Fabrication and Characterization of Eco-Friendly Non-Isocyanate Polyurethane Nanocomposites for Electromagnetic Shielding by Absorption

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***Abstract* — This study presents a novel approach to use nonisocyanate polyurethanes (NIPU) as a host matrix for carbon nanotubes (CNT) to fabricate CNT-NIPU nanocomposites for electromagnetic shielding applications. The NIPU was formed using trimethylolpropane tricarbonate (TMPTC) and m-xylylene-diamine (XDA). Different compositions (0.1% and 0.2%) of CNT were incorporated into the NIPU matrix. The CNT-NIPU nanocomposites were successfully prepared by mixing and curing and then characterized using a vector network analyzer (VNA) at room temperature. The nanocomposites' reflection coefficient (R) and shielding effectiveness (SE) against electromagnetic interferences (EMI) were measured in the 26.5 – 40 GHz frequency range. It was found that a 0.2% CNT sample had an SE of 20 dB/cm and a maximum absorption of 90 %. Increasing the CNT content from 0.1% to 0.2% significantly enhanced the SE and absorption.**

***Keywords*—non-isocyanate polyurethane, carbon nanotubes, electromagnetic shielding, eco-friendly, microwave absorption.**

I. INTRODUCTION

Electromagnetic interference can cause malfunctions in our everyday devices, which contain electronic components sensitive to electromagnetic radiation. The EMI can affect a wide range of applications such as medical, automotive, wireless communications, and aerospace. Therefore, shielding against EMI has become a widespread challenge for twenty years [1]. Metals have the best shielding capabilities, but their low corrosion resistance, high cost, and heavy weight are disadvantages [2]. Therefore, conductive polymer composites have emerged as alternative materials due to their low cost, versatility, and light weight [3].

Carbon nanotubes are promising inclusions for microwave absorbers because of their superior electrical properties, relatively low density, and high specific surface area, which are used in multifunctional composite materials [4]. The CNTs have been incorporated into a wide range of matrices, to enhance the EMI shielding performance, such as polyethylene (PE) [5], poly(vinylidene fluoride) (PVDF) [6], poly(lactic acid)/ polycaprolactone [7], carbonized melamine [8], poly (butyleneadipate-coterephthalate) [9], polylactide acid/polystyrene [10], and acrylonitrile–butadienestyrene [11].

Polyurethane (PU) is a common polymer with good tensile, flexibility, and mechanical properties [12]. The PU foam is used in a wide range of applications such as fibers, high-efficiency coatings, insulators, and advanced controllers. It is also considered as an attractive material for the EMI SE applications [13]. Different types of fillers were incorporated into the PU matrix, to enhance the shielding performance, such as chemically reduced graphene (CRG), thermally reduced/annealed graphene (TRG) [14], nickel-coated carbon fiber, and CNT [15]. Traditional PU is commonly obtained from polyols, polyisocyanates, and chain extenders. However, the main starting materials (isocyanates), used in the process, raise severe health hazard concerns [16]. Therefore, NIPU materials have attracted great attention, compared to the traditional PU, because they are considered ecofriendly and nontoxic in nature. Since NIPU does not proceed through toxic isocyanates, this procedure can be considered safe for the environment and humans, thus, it gained fame as green PU [17].

Several studies have recently focused on the synthesis and usage of NIPU for coating [18] and foam materials [19]. Other studies investigated embedding the CNT into a hybrid NIPU matrix for coating applications [20]. However, limited research has explored the usage of CNT-NIPU coating for microwave absorption applications such as the study conducted by Doley at el. in the 8.2 – 12.4 GHz frequency range [21]. They used the polyaddition route in the NIPU preparation which is considered the eco-friendliest path [22] but their process involves several steps and the use of solvents. We aim to fabricate CNT-NIPU nanocomposites using the same route, but with a simpler and solvent-free method. This also enables us to produce thicker CNT-NIPU samples that can be used in a wide range of EM shielding applications.

Cyclic carbonates are easily produced by the transformation of CO_2 with epoxides [23]. These heterocycles have found an utility as monomers in the preparation of isocyanate-free polyurethanes by polyaddition with amines. Over the last decade, these NIPUs have been used in the fabrication of coatings and adhesives, (self-blowing) foams or biomaterials. Herein, we extend the scope of utilization of NIPU to EMI shielding applications. NIPU thermosets have been synthesized from a trifunctional cyclic carbonate (trimethylolpropane tricarbonate, TMPTC) and *m-*

xylylenediamine hardener (XDA), under controlled heat conditions.

The incorporation of XDA can endow the composites with an expanded conjugation structure that significantly enhances the thermal stabilities and mechanical properties [24]. The XDA was used as a curing agent to prepare cellulose nanofibers and Ti_3C_2Tx Mxenes [25] and nitrogen-doped graphene aerogels [26] for EMI shielding applications.

The novelty of this study is fabricating thick and solid structural CNT-NIPU nanocomposites which can be used in a wide range of microwave absorbing applications, using an eco-friendly process. The scattering parameters (S_{11} and S_{21}) of CNT-NIPU composites are measured using a VNA in the 26.5 – 40 GHz frequency range. The impact of increasing the CNT content in the composites on EMI shielding and absorption is also presented.

II. Materials and Methods

A. Materials

In this study, three materials were used to fabricate the nonisocyanate polyurethane composites: multiwall carbon nanotubes (CNT) in pre-dispersed form, m-xylylenediamine (XDA), and trimethylolpropane tricarbonate (TMPTC). EPOCYL^{TM} 128-05 multiwall carbon nanotubes dispersion (2 wt%) in an epoxy matrix (2 wt%) was provided by Nanocyl SA company (Belgium). The XDA with a molecular weight of 136.19 g/mol was provided by Merck company. The trimethylolpropane tricarbonate (TMPTC) was synthesized from CO_2 and trimethylolpropane triglycidyl ether in a high-pressure vessel, following a previously described procedure [27, 28].

B. Fabrication of CNT-NIPU samples

TMPTC (21.7 g) and XDA (9.3 g) were mixed in a 7/3 weight proportion. The mixture was homogenized, then the appropriate amount of Epocyl (1.55 g or 3.1 g) was added to the mixture for reaching the expected CNT content in the final material, i.e. 0.1 and 0.2 wt%. The mixture was then transferred to a rectangular silicon mold (8.4 cm × 4 cm) and first left to cure for 1 day at room temperature and then 1 day at 80°C in an oven. The rigid samples were finally demolded.

The samples were polished using a Bernardo (KF50) drilling machine and sandpaper to obtain a flat and smooth surface on both sides for higher accuracy measurements. The two samples shared the same surface area of 8.4 cm × 4.0 cm, but the thicknesses T of 0.1% CNT and 0.2% CNT samples were 5.12 mm and 4.57 mm, respectively.

C. EM Characterizations

The measurement of the reflection coefficient (S_{11}) and transmission coefficient (S_{21}) was conducted using a rectangular waveguide connected to an Anritsu VNA (model MS4644B) in the 26.5 – 40 GHz frequency range. A prior standard short-open-load-through (SOLT) calibration method for 201 points, was performed. Then, the material under test (MUT) was inserted between the two WR28 adapters as presented in Fig. 1, according to the method described in [29]. The measurements were conducted at room temperature (22.5 °C). The following equations were used to calculate the shielding effectiveness (SE) and absorption (A), and reflection coefficient (R):

$$SE\ (dB) = -\ 20\ Log_{10}\ (S_{21}) \quad (1)$$

$$A = 1 - S_{11}^2 - S_{21}^2 \quad (2)$$

$$R\ (dB) = 20\ Log_{10}\ (S_{11}) \quad (3)$$

As the two samples do not have the same thickness, for the sake of exact comparison, the SE and A results were plotted for the same 0.457 mm thickness corresponding to the sample of 0.2 % concentration. Therefore, the A and SE of the 0.1% CNT sample were recalculated using the following formulas:

$$A_{0.1\%}\ recalculated = A_{0.1\%} \times \frac{0.457}{0.512} \quad (4)$$

$$SE_{0.1\%}\ recalculated = SE_{0.1\%} \times \frac{0.457}{0.512} \quad (5)$$

The results of the 0.2% CNT sample were not recalculated since they already correspond to the 0.457 mm thickness.

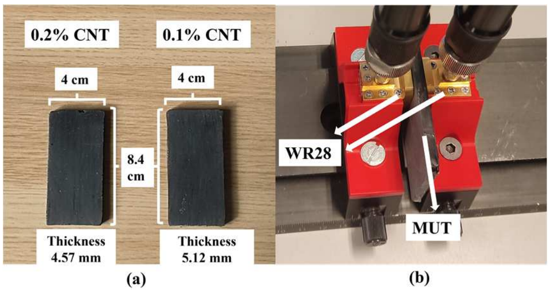

Fig. 1. Measurement setup and samples; a: CNT- NIPU nanocomposites; b: MUT inserted between WR28 adapters.

III. RESULTS AND DISCUSSIONS

The R, SE, and A of CNT-NIPU are presented in Figs. 2, 3, and 4, respectively. The results of SE and absorption are presented for the same thickness of 4.57 mm as explained in Section II.C. The noise observed in the SE curves is attributed to artifacts during the calibration. As expected, increasing the content in conductive CNT loads caused an increase in the SE and absorption A. The 0.2% CNT sample absorbs more microwave signal compared to the 0.1% CNT sample due to the increment in conductivity. The absorption A shows a level close to 90 %, for a 0.2% CNT concentration. The EMI SE and A performance can thus be significantly enhanced by increasing the CNT content. In this work, the EMI shielding is achieved by an absorption mechanism whereby electric dipoles in the samples interact with the EM signals [30].

The structures of TMPTC and XDA are classified as insulating (non-conductive) materials. On the other hand, CNT filler is a highly conductive material [31], making it ideal to absorb EM waves. Incorporating the conductive CNT with the insulating XDA and TMPTC resulted in the Maxwell-Wagner-Sillars effect (interfacial polarization). This polarization type is associated with the accumulation of polarized charges arising from the difference in the permittivities and conductivities of the constituents [32]. This mechanism is responsible for the good absorption of the 0.2 % CNT sample. The absorption peaks in 29 GHz and 35.5 GHz, presented in Fig. 4, are associated with R minima shown in Fig. 2. This behavior is expected since higher absorption restricts the EM signal from reflecting to the source, leading to higher reflection coefficient.

The sample with 0.2% CNT can achieve an SE exceeding 20 dB, which is the target value for commercial applications, with a thickness of 1 cm (i.e. roughly twice the thickness considered in Figs. 3 and 4) [33].

Table 1 shows that the SE of our 0.2% CNT sample is greatly superior to previously reported CNT-based composites based on β factor. The β factor takes into consideration the sample thickness and filler percentage as follows:

$$\beta = \frac{\frac{SE\,(dB)}{Thickness\,(mm)}}{CNT\%} = \frac{SSE(^{dB}/_{mm})}{CNT\%} \tag{6}$$

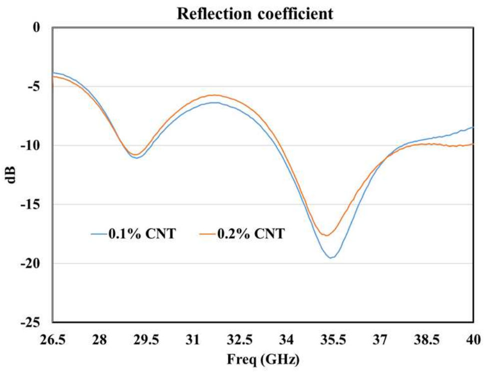

Fig. 2. Reflection coefficient of CNT- NIPU composites.

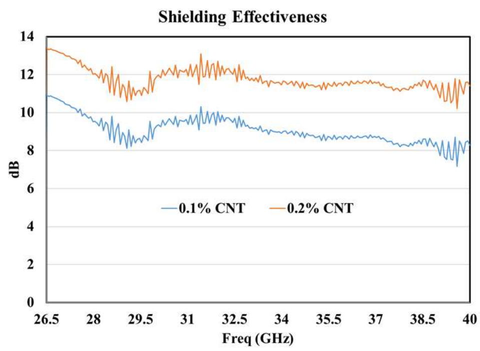

Fig. 3. SE of CNT- NIPU composites for a thickness of 4.57 mm.

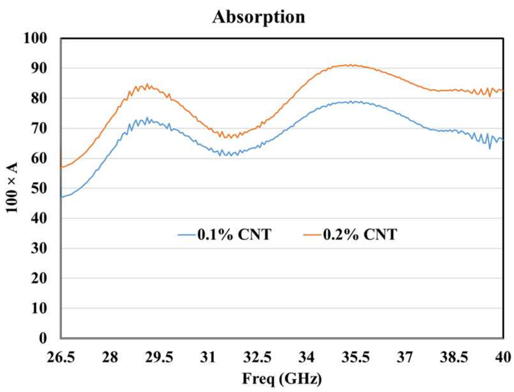

Fig. 4. Absorption A of NIPU composites for a thickness of 4.57 mm.

Table 1: The SE and β of different CNT-based composites at 26.5 GHz.

Material	**CNT %**	**SE (dB)**	**T (mm)**	**SSE (dB/mm)**	**β**	**Ref.**
PU-CNT	10	20	1.4	14.3	1.4	[34]
PVDF-CNTs	10	27	1.8	15	1.5	[35]
PE/PVDF/CNTs/Fe_3O_4	10	30	1.4	21.4	2.1	[36]
PMI*CNT-9/Ag	9	45	8	5.6	0.6	[37]
CNT-NIPU	0.2	13.4	4.57	2.9	14.7	This study

*: Polymethacrylimide.

IV. Conclusion

In this work, novel eco-friendly CNT-NIPU nanocomposites were successfully fabricated for electromagnetic shielding applications. The scattering parameters of 2 samples with different CNT concentrations were characterized at room temperature using a VNA in waveguide configuration in the 26.5 – 40 GHz frequency range. The 0.2% CNT sample achieved the target 20 dB SE level needed for commercial applications with a reduced thickness of 10 mm. In the future, the EM behavior of the samples can be investigated in the 6 GHz - 110 GHz frequency range. Investigating the mechanical properties of CNT-NIPU samples with different percentages of XDA and CNT is also recommended to co-optimize the mechanical and microwave absorption performances.

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