB.[20] However, at 140°C after 28 min the LP:LF blends showed similar residual weight% as LP and the other blends, and hence why the composite with LP:LF blends were prepared at 140°C.

3.3 | DSC

Figure 2 shows DSC analysis of the LP:H-HB films of 90–10 and 80–20 composition from room temperature to 200°C. A peak was identified for LP:H-HB 80–20 at 165°C (Figure 2) whereas no such peak was found for the heat treated LP:H-HB 90–10. This peak indicated that after crystallization of the ethyl chain end ($-CH_2-CH_3-$) for H-HB in LP:H-HB 80–20 blends may have occurred post heat treatment at 200°C. For the LP:H-HB 90–10 absence of this peak indicated that 10 wt% of H-HB in the blend was not sufficient enough to cause any significant crystallization in the blend.

3.4 | Mechanical properties

3.4.1 | Tensile test

The tensile modulus data of LP and blends both at room temperature (R.T) and heat treated (H.T) are presented in Figure 3(A, B), respectively. At R.T the tensile modulus of all polymer blends was found to be statistically significantly ($p < 0.05$) lower in comparison to the LP alone. The lower modulus of LP:HB and LP:H-HB blends at R.T could also be explained in
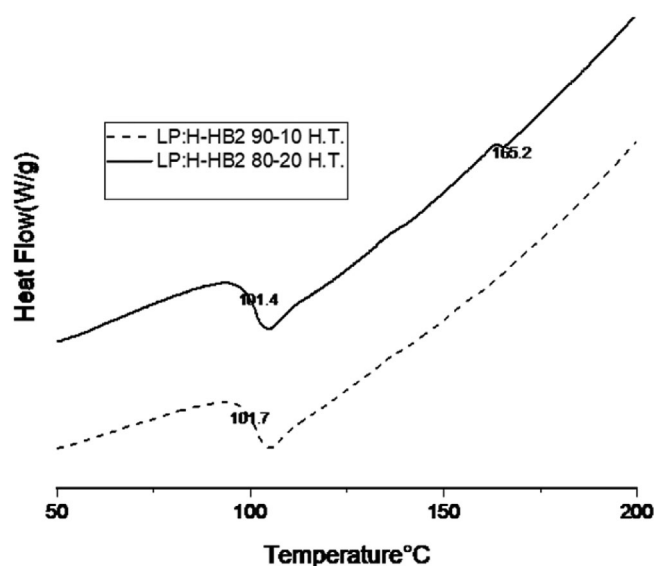
FIGURE 2 DSC thermograms of heat treated LP:H-HB 90–10 and LP:H-HB 80–20

terms of the absence of crosslinking and polymer chain entanglements of HB and H-HB at room temperature. It has been reported that HB polymers possess poor mechanical properties and brittleness in comparison to their linear counterparts due to higher branching and absence of chain entanglement.[21] The tensile modulus of LP:LF blends was also statistically significantly ($p < 0.05$) lower than LP, which was again suggested to be due to the lower molecular weight of the LF polymer. Although LF polymer had a lower molecular weight than for HB and H-HB, the tensile modulus of LP:LF 90–10 and 80–20 was statistically significantly higher ~15% ($p < 0.05$) in comparison to the LP:HB 90–10 and 80–20, respectively. At room temperature (in absence of crosslinking) both HB and H-HB possessed a globular, three-dimensional structure whereas LF possess a most likely linear structure like LP with few functional groups, since the monomer for LF was only 1% of divinyl benzene and 99% styrene.[15] So, it can be said that the highly branched structure at R.T may have been responsible for the statistically significantly ($p < 0.05$) lower modulus value for LP:HB and LP:H-HB in comparison to LP:LF. However, no statistical significant ($p < 0.05$) difference was observed for LP:HB and LP:H-HB tensile modulus value.

After heat treatment, the tensile modulus of LP decreased by 24% ($p < 0.005$). The decreased modulus value of LP could be attributed to the development of free volume and residual stress after heat treatment.[15,22] To study the effect of thermal treatment and quenching on thermal and mechanical properties of linear polystyrene, Rouabah et al.[23] carried out heating and quenching of linear polystyrene to different temperatures. They reported the lowest elastic and flexural modulus for linear polystyrene after quenching, and stated that this lower modulus was due to the development of free volume during quenching (as all polymer chains can have sufficient time to reorganize and thus free volume is induced) and residual tensile stresses developed, which may have increased the total tensile stress applied to the sample.[22,23]
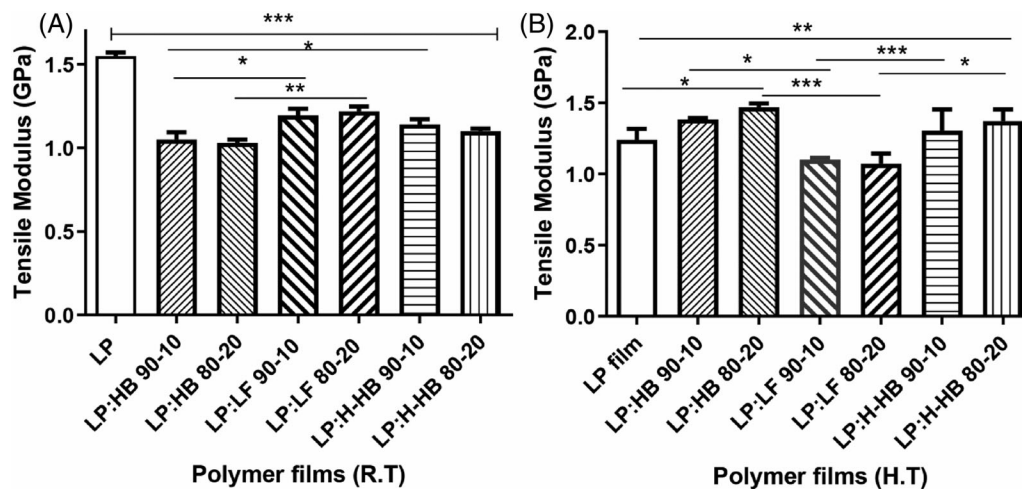
FIGURE 3 Tensile modulus of pure LP and blends (A) at room temperature and (B) heat treated

Since the heating and cooling process for both LP and the blends was similar, a decrease in tensile modulus value after heat treatment was also expected for blends. However, the heat treated LP:HB 90–10 and 80–20 blends experienced a 26% ($p < 0.005$) and 30% ($p < 0.005$) increase in tensile modulus, respectively, in comparison to LP:HB 90–10 and 80–20 blends at R.T. This increased modulus value of heat treated LP:HB 90–10 and 80–20 blends was attributed to the crosslinking of HB polymer at 200°C due to the presence of —CH=CH$_2$ at its chain end group.[24] Moreover, the modulus of heat treated LP:HB 80–20 was found to have increased statistically significantly by 18% ($p < 0.05$) in comparison to that of heat treated LP.

H-HB polymer possessed non-entangled polymer chains with non-reactive ethyl (-CH$_2$–CH$_3$) chain end groups. The ethyl (—CH$_2$—CH$_3$) chain end crystallization of H-HB at 165°C (Figure 2) had significantly ($p < 0.005$) increased the tensile modulus value of the LP:H-HB 80–20 blends (by 27%) than their value at R.T Malmstrom et al.[25] investigated the effect of alkyl chain end groups on the crystallinity of HB polyester and reported the crystallization of HB polymer chain ends with sufficiently long alkyl chain (C12-C16) length. However, they did not observe any crystallization with short alkyl chain lengths with 3–6 carbons. Schmaljohann et al.[26] also did not observe any crystallization effects for HB polymer with short alkyl chain (C4) ends. However, they did report crystallization for polymers containing C14 and C18 long alkyl chain ends. The H-HB polymer used in this study contained short (C2) alkyl chain ends, and crystallization may have occurred since the LP:H-HB blends were subjected to heat treatment at 200°C for 20 min and then cooled down to below the T_g value (100°C), which could have caused reorganization of the ethyl (—CH$_2$—CH$_3$) chain ends. However, for LP:H-HB 90–10 blend no significant ($p > 0.05$) improvement in tensile properties was observed in comparison to the value of the blend at R.T due to the absence of chain end crystallization (Figure 2).

The tensile modulus value of heat treated (140°C) LP:LF 90–10 and 80–20 also decreased by 9% and 12%, respectively ($p < 0.05$), in

comparison to the heat treated LP (at 200°C). Since LF has a linear structure with few —CH=CH$_2$ functional groups, the decrease in modulus may have been the same as for LP.

Figure S3a,b presents a comparison of the tensile strength data of LP:HB, LP:H-HB, and LP:LF blends with LP for both at R.T and heat treated (H.T). At R.T the tensile strength value of all polymer blends appeared to be statistically significantly ($p < 0.005$) lower in comparison to LP. However, after heat treatment the tensile strength of LP decreased by 20% ($p < 0.05$) as compared to R.T values. The lower tensile strength of LP after heat treatment may have been due to the fact that when external load was applied the stresses developed were superimposed with the tensile residual stresses (due to heat treatment) and the LP broke down at a lower load.[23] LP:HB 80–20 also experienced a decrease in tensile strength by 70% ($p < 0.005$) compared to LP alone. With increase wt% of HB in the blend, the crosslinking density of HB also increased and the tensile strength decreased. Kim et al.[27] prepared crosslinked polymer films with HB polyglycidol containing hydroxyl (—OH) group and used carboxyl (—COOH)-terminated poly (ethylene glycol) as a crosslinking agent. They reported a lower tensile strength value at 0.139 MPa for higher crosslinking concentration (mole ratio [—COOH]/[-OH];0.75) whereas higher tensile strength value at 0.22 MPa for lower crosslinking concentration ([—COOH]/[—OH];0.25). On the other hand, the tensile strength of heat-treated LP:H-HB 80–20 increased statistically significantly ($p < 0.005$) in comparison to its value at R.T The LP:LF 80–20 also experienced statistically significant ($p < 0.005$) decrease in tensile strength value.

A comparison table for the tensile strength of all polymer films both at room temperature and heat treated is presented in Table 2.

3.4.2 | Flexural test

For the flexural modulus data of the composites (Figure 4(A)) the lower flexural modulus was observed for LP:HB 90-10-GF and 80–20

TABLE 2 A comparison of the tensile strength value of pure LP and blends (LP:HB, LP:H-HB, and LP:LF) for both at room temperature (R.T) and heat treated (H.T)

| Polymer films	Tensile strength (R.T) (MPa)	Tensile strength (H.T) (MPa)	(%) increase or decrease	p value
LP	25.01	20.8	20% decrease	(p < 0.01)
LP:HB 90–10	15.65	13.51	15% decrease	(p > 0.01)
LP:HB 80–20	13.29	6.88	93% decrease	(p < 0.005)
LP:H-HB 90–10	16.75	18.08	8% increase	(p > 0.05)
LP:H-HB 80–20	12.22	19.78	61% increase	(p < 0.005)
LP:LF 90–10	12.66	14.92	15% increase	(p > 0.05)
LP:LF 80–20	14.66	11.33	29% decrease	(p > 0.01)
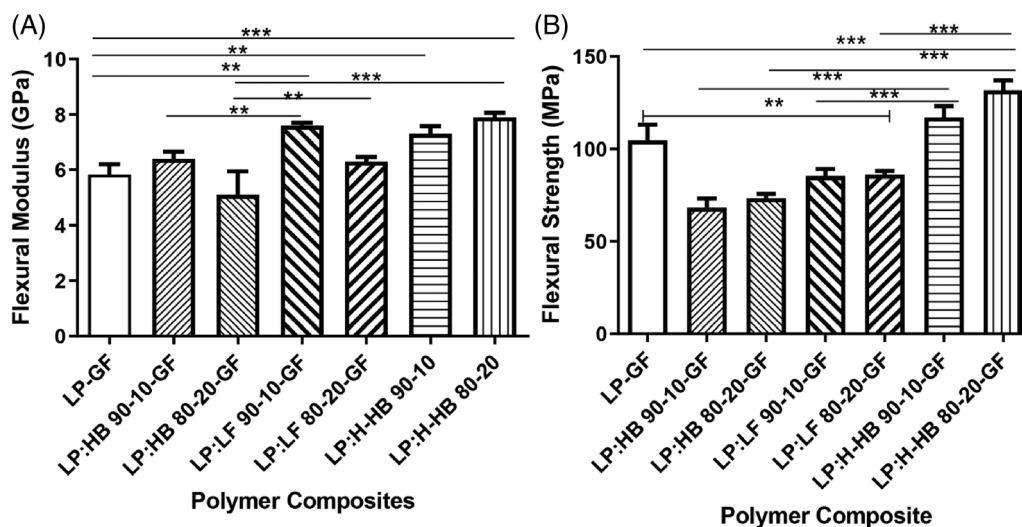
FIGURE 4 (A) Flexural modulus (B) Flexural strength for composites with 21 wt% E-glass fiber (woven mat) produced using LP and blends

composites at 5.5 and 5.1 GPa, respectively. However, this value was not statistically significantly lower than that of LP-GF composite (5.8 GPa). From our previous study[15] the rheological data showed that the storage modulus of LP:HB blends was higher than the loss modulus across the temperature region examined and did not show any flow behavior before being crosslinked. As a result, wetting of fiber with matrix was minimal and resulted in low a modulus value. Other studies also reported lower flexural properties for composites prepared with crosslinked HB polymers. For example, Ratna et al.[28] manufactured epoxy/clay nanocomposite using a matrix, which was a blend of epoxy and 15 wt% epoxy functional HB polymer and utilized a crosslinking agent for the HB with epoxy. They reported a significant decrease in flexural modulus value for the nanocomposites with 15 wt% HB (2.5 GPa) in the matrix as compared to the composite without HB (5.0 GPa) in the matrix. They attributed this decrease in composite modulus to the lower modulus value of the HB polymer.

On the other hand, in comparison to the LP-GF composite the flexural modulus of LP:H-HB 90-10-GF and 80–20 increased by 25% and 36%, respectively. Moreover, the flexural strength for LP:H-HB 80-20-GF had increased statistically significantly by 31% compared to the LP-GF composite. This increase in modulus and strength indicated better adhesion between LP:H-HB matrix and the fiber due to

potentially enhanced wettability of the fiber by the LP:H-HB matrix in comparison to LP matrix at the composite processing temperature (200°C). The improved wettability of the LP:H-HB matrix can be supported by the lower viscosity at lower strain rate (0.01%) (see Figure 1) and also by the flow behavior (from rheological data[15]) at lower temperatures ~170°C (for both LP:H-HB 90–10 and 80–20 blends) in comparison to the LP (~190°C). Hyperbranched polymers have been previously reported for use as matrix modifiers for thermoplastic polymer composites to improve processability.[7] Lu et al.[9] used a carboxy terminated HB polymer as compatibilizer for composites with sisal fiber (as reinforcing agent) and polypropylene (as matrix) and reported an increase in flexural modulus to 2.13 GPa and flexural strength to 42.6 MPa with addition of 2% HB whereas for neat polymer and sisal fiber composite the values were reported to be 1.84 GPa and 35.7 MPa, respectively. They explained that this increase in flexural properties was due to the uniform distribution of sisal fiber in the HB modified polymer matrix.[9] Moreover, during composite manufacture alkyl chain end crystallization was suggested to have occurred for LP:H-HB 80–20, which contributed to the higher mechanical properties of the LP:H-HB 80-20-GF composite.[29]

However, the flexural strength value of both LP:LF 90-10-GF and 80-20-GF composites decreased (by 18%, p < 0.005) as compared to
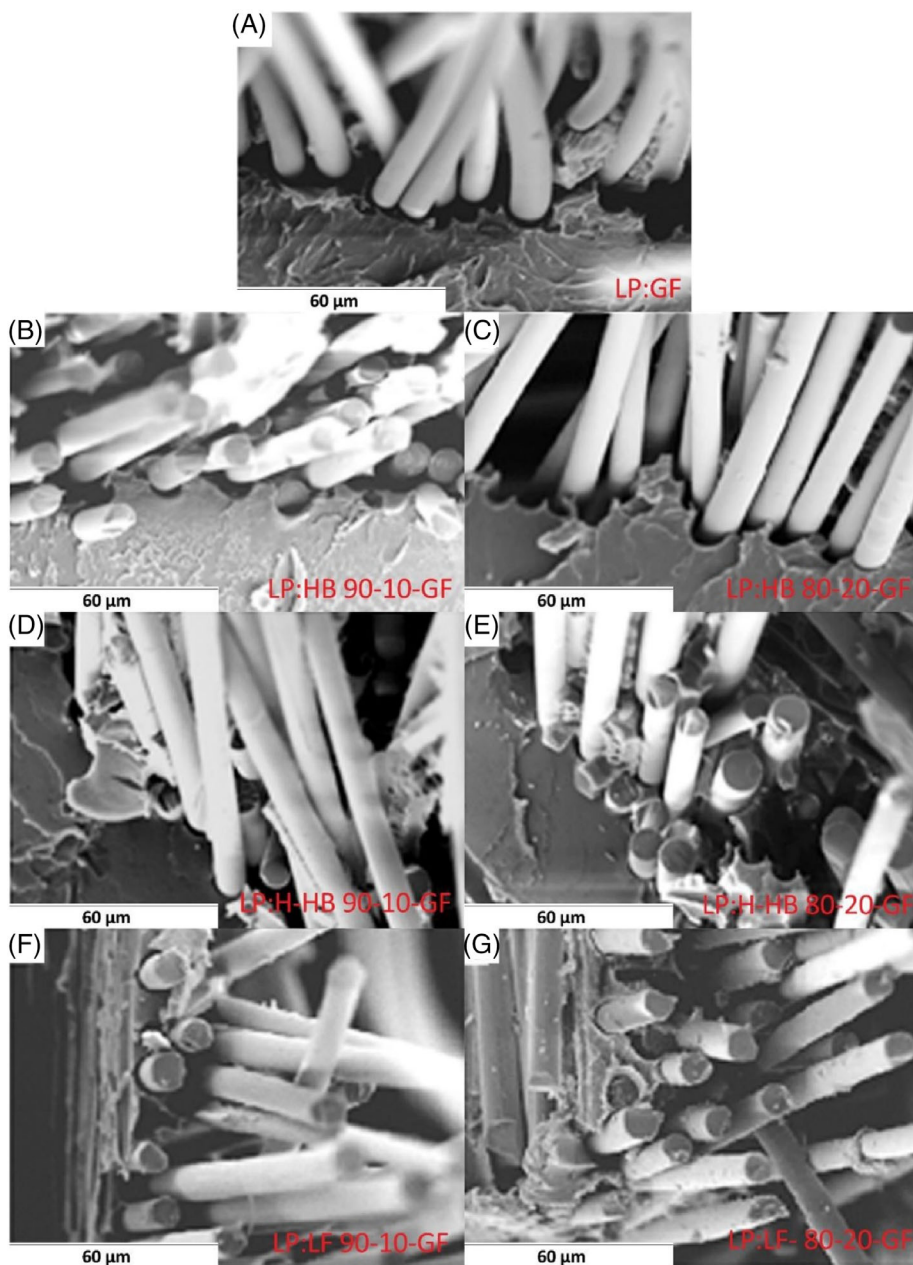
FIGURE 5 SEM micrographs of fracture surfaces of composites (A) LP-GF (B) LP:HB 90-10-GF (C) LP:HB 80-20-GF (D) LP:H-HB 90-10-GF (E) LP:H-HB 80-20-GF (F) LP:LF 90-10-GF (G) LP:LF-80-20-GF

the LP:LF 90-10-GF composite. Although LP:LF blends melted at ~140°C,[15] the viscosity of both LP:LF 90–10 and 80–20 blends were significantly higher at 140°C than LP at 200°C. The higher viscosity of the LP:LF blends may have been responsible for the comparatively poor wettability compared to the LP.[30]

3.4.3 | Scanning electron microscopy (SEM)

Figure 5 shows the surface morphology of the fractured composites and in the case of LP-GF (Figure 5(A)) and LP:HB-GF (Figure 5(B, C)) composites the fibers appeared to have de-bonded from the LP matrix indicating poor adhesion between the fibers and the matrix. De-

bonding was also observed for LP:LF-GF composites (Figure 5(F, G)), however, less than LP-GF and LP:HB-GF. For the LP:H-HB composites (Figure 5(D, E)) better adhesion between the fiber and matrix was observed after composite fracture in comparison to the other composites. This result was also in agreement with data from mechanical tests.

4 | CONCLUSIONS

In conclusion, after heat treatment the tensile modulus of LP:HB of 90–10 and 80–20 increased significantly in comparison to LP (p < 0.005), which was suggested to be due to crosslinking, and their

tensile strength properties decreased. For the LP:H-HB 80–20 blends a significant ($p < 0.005$) increase was observed for both tensile modulus and tensile strength value, which was suggested to be due to the ethyl chain end crystallization of H-HB after heat treatment. Moreover, for the composites, the highest flexural modulus and strength was found for LP:H-HB 80-20-GF at 7.9 GPa and 131 MPa, respectively, which was suggested to be due to enhanced wettability of fiber by LP:H-HB 80–20 matrix and chain end crystallization. This observation was also supported by SEM analysis where better adhesion between the fiber and matrix was observed for LP:H-HB 80-20-GF.

DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available in the supplementary material of this article.

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SUPPORTING INFORMATION

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