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ABSTRACT

Boron nitride nanotubes (BNNTs) have experienced considerable growth in ent due to their unique intrinsic properties, in particular for the fabrication of polymonal omp Dispersion of pure BNNTs in nanocomposites is often difficult due to their pocompatibility with most polymer matrices. An approach involving the creation of h droxy groups on their surface could improve their dispersion. While some harsh oxidation est es have been reported so far, a mild oxidation of BNNTs using air as the oxidant is report here. This new catalytic ectenzed by SEM, XPS, FTIR and reaction leads to slightly oxidized BNNTs, which were TGA. Polycarbonate nanocomposites were then fabricated sing pristine and oxidized BNNTs as easing linearly with the mildly oxidized nanofillers. The measured thermal conductivity BNNTs content. It reached a five-fold increase t ▶ 1.19 W/m.K at 15% vol. content which is significantly improved over nanocomposite cated with severely oxidized BNNTs, while the electrically insulating character remained underfiged.

1. INTRODUCTION

Boron nitride-based nanomaterials are continuously drawing interest from scier tific community [1,2]. They are used in a variety of applications and especially in wher dissipation is of primary consideration [3,4]. Among these boron nitride-based. nomaterials, two nanostructures have attracted particular attention for applications as nanofilers in polymer nanocomposites: boron nitride nanosheets (BNNS, 2D) and boron nitrid notubes (BNNTs, 1D). Although BNNS have been of great interest in the development of bernally conductive polymer nanocomposites [5–7], this paper focuses specifically on BNNTs. When recent development [8,9], for keat dissipation applications [10– BNNTs are now emerging as very promising 1D nanofills. 12]. They are geometrically very close to carbon n notice (CNTs) except that the carbon-carbon bonds are replaced by alternating boron-nition bonds. While they possess very good thermal parable to those of CNTs, BNNTs are electrically conductivity and mechanical proper insulating (band gap > 5.5 eV) and thermally stable up to 1000 °C under air [13,14].

For many applications in nanceemposites, the pristine form of the BNNTs is not fully satisfactory due to insufficient stabilizing interactions with the polymer matrices. This often leads to poor dispersion resulting in the formation of BNNTs bundles in the polymer matrix. Although BNNTs are practically sherincally inert ant quite resistant to oxidation [15], several approaches involving chemical functionalization of the nanotubes have been developed to improve their

dispersion [12-21] It should be mentioned that much effort has also been devoted to the functionalization of boron nitride nanosheets (BNNS), the 2D counterpart of BNNTs [22-25]. The first step of BNNT functionalization is commonly based on the oxidation of the nanotubes to activate the surface, followed by various reactions with molecules of interest. Different functionalization routes using hydroxylated BNNTs have been reported to be effective in

providing greater solubility or dispersion of the nanotubes through stabilizing interactives [26–30].

One of the main difficulties of the reported oxidation processes is to reac ficien of oxidation on the surface of the nanotubes to ensure a good density of hydrox groups, without being too harsh to avoid over-oxidation. Indeed, Liao et al. [31] showed that over oxidation related d end-caps, sharpened to severe reaction conditions leads to the nanostructure destruction rep f the remarkable properties. ends, thinned sidewalls and shortened lengths), resulting in a loss Since the intrinsic chemical reactivity of BNNTs is quite low, or we a few oxidation routes have been successfully tested so far, especially under harsh con tions. Such severe oxidation protocols include the use of nitric acid [27,30,32], perchloric acid [26], concentrated sodium hydroxide solution [28,33], excess bromine in water [3 1 or hydrogen peroxide under pressure [38,39]. A fine control of the nanotube oxid onewhat difficult due to these harsh conditions. It should also be noted that gas-phase oxidation of BNNTs exists [40–43].

Among various oxidation reactions used in organic chemistry, a catalytic free-radical reaction based on N-Hydroxyn than mide (NHPI) has been widely developed for the air oxidation of organic molecules that a manes, alcohols or aldehydes [44–46]. This oxidation reaction is known to give better enversion and selectivity than conventional autoxidations [47]. A main advantage of this system telies on the use of air as the final oxidant of the reaction. To the best of

our knowledge, this catalytic system has never been used for oxidizing inorganic compounds. In most cases, the oxidation reaction of BNNTs occurs through a concerted mechanism [27,34]. However, some recent reports revealed that BNNTs could undergo surface activation through freeradical reactions [48,49]. Shin et al. [48] predicted via theoretical study and experimentally verified the functionalization of pristine BNNTs using chemically reduced nanotubes with sodium

naphthalide followed by reactions with free radicals. Lin et al. [49] used thermally labile provides to covalently functionalize BNNTs. Upon heating, the peroxides decompose to generate relicals that are capable of reacting with the BNNTs.

In this article, it is demonstrated that such a catalytic system based on NHPI efficiently catalyses the air oxidation of BNNT and affords a straightforward route to the fabrication of mildly oxidized BNNTs.

The advantages of using mild over harsh oxidation conditions and the effects of such oxidation protocols on thermal properties of polymer nanocomposites are also highlighted. The BNNTs were used as nanofillers dispersed in a polytochonau matrix. Contrary to what had been reported with nanotubes oxidized according to the usual protocols [37], the moderately oxidized BNNTs behave like raw BNNTs, i.e. they allow ustrong increase of the thermal conductivity (500% increase at 15 vol%) while maintaining a marked electrically insulating character.

2.1 Materials

N-hydroxyphthalimide (NHPI, 97%), manganese(II) acetate (Mn(OAc₁₂, 98%)) cobal(II) acetate (Co(OAc)₂, 99.9%), acetic acid (AcOH, glacial), sodium hydroxide (NaOH) and tetrahydrofuran (THF, 99.9%) were purchased from Sigma-Aldrich (USA), which are as received. Nitric acid (HNO₃, 69.5%) was purchased from Carlo Erba (Germany). Beron nitride nanotubes (BNNTs) were purchased from BNNano (USA) as Nanobar¹⁰T^M (pure 90%, diameter \approx 250-300 nm / length \approx 20 µm) and used as received without any prification treatment. Polycarbonate (PC, grade Makrolon LED2045) was purchased from Sovesta (Germany).

2.2. Experiments

2.2.1. Oxidation of BNNT

BNNT-OH through a catalytic reaction based on NHPI and BNNTs were oxidized in transition metals such as mangan se and cobalt. In a typical experiment, 200 mg of pristine BNNTs were firstly dispersed in 159 mL of glacial acetic acid for 30 min in an ultrasonic bath. Simultaneously, 260 m (20 mol%) of NHPI, 7 mg (0.5 mol%) of Mn(OAc)₂ and 7 mg (0.5 mol%) of Co(OAc)₂ were dispersed in 50 mL of glacial acetic acid for 30 min. Once fully dispersed, the $NHPI + Mn(OAc)_2 + Co(OAc)_2$ solution in glacial acetic acid were put **BNNTs** solut and under a reflux heating set at 100 °C with magnetic stirring and controlled air together and bubblin The/ eaction mixture was left under these conditions for 64 h. The resulting hydroxylated [NTs (**I**NNT-OH]/*NHPI*]) were finally vacuum-filtered and washed four times with 200 mL of deionized water to remove catalysts and residual NHPI. The purified BNNT-OH|*[NHPI]* cowder was then dried in an oven set at 80°C for several hours before any further experiment

For comparison purposes, pristine BNNTs were also treated with concentrated here acid (HNO₃ 69.5%) for 3 h in an ultrasonic bath (BNNT-OH $|[HNO_3]$) and concentrated socium hydroxide aqueous solution (NaOH 10 M) for 20 h at 100 °C (BNNT-OH|[NaOH]).

2.2.2. Nanocomposite preparation

PC-BNNT and PC-BNNT-OH nanocomposites were synthwized through the solution mixing technique. Briefly, PC was firstly dissolved in Thr the stirring at room temperature) and simultaneously, BNNTs or BNNT-OH were dispersition Threat a concentration of 1 mg/mL (10 min stirring at room temperature followed by 10 min in an ultrasonic bath). Then, the BNNTs/THF or BNNT-OH/THF solution was incorporated into the PC/THF solution and stirred for 30 min. Finally, the excess of THF was removed using a rotary evaporator. The resulting dry nanocomposite flakes were lefting night under a fume hood for an additional drying.

PC-BNNT and PC-BNNT-OR panocomposite flakes were then used to produce bulk samples (disk-shaped, diameter = 15 mm, thickness = 1.2 mm). The disk-shaped samples were obtained by hot pressnet the home composite flakes under a uniaxial hot press set at 270 °C (Carver 30T 4128, Carver 100 USA). Prior to molding, the nanocomposite flakes were dried in an oven set at 120 °C for advant 9 h. Then, the nanocomposite flakes were put inside a pressing die and

preheated 20 min 2 270 °C. Finally, a 5 min pressing at 270 °C of the nanocomposite flakes resulted in the desired disk-shaped sample. The pressing die was then cooled down to room temperature. Different nanofiller weight fractions (wt%) were investigated in this study. For comparison purposes, they were also converted into volume fractions (vol%) using the following

fornula:

$$vol\% = \frac{wt\%}{wt\% + (\rho_m) * (1 - wt\%)}$$

where ρ_f is the density of the filler ($\rho_{BNNT} = 2.3 \text{ g cm}^{-3}$) and ρ_m is the density T the potential matrix ($\rho_{PC} = 1.2 \text{ g cm}^{-3}$).

2.3. Characterizations

The morphology of BNNTs and BNNT-OH was observed us becaused-emission - scanning electron microscope (FE-SEM, LEO 1530 VP Gemini, Zeiss, German V Diameters and lengths of BNNTs and BNNT-OH were measured using the digital time processing software ImageJ. The dispersion of BNNTs and BNNT-OH inside the polycarchate matrix was also studied by FE-SEM coupled with energy dispersive X-ray spectroscopy (EDX, XFlash Detector 5030, Bruker, Germany) on bulk nanocomposites fracture surface. Before any observation, all samples were metalized by platinum sputtering.

Infrared spectra of BNNTs and BNNTOH samples were obtained with a Fourier transform infrared (FTIR) apparatus used in transmission mode (Vertex 70, Bruker Optics, Germany). In a typical analysis, a spatula time of BNNTs or BNNT-OH powder was mixed with KBr grinded crystals and disk-surped onder a uniaxial hydraulic press. All KBr samples were dried in an oven set at 80 °C before by FTIR analysis to avoid water contamination.

X-ray photoelectron spectro of BNNTs and BNNT-OH were obtained with a X-ray photoelectron spectroscop (XPS) apparatus (Versaprobe-II, Physical Electronics, USA).

Mass loss percentage with increasing temperature was measured by thermogravimetric narbits (TOA) using a STA 449 from Netzsch, Germany. Two measurements were carried out or shouterial. A heating rate of 5 °C/min up to 600 °C was applied under air atmosphere.

Thermal conductivity values (λ) were calculated using the formula $\lambda = \alpha * \rho * C_{P}$ where α is the measured thermal diffusivity, ρ is the measured bulk density and C_{p} is the calculated heat capacity based on the rule of mixtures. Through-plane (\perp) and in-plane (//) thermal definitivity measurements were performed using a laser flash apparatus at 25 °C (LEA447 MicroFlash, Netzsch, Germany). For in-plane measurements, the disk-shaped samples were put into \approx 1.2 mm-wide strips using a diamond-coated wire saw, rotated 90° and placed inside a square sample holder. Bulk density was measured in a 1 cm³ cell with a He gas displacement pw/nometry system at 25 °C (Accupyc II 1340 from Micromeritics, USA). The average value was calculated from 25 measurements.

Electrical resistivity was measured using a meresistivity measurement system mounted with a UR-SS probe (Hiresta-UX, MCP-HT, Mitsteini Chemical Analytech, Japan).

3. RESULTS AND DISCUSSION

3.1. Synthesis and characterization of oxidized BNNTs (BNNT-OH)

The objective of this budy was to mildly oxidize BNNTs through a soft and straightforward need using air as the final oxidant. The oxidation reaction of BNNTs was carried out in a conventional benchtop setup, with a flow-regulated air bubbler placed in the solution, as simplayed in figure 1.



Figure 1. Schematic view of the catalytic air oxidation process of BI

After reaction, the BNNT-OH were filtered, wa ed, drived and then analyzed by a set of characterization techniques. High-resolution SEM ma of the nanotubes were compared before and after the oxidation reaction. They are dis xed in gure 2. Although the BNNTs appeared slightly modified after the reaction with NHPI (slight modification of the nanotube diameter), their overall integrity was maintained (figure 20.b)). BNNTs entanglement made length measurements difficult, however it appears the BNNT-OH (figure 2(b)) were slightly shorter than pristine BNNTs (figure 2(a)). In contract, BNT-OH obtained after HNO₃ or NaOH based reactions underwent significant degradation as shown in figure 2(c-d). These degradations are typical of severe oxidation proce as and include thinned sidewalls (drastic reduction of the nanotube diameter in BNNT OH, NO3 and BNNT-OH [NaOH] samples), sharpened ends and tearing or gure 2(c)) [31]. SEM images of oxidized BNNTs are shown in figure S1. breakage of r



Figure 2. SEM images of (a) pristine **(b)** T₅ (b) BNNT-OH[*[NHPI]*, (c) BNNT-OH[*[HNO₃]* and (d) BNNT-OH[*[NaOH]*. Insets show typical high magnification images of individual BNNTs.

Oxidized BNNTs were enalyzed by PTIR. The full-scale FTIR spectra of pristine and oxidized BNNTs are displayed in figure 3(a). An inset of the 2800-4000 cm⁻¹ region is also presented in figure 3(b). The R spectrum of pristine BNNT is similar to previous reports in the literature [50,51]. Two major is sorption bands are observed at 811 and 1380 cm⁻¹ which are indicative of the conf-plane B-N-B bending and the in-plane B-N stretching vibrations respectively. This is unital of hexagonal boron nitride with symmetries of A_{2u} and E_{1u} [52,53]. The comparison of the 2800-4000 cm⁻¹ region between pristine BNNTs and BNNT-OH shows the appearance of apeak at 3435 cm⁻¹, which can be ascribed to the vibration frequency of the hydroxyl groups. The BNNT-OH]/*NHPI*] sample exhibits the highest relative absorbance intensity compared to BNNT-OH]/*HNO*₃] and BNNT-OH]/*NaOH*] (figure 3(b)).

The comparative XPS analysis of the pristine and oxidized BNNT reveals a shift but significant modification of the spectrum as displayed in figure 3(c-f). The peak around 12.03 eV was attributed to the B-N bond [39]. In pristine BNNTs (figure 3(c)), the B1s peak is symmetric with respect to its center located at 190.3 eV and well fitted with a single Gaussian component. On the contrary, for oxidized BNNTs (figure 3(d-f)), the B1s peak appears asymmetric with shoulders at higher binding energies. After peak deconvolution, the presence of a second Gaussian component centered at 191.3 eV in BNNT-OH|*/NHPI*] and BNNT-OH|*/bNO₃*] samples can be assigned to the B-O bond [38,39,54] thus confirming for surface oxidation of BNNTs. Interestingly, the B1s peak in the BNNT-OH|*/NaOH*] sample (have 3(f)) display less asymmetry, suggesting a lower hydroxyl density after functionalization.

TGA experiments were also carried by to colfirsh the presence of -OH groups after the oxidation reaction. TGA curves of pristine and oxidated BNNTs are presented in figure S2. While pristine BNNTs remained thermally stable over the entire temperature range (no noticeable mass loss), BNNT-OH underwent a probet mass loss between 250 and 450°C. This mass loss corresponds to the elimination of the hydroxyl group (de-hydroxylation) [30,55], confirming the presence of -OH groups at the surface of BNNTs after oxidation. However, it should be noted that the mass loss is slightly differencedepending on the oxidation process employed. The most important mass loss (about 0.77%) is a trained with the BNNT-OH *[NHP1]* sample, which is consistent with both FTIR and XPS barace azation results.



Figure 3. (a) FTIR spectra of pristine and condized BNNTs, (b) zoom of the FTIR spectra in the 2800-4000 cm⁻¹ range. Narrow B1s scans of high resolution XPS spectra of (c) pristine BNNTs and (d-f) oxidized BNNTs.

3.2. Thermally conductive procomposites

pared using polycarbonate (PC) as the polymer matrix. PC is a Nanocomposites were pr sistant thermoplastic polymer with very good mechanical properties high-performance and heat and dimensional stability ven at high temperatures. PC nanocomposites with various nanofiller loadings were q ried out through the solution mixing technique. The thermal conductivity mposites prepared with pristine and oxidized BNNTs are plotted in figure measuremen nanc ment realized without BNNTs confirmed the expected thermal conductivity 4(a). A 23 W/m.K [56]. The reference material was chosen as the pure PC loaded with of PC modified BNNTs (black data points in figure 4(a)). The thermal conductivity of the PC-BNNTs ur

panocomposites was found to increase linearly with the BNNT content with a maximum through-

plane value $\lambda_{\perp} = 0.87$ W/m.K and in-plane value $\lambda_{//} = 1.08$ W/m.K at 15% vol. cont This corresponds to more than a four-fold increase compared to the pristine polymer, stown that BNNTs are very efficient nanofillers for increasing the heat dissipation capacity of the vmer. Regarding oxidized BNNTs, the thermal conductivity values measured on PC_NNT-OX[[HNO₃] and PC-BNNT-OH *[NaOH]* nanocomposites are clearly worsened. These results obtained with OH|[NaOH]) are fully consistent with the recent report of Zandieh et al. [37]. In this study, the authors found similar results on the thermal conductivity on Perspective filled with pristine BNNTs and BNNTs oxidized with excess bromine in water, which is equally considered as a harsh oxidizer. Interestingly, the BNNTs treated with our proposal based on the NHPI catalytic oxidation did not alter the thermal conductivity of th C nano or posite (blue data points in figure 4(a)), they even slightly improved the in-plane thermal conductivity with a value of $\lambda_{l/l} = 1.19$ W/mK at 15% vol. content. At high filler loadings, the in-plane thermal conductivity of PC-BNNT-OH|[NHPI] was clearly higher than the one of PC-BNNTs (figure 4(b)), suggesting a better phonon diffusion throughout the whole is no composite. The difference between through-plane and in-plane thermal conductivity results observed in figure 4(a-b) can be ascribed to a partial alignment of the BNN s perpendicularly to the pressing direction during the disk-shaping process, favoring a phonon rans, ort in the in-plane direction [57–59]. SEM images and EDX mappings of PC and PC nanocomposites filled with BNNT-OH fillers are presented fracture surfa of p e EDX mapping images suggest a better dispersion of hydroxylated BNNTs b) T in figure S3 within he PC natrix compared to pristine BNNTs which tend to form large agglomerates (figure (a)). However, no significant difference was observed regarding the quality of the filler/matrix S1 interface in the different samples with BNNT-OH as nanofillers (figure S3(b)). The lower thermal

HNO₃, conductivity recorded for nanocomposites using BNNTs oxidized under harsh conditions NaOH, Br₂/H₂O) can thus be ascribed to the creation of large defects inside the BNN is su cture (figure 4(c)), as observed in figure 2 and figure S1. As surface hydroxylation implies the avage of several B-N bonds, the damaging of the h-BN lattice certainly induces similarity of the nanomaterial properties, thus amplifying the phonon-defect scattering which result in a decrease of the overall thermal conductivity. The results obtained with ETNTS acated under mild conditions (BNNT-OH [NHPI]), suggest a controlled oxidation rate, with less defects (figure 4(d)). The phonon-defect scattering is therefore minimized and the mermal conductivity of the nanocomposite not significantly altered. Electrical resignity was also measured on the different nanocomposites. No significant change was observed with respect to the pure PC (figure 4(e)). It that are wide band gap insulators. This is consistent with the expected properties BNNT confirms the high potential of these nanofillers to far icate nanocomposites being both thermally conductive and electrically insulating.



Figure 4. (a) In-plane and through-plane thermal conductivities of PC nanocomposites with pristine and oxidized BNATE, (b) m-plane and through-plane thermal conductivities of PC-BNNTS vs PC-BNNT-OH*UNHPI*. Schematic representation of oxidized BNNTs (c) under harsh and (d) under mild oxidizing contations. (e) Electrical resistivity of PC nanocomposites filled with pristine and oxidized BNNTs.

4. CONCLUSION

In summary, three oxidation routes of pristine BNNTs have been tested luding severe oxidation protocols (concentrated HNO₃ and concentrated NaOH) and a pew ild ox reaction. To our knowledge, the catalytic air oxidation of BNNTs is reported. rein for the first time. All the oxidized BNNTs were characterized by a set of techniques demonstrating unambiguously the presence of hydroxyl groups on their surface Ŀ Intrast to the severely oxidized BNNTs, those oxidized by the NHPI route have largely reasoned their structural integrity. The oxidized BNNTs were used as nanofillers for the fabrication of nanocomposites with a PC gradation of the thermal conductivity matrix. Though severely oxidized BNNTs resulted in the h. 1. oxidized BNNTs allowed a five-fold of PC nanocomposites compared to the pristine on s, r improvement of the thermal conductivity at h vol. content. Functionalization of the mildly ported protocol appears as a promising way to further oxidized BNNT prepared according increase the dispersion within the matrix, without damaging the integrity of the nanotubes, and thus to enhance the performances the nanocomposites.

ASSOCIATED CONTENT

Supporting Information

Figure S1: High-resolution SEM images of pristine BNNTs and BNNT-OH.

Figure S2: TGA curves of pristine and oxidized BNNTs.

Figure S3(a): SEM images and EDX mappings of fracture surfaces of the nocomposites for assessment of BNNTs dispersion.

Figure S3(b): SEM images of fracture surfaces of PC procomposites for assessment of filler/matrix interface quality.

NOTE

The authors declare no competing financial in erea

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DATA AVAILALUTY STATEMENT

The data that support the findings of this study are available upon reasonable request from the

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