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$NaBF_4$ as a hygrothermal durability enhancer for glass fibre reinforced polypropylene composites

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ABSTRACT

The long term performance of composite materials is highly desired for their expanding application range. Tuning the interphase properties has been proven to be a practical way to enhance the performance of composites. In this study, short glass fibre (GF) reinforced polypropylenes (PPs) with improved hygrothermal durability were obtained by incorporating $NaBF_4$ into the sizing and thus the interphases of GF/PP composites. Detailed investigations were performed on the surface properties of sized GFs and the mechanical properties of virgin and aged composites. It was found that the retention in both ultimate tensile strength and Charpy impact toughness of aged composites monotonically increased with increasing $NaBF_4$ content. The improvement in hygrothermal durability was related to the enhanced fibre/matrix adhesion strength induced by the presence of $NaBF_4$ as indentified by fracture surface analysis using field-emission scanning electron microscopy and single fibre pull-out test.

1. Introduction

Owing to the combination of great static/dynamic mechanical properties, recyclable feature, low cost, and tailor-able polymer structure, PP is one of the most intense used semi-crystalline polymers, gaining a wide variety of applications [1,2]. Furthermore, the incorporation of high stiffness and high strength fibres into PP realized fibre reinforced PP composites with significantly improved stiffness and strength, which greatly expands the use range of PP to more broader application fields, such as structural or semi-structural materials in automotive, offshore, and marine structures [3,4]. This, in turn, demands fibre reinforced PP composites with improved long term performance in different environments, such as moisture, temperature, radiation.

Influenced by moisture and elevated temperature, i.e. hygrothermal aging, fibre reinforced polymers usually suffer significant performance degradation [5,6]. Several mechanisms accounting for the performance reduction have been proposed involving the following interactions between water and the constitutes of composites [7,8]. It has been observed that water molecules could (1) diffuse to matrix and reinforcing fibre leading to the degradation of matrix and fibre, (2) penetrate to the interphase between matrix and fibre resulting in de-bonding, and (3) transport through microcracks or other forms of microdamages, such as pores or small channels, giving rise to the build up of stress. Experiments also revealed that the uptake of moisture mostly follows Fick's law of diffusion with different diffusion coefficients, which increase with increasing temperature but decrease with increasing water salinity [9]. In addition, it was estimated that water penetrating through interphases was more than 450 times faster than through matrix [10]. Hence, surface modification of reinforcing fibres with sizings/coatings and incorporation of matrix modifier are two common means used to improve the hygrothermal stability of fibre reinforced polymers by enhancing the interfacial adhesion strength or impenetrability [10–12]. Thus, the water penetration was limited and the deterioration on matrix, fibre and interphase was slowed down [10].

The interphase between reinforcement and matrix plays an important role in determining the mechanical properties of composites [13]. In GF/PP composites the interphase between GF and PP is formed by the interdiffusion of matrix PP and the sizing of GFs. This results in the interpenetrating networks (IPNs) of polysiloxane and PP, where siloxane groups and maleimide groups are created for polysiloxane/GF and polysiloxane/maleic anhydride grafted PP (MAH-*g*-PP, matrix modifier), respectively [14]. Consequently, stress can be efficiently transferred from matrix to load bearing reinforcing fibres leading to GF/PP composites with great performance. Besides these perfect covalent bondings, there are still some unreacted silanol groups, polar groups of lubricants or surfactants [15] and other weak points in the interphase, which are liable to interact with [16] and accommodate water molecules, leading to the degradation of interphase properties, correspondingly, the mechanical properties of composites. When the non-hygroscopic features of

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GFs and PP are taken into consideration [17], it becomes obvious that proper interphase design holds great promise to improve the hygrothermal durability of composites [3]. However, as yet reports addressing the further improvement of the hygrothermal durability of GF (the most widely used fibre reinforcement globally) reinforced PP composites are rather limited.

Tetrafluoroborate ion (BF_4^-) is being used as the counter ion of templating agents for the preparation of mesoporous silica with higher thermal and hydrothermal stabilities in comparison with fluoride ion, which is mainly attributed to the less hydrophilic BF_4^- promoting the hydrolytic condensation of alkoxysilanes [18,19]. Meanwhile, it has been reported that O–B–F was formed in hydrothermally synthesized borophosphates [20] or the hydrolysis of BF_4^- ion [21]. It suggests that F could be chemically coupled to silica. Taking into consideration the chemical similarity for silica, GF and the polysiloxane in the interphase of GF/PP, the introduction of tetrafluoroborate ions into the interphase might lead to interphases with higher hydrophobic character and higher hygrothermal stability, correspondingly, GF/PP with higher hygrothermal durability.

In this work, we present the results on the concept: Enhancing the hygrothermal durability of composites by "hydrophobizing" the interphase. The potential of $NaBF_4$ was assessed as "interphase hydrophobizer". The work focuses on the influence of $NaBF_4$ content on the fibre properties and hygrothermal stability of short GF/PP composites with both PP homopolymer and PP-polyethylene copolymer as matrices. Field-emission scanning electron microscopy (FE-SEM) was used to investigate the fracture surfaces of tensile test specimens. Single fibre pull-out test (SFPO) was used as a complemental method. The correlation between fibre/matrix adhesion strength and hygrothermal durability is discussed.

2. Experimental details

2.1. Materials and sample preparation

E-GFs sized by 3-aminopropyltriethoxysilane (AMEO, Evonik Degussa GmbH, Rheinfelden, Germany) in conjunction with a PP film former (Permanol 602, Clariant, Switzerland) in presence of or free of additive ($NaBF_4$, Sigma–Aldrich, Germany) were spun at the Leibniz Institute of Polymer Research Dresden using continuous spinning devices comparable to industrials ones. The average diameter of used sized GFs was 17 μm. The content of $NaBF_4$ in sizings was 0.0, 0.08, 0.16, and 0.32 wt.%, respectively. The addition of $NaBF_4$ did not affect the pH value of the sizings. These sized GFs are referred to as GF-00, GF-08, GF-16, and GF-32, respectively. An isotactic PP homopolymer (Hostalen PP W2080, LyondellBasell Industries) and a PP copolymer (Moplen EP240T, LyondellBasell Industries) compounded with 2 wt.% PP-*g*-MAH (Exxelor PO1020) were used as matrices and referred to as PPH (crystallization enthalpy ΔH_c = 110.9 J/g) and PPC (ΔH_c = 81.4 J/g), respectively. GF/PPs with 30 wt.% GF (13.2 vol.%) were compounded using a corotating twin-screw extruder ZSK 30 (Werner & Pfleiderer, Stuttgart, Germany). Consequently, eight composites were made, they are designated by (matrix type)-($NaBF_4$ content). For example, PPH-32 is the PPH based composite reinforced with GF-32. The dog-bone shaped specimens (160 × 10 × 4 mm, according to DIN 53455, specimen No. 3, ISO 527.2) and plates (80 × 4 × 2 mm) were made on the injection moulding machine Ergotech 100 (Demag Ergotech Wiehe GmbH) for tensile strength test and Charpy impact test, respectively.

2.2. Characterizations

The loss on ignition (LOI) of sized GFs was determined according to ASTM D4963-04 by means of high temperature pyrolysis at 625 °C. Fibre content of composites was also estimated gravimetrically by the resin burn-off method (ASTM D2584).

Tapping mode Atomic Force Microscope (AFM) investigations were carried out on a Dimension 3100 (Digital Instruments, Santa Barbara) at room temperature. The values of root-mean-square roughness (R_q) and maximum height roughness (R_{max}) were calculated after 2nd flatten over the whole captured area (3 × 3 μm^2).

Dynamic advancing contact angle (θ_a) and receding contact angle (θ_r) measurements on single GFs were performed on a tensiometer K14 (Krüss GmbH, Hamburg, Germany).

X-ray photoelectron spectroscopy (XPS) investigations were performed on a Kratos AXIS Ultra X-ray photoelectron spectrometer. Areas of approximate 300 × 700 μm^2 were analyzed with a monochromatic Al Kα X-ray source. The survey spectra were collected over a wide binding energy range (0–1300 eV) and were used to evaluate all of the elements present (except H and He) within the sample surface. The survey spectra were acquired at a pass energy of 160 eV and a step size of 1 eV. The high resolution spectra were obtained at a pass energy of 20 eV and dissected by means of the spectra deconvolution software. The parameters of the component peaks were their binding energy, height, full width at half maximum, and the Gaussian–Lorentzian ratio. The maximum information depth of 8 nm was probed with take-off angle 90°.

The modulated DSC was carried out on a Q 2000 MDSC (TA Instruments, USA) at a temperature change rate of 10 K/min.

Hygrothermal aging was carried out in 95 °C de-ionized water for 10 days in an autoclave (CV-EL 18 L GS, CertoClav Sterilizer GbmH, Traun, Asutria). Hygrothermal aging led to water uptake in the range of 0.23–0.32 wt.%, which did not show clearly correlation with $NaBF_4$ content. The aged specimens were stored in air-conditioned room (50% relative humidity, 23 °C) for 24 h before mechanical property test.

Tensile tests were performed on a Zwick 1456 Universal Testing Machine (Zwick GmbH, Ulm, Germany) according to ISO 527-2/1A/5. The presented results are averaged values based on ten specimens for each test series. Unnotched Charpy impact tests were carried out on a PSW 4J (Zorn GmbH, Stendal, Germany) in accordance with ISO 179/1eU. The presented results are averaged values based on five specimens for each test series.

The retention of composite tensile strength and Charpy impact toughness after hygrothermal aging is defined as:

$$\Delta\sigma = \sigma_{aged}/\sigma_{DAM} \times 100\% \quad (1)$$

and

$$\Delta a_{cU} = a_{cU_{aged}}/a_{cU_{DAM}} \times 100\%, \quad (2)$$

respectively, where σ_{aged} and σ_{DAM} are the ultimate tensile strength of aged and dry as molded (DAM) composites, respectively. $a_{cU_{aged}}$ and $a_{cU_{DAM}}$ are the Charpy impact toughness of aged and DAM composites, respectively. In order to further reveal the impact of $NaBF_4$ content, the relative change in mechanical properties of composites with $NaBF_4$ over composites without $NaBF_4$ is calculated using following equations:

$$\Delta\sigma_{DAM} = (\sigma_{DAM,NaBF_4\%} - \sigma_{DAM,0.0\%})/\sigma_{DAM,0.0\%} \times 100\%, \quad (3)$$

$$\Delta\sigma_{aged} = (\sigma_{aged,NaBF_4\%} - \sigma_{aged,0.0\%})/\sigma_{aged,0.0\%} \times 100\%, \quad (4)$$

$$\Delta a_{cU_{DAM}} = (a_{cU_{DAM,NaBF_4\%}} - a_{cU_{DAM,0.0\%}})/a_{cU_{DAM,0.0\%}} \times 100\%, \quad (5)$$

and

$$\Delta a_{cU_{aged}} = (a_{cU_{aged,NaBF_4\%}} - a_{cU_{aged,0.0\%}})/a_{cU_{aged,0.0\%}} \times 100\%. \quad (6)$$

Eqs. (3) and (4) give the relative tensile strength changes for DAM and aged composites, respectively. Eqs. (5) and (6) present the relative Charpy impact toughness changes for DAM and aged