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EROSION-RESISTANT NANOCOATING DERIVED FROM POLYPROPYLENE AND BAMBOO-BASED BIO NANO CARBON (PP-BNC) TO ENHANCE ENERGY EFFICIENCY OF PETROLEUM PIPELINES

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ABSTRACT

Oil and gas transportation efficiency is hindered by petroleum pipeline erosion where the pipelines are exposed to solid particles, viscous fluids, processing temperature and pressure, surrounding conditions and accompanied gasses. The current issue is to solve the erosion of petroleum pipelines problem by developing an erosion-resistant nanocoating. The development of erosion resistant nanocoating which is derived from polypropylene and bamboo-based bio nano carbon (PP-BNC) is the main focus of this research. PP-BNC nanocomposite were prepared by using thermal composition method to obtain the bamboo BNC or also known as carbon black, followed by coagulation method to obtain PP-BNC nanocomposites (10 wt%, 20 wt%, 30 wt%, 40 wt% and 50 wt%) and lastly compression moulding method for the nanocomposite to become nanocoating thin film. During the thermal composition method, the grinded bamboo powder were combusted in tube furnace at 400°C, holding time for 30 minutes at 10°C/min rate in Nitrogen atmosphere. The solvents that were used are Toluene and Methanol during coagulation method. The structural, thermal and morphological properties of PP-BNC nanocomposites were characterised by Differential Scanning Calorimetry (DSC), X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). Whereas the mechanical properties such as tensile and abrasion resistance along with its weight loss were evaluated by tensile and abrasion resistance tests. PP with 20 wt% BNC has the best results as the weight loss and wear index are the lowest which is 0.001 g and 0.033 mg/cycles respectively, great tensile strength with the value of 20.52 MPa and able to withstand high temperature up to 163°C where the highest temperature underwater is only up to 100°C.

Keywords: *bamboo, polypropylene, bio nano carbon, carbon black, nanocomposite, thin film, tensile, abrasion, wear index.*

INTRODUCTION

Nanocoating is a nanoscale thin film that is derived from nanocomposites which will be applied to surface in order to improve a material's functionality. As illustrated in Figure 1, the nanocomposite is a combination of two or more different materials which makes it stronger than the individual materials alone with the grain size of 1 nm to 100 nm. Basically, nanocomposite material is the combination of fiber and matrix where fiber is to provide strength and stiffness while the matrix is

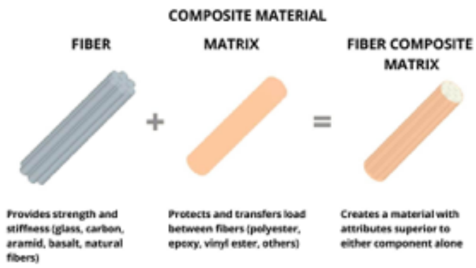

Figure 1 Composite material composition
Source: https://www. engineeringchoice.com/composite-

to protect and transfers load between fibers. In this research, the fiber will be bamboo-based bio-nano carbon (BNC) and the matrix will be polypropylene (PP). When the two materials are combined together, it will become PP-BNC.

As mentioned previously, the fiber is bamboo-based BNC which will act as the nanofiller. The bamboo that will be used is from Gigantochloa Ligulata species or its malay name is Buluh Tumpat. Bamboo is used due to its lightweight, flexible, tough, high tensile properties and it is cheap as compared to steel.

Meanwhile, the matrix is PP. PP is a type of thermoplastic polymer with propylene as its monomer. Thermoplastic is a type of plastic that can be moulded under heat. PP has a low density among commodity plastics which is between 0.895 g/cm^3 to 0.92 g/cm^3 [1]. PP also has high melting point, 160°C, good chemical and heat resistance, tough, flexible, high durability and light weight. Besides that, one of PP mechanical properties is its Young's Modulus value between 1300 N/mm^2 to 1800 N/mm^2 [2].

Next, the nanocoating that will be produced will be erosion resistant. Erosion and corrosion have a small difference from each other. In distinguishing erosion and corrosion, erosion is a physical phenomenon that involves the movement of tiny fragments of rocks or dirt as a result of natural forces such as gravity, wind, water and other natural agents, while corrosion is a chemical process that causes things to corrode such as oxidation which leads to rust. In this research, the nanocoating will be focusing to enhance the wearability of the petroleum pipelines. The causes of pipelines erosion are material of pipelines (current material used is epoxy resin [3], or fusion-bonded-epoxy (FBE) [4]), the acidity of the water (average ocean pH = 8.1, alkaline), temperature (as high as up to 100°C [5], but typically 21 – 38°C [6]), flowrate (2000 – 9200 m^3/day [7]) and pressure (51 – 720 psi [8]) of fluid flowing through pipelines and lastly, the exposure to solid particles such as sand, rock and dirt. As mention previously, the selected material is PP because PP has low density, low hardness, high erosion rate and efficiency [9] as compared to TPU [10], but when combined with certain ratio of bamboo-based BNC, it will enhance its mechanical properties due to its high tensile strength.

Solid particle erosion caused by the repeated impact of small particles on a surface is a typical wear mode involving progressive loss of materials. It is an important issue in oil industries because their pipes are often exposed to aggressive erosive environments. To improve their wearability and add on high strength, abrasion resistance and modulus properties nanocarbon synthesised from bamboo can be used as nanofiller.

Problem Statement

Erosion is a common cause of deterioration in petroleum pipeline systems that are exposed to solid particles, viscous fluids, processing temperature, and accompanying gasses such as air, methane, mixed gas and oil-gas. A small number of solid particles may cause significant erosion since the pipelines will be exposed to the solid particles daily as the fluid flowing through come from a natural source that has solid particles. The solid particles may have a fine grain size that is difficult to separate or filter first. Thus, solid particles cause the erosion of pipelines. Besides that, the viscous fluids flowing through which has the difference in temperature with the surrounding temperature also one of the causes of erosion pipelines. The temperature of the fluids inside the pipelines is normally high. The average temperature is around 21°C to 38°C [6]. However, it could also go up to 100°C [5] as compared to the surrounding temperature, from -20°C to 15°C [11] and the seabed maintained at around 5°C [5] because of the location of the pipelines is usually located under seawater.

This research aims to develop an erosion-resistant nanocoating derived from polypropylene and bamboo-based bio nano carbon, which has been a major concern in oil industries due to its steady nature. Developing nanocoating would help overcome the problem of certain eroded parts of petroleum pipelines instead of replacing the whole pipeline. The material's functionality and wearability to coat the pipelines' surface are important in order to transport oil and energy efficiently without any loss as oil and gas is limited, and every drop is precious since oil and gas is predicted to be depleted in the future.

Scope of Study

This research aims to produce an erosion-resistant nanocoating for petroleum pipelines. The current concern is that the ideal material for pipelines has yet to be developed as the pipelines surface will need to be replaced after some time as it is exposed to solid particles and fluids flowing through every day, leading to erosion. In addition, replacing the pipelines is not an easy process since the pipelines are located deep underwater and it would take up some cost for the materials and the service charges.

In this research, the materials that will be used are PP and bamboo as the nanocomposite and Toluene and Methanol as the solvents to dissolve PP and BNC during sample preparation. Bamboo as nanofiller will enhance PP's functionality in terms of tensile and erosion resistant due to its unique natural composite structure of fibers. The proposed methods are ultrasonication, thermal decomposition method or also known as carbonisation process to obtain carbon black for BNC, coagulation method to produce PP-BNC nanocomposite, which is a common technique used by researchers [1],[10] and compression moulding method to transform nanocomposite into nanocoating which is similar to hot pressing method [10]. There is an alternative technique which is igneous high-speed melting stretching [12] and two stir casting technique [13] to prepare the nanocomposites, but these techniques consist of long steps and require a lot of heat respectively.

The materials and methods proposed are not only green but also practical and accessible because it uses common materials, short methodology and is energy efficient. Therefore, this research hopes to find a way to contribute and implement in the future, even in a minor yet crucial part of petroleum refineries, by producing nanocoatings to place on the surface of the pipelines instead of replacing the whole pipeline.

Figure 2 PP beads

Figure 3 Bamboo Tumpat, Gigantochloa Ligulata

METHODOLOGY

Materials and Reagents

The main materials used in this research are Polypropylene (PP) and bamboo-based Bio Nano Carbon (BNC). PP beads (2~3 mm) was purchased from Kimbee Farm as shown in Figure 2 while the bamboo Tumpat, Gigantochloa Ligulata was from Hulu Langat, Selangor as shown in Figure 3. The bamboo-based BNC will be prepared from scratch through the thermal decomposition method, while the PP-BNC nanocomposite will be prepared by using the coagulation method and hot pressing. The solvents that will be used include Toluene and Methanol.

Sample Preparation

The samples were prepared by ultrasonication, thermal decomposition (carbonisation), coagulation, and compression moulding.

Preparation of Bamboo BNC (Carbonisation)

Bamboo BNC will be prepared using thermal decomposition method. First, the bamboo will be cut into small segments and dried in oven at temperature 100°C for 48 hours to remove any moisture. Next, the dried bamboo strips will be granulated and sieved to a mesh size of 150. Then, the bamboo granulates will be combusted in a tube furnace that is supplied with inert gas flow until it becomes carbon black or BNC with the carbonisation parameter at 400°C, holding time for 30 minutes at the rate of 10°C/min in a Nitrogen atmosphere.

Preparation of PP-BNC Nanocomposite

PP-BNC nanocomposite was prepared using coagulation method and compression moulding method. First, the 0.2 g of bamboo BNC was mixed with 50 mL Toluene and the mixture was ultrasonicated for 30 minutes to disperse the BNC particles homogenously. Next, 0.8 g of PP was fully dissolved in 50 mL Toluene separately using a hot plate at 140°C for 40 minutes. Then, the two solutions were left to stir on a hot plate for 24 hours without heat. The solution must be kept stirred all the time to avoid the PP from hardening and becoming a white solid and ensure that the PP and BNC are well mixed, so the sample outcome has a smooth surface. After that, the mixed solution was ultrasonicated for 30 minutes. 50 mL Methanol was added to the solution stirred on a hot plate at 30°C to obtain the flocculate of PP-BNC nanocomposite. The flocculate will be filtered and dried for 5 hours at 80°C under vacuum.

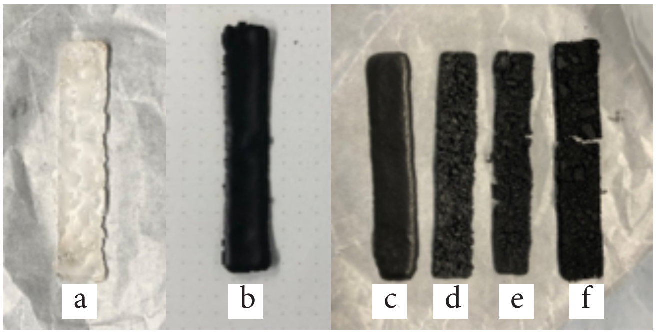

Figure 4 Nanocoating of (a) pure PP, (b) PP-BNC 10 wt%, (c) PP-BNC 20 wt%, (d) PP-BNC 30 wt%, (e) PP-BNC 40 wt% and (f) PP-BNC 50 wt%

Fabrication of PP-BNC Nanocoating

The flocculate was hand crushed by a mallet before undergo compression moulding. The flocculate was pre-heated for 1 minute under 0.8 tonne. Then, the flocculate was pressed into a 3 mm film at 190°C for 15 minutes under 20 tonnes and cooled afterwards for 20 minutes under 2 tonnes as demonstrated in Figure 4.

Microstructure Characterisation

DSC, XRD and SEM characterised PP-BNC nanocomposites' structural, thermal and morphological properties.

Differential Scanning Calorimetry (DSC)

The thermal behaviour and crystallinity of the PP-BNC nanocomposite were analysed by DSC instrument (Q2000 Version 24.11) with TA Universal Analysis software (Version 4.5A) under an inert nitrogen stream. About 5 mg of specimen was sealed in an aluminium pan and the DSC scans were recorded while heating from 30°C to 380°C at a heating rate of 10°C/min, hold for 5 minutes and cooled back to 30°C. The melting point of the PP-BNC nanocomposite can be determined by analysing the graph obtained.

X-Ray Diffraction (XRD)

X-ray diffractograms were collected with an PANalytical X'pert PRO (DY 2536) instrument using Ni-filtered CuKα1 radiation (λ = 0.1542 nm) at 45 kV and 40 mA. The intensities of the XRD patterns were recorded in the 2θ range of 4–40° with a scan rate of 2°/min.

Scanning Electron Microscopy (SEM)

For the morphology characterisation of the PP-BNC nanocoating, the surface of the PP-BNC nanocomposite will be observed before and after mechanical testing to inspect surfaces after the abrasion resistance test by Phenom ProX SEM instrument. All samples will be sputtered with a thin layer of gold for the samples to be conductive and to ensure clear imaging. The image of PP-BNC can be observed and analysed at the magnification of x100, x500, x800, x5000 with Phenom Pro Suite software.

Mechanical Properties Testing

The mechanical properties such as tensile strength and abrasion resistance with its weight loss and wear index are evaluated by tensile and abrasion resistance tests.

Tensile Testing

The tensile properties, including the tensile strength, were assessed with rectangular-shaped samples at a 5 mm/min loading speed by 5 kN Universal Testing Machine (UTM) (Shimadzu MSC-5/500, Japan). The specimens will be prepared in a mould with the dimension of 60 mm (L) x 10 mm (W) x 3 mm (T).

Abrasion Resistance Test

The abrasion resistance test or for short, abrasion test was conducted to test the wearability of PP-BNC and as a simulation for erosion but instead of natural agents such as sand, dirt and rocks, a Taber Rotary Abraser

(Model 5131) as shown in Figure 5 which consists of two 1000 g abrasive wheels and a rotating abrasive disc with a grit paper that has a rough surface which is quite similar to sandpaper was used. A small piece of PP-BNC nanocoating was placed on the rotating abrasive disc and tested for 30 cycles under a vacuum level of 50 Pa. The weight loss of PP-BNC that was exposed to a rotating abrasive disc was measured every ten cycles. The wear index can be calculated by using the following equation:

$$\text{Weight loss (g)} = \text{Weight Before Test} - \text{Weight After Test}$$

$$\text{Wear Index (mg)} = \frac{\text{Weight loss} \times 1000}{\text{no. of test cycles}}$$

RESULTS AND DISCUSSION

DSC Analysis

Figure 6 illustrates all PP-BNC nanocomposites (except PP-BNC 10 wt%) exhibit an endothermic peak with the same value of melting temperature, Tm of 163°C which is also the melting temperature for pure PP. PP-BNC 10 wt% DSC curve is not reported in this paper but expected to have the melting temperature in the range of 163°C. Although bamboo-based BNC was added to PP, the melting temperature is closer to pure PP's melting temperature rather than BNC's melting temperature which is approximately 3652°C according to the safety data sheet of activated carbon. This is because PP's melting temperature is much lower than BNC's melting temperature, therefore the PP will melt first, and the composition of the nanocomposite is dominated by PP.

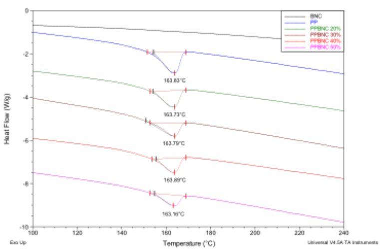

Figure 6 DSC curves of melting temperature of BNC, pure PP and PP-BNC (20 wt%, 30 wt%, 40 wt% and 50 wt%

Besides that, the peaks from PP to PPBNC 50% become less intense or more broad due to the increase in the amount of nanofiller, which showed that the nanocomposites shifted from crystalline to amorphous [14].

XRD Analysis

As illustrated in Figure 7, it showed that PP is crystalline, while BNC is amorphous. From PP-BNC 20 wt% to PP-BNC 50 wt%, it can be observed that the peaks shifted from crystalline to amorphous as the percentage of BNC increases. Similar results were reported by Adamu et al. [14]. When BNC is added to PP, PP-BNC 20 wt% showed the most intense peaks which indicate high crystallinity among all nanocomposites and as the percentage of BNC increases, no sharp peaks indicate low crystallinity of the nanocomposites due to the composition of nanocomposite is dominated by BNC which contributed to the factor of the brittle state of the nanocoating [15]-[17]. This is why the tensile test cannot be done on PP-BNC 40 wt% and PP-BNC 50 wt%. PP-BNC 50 wt% has the lowest crystallinity due to the least intense peak illustrated. (PP-BNC 10 wt% XRD peak is not reported in this paper).

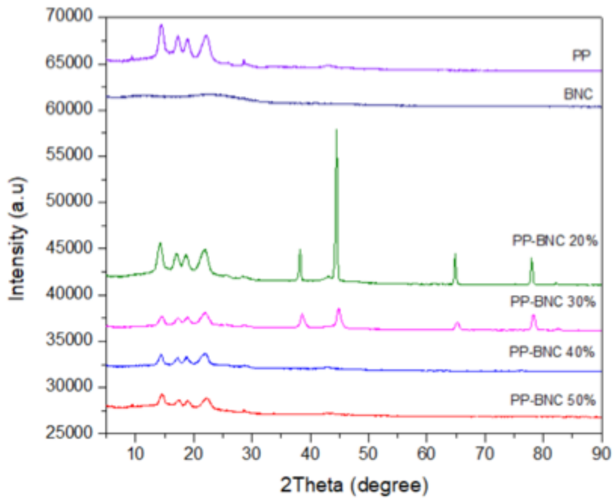

Figure 7 XRD graph of pure PP, BNC and PP-BNC (20 wt%, 30 wt%, 40 wt% and 50 wt%)

SEM Analysis

The SEM images obtained are taken before and after mechanical testing which is tensile test and abrasion resistance test (30 cycles). Figures 8a, 9a, 10a and 11a showed the SEM images before the mechanical testing for pure PP, PP-BNC 10 wt%, PP-BNC 20 wt% and PP-BNC 30 wt%, respectively. Figures 8b, 9b, 10 b and 11b displayed the SEM images after the mechanical testing for pure PP, PP-BNC 10 wt%, PP-BNC 20 wt% and PP-BNC 30 wt%, respectively. For pure PP, PP-BNC 10 wt% and PP-BNC 30 wt%, after mechanical testing, the surface of nanocoating is rough and has obvious scratched lines, which indicates worn or eroded surfaces from abrasion

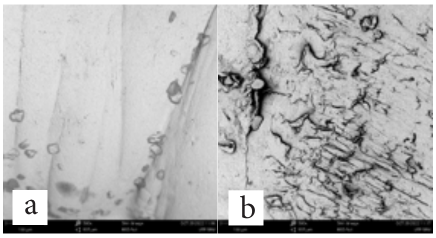

Figure 8 Pure PP nanocoating
(a) before and (b) after abrasion test

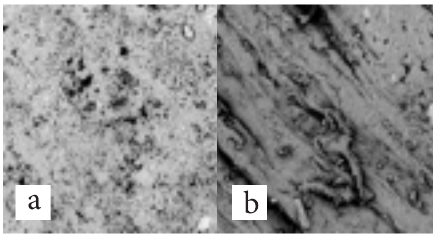

Figure 9 PP-BNC 10 wt% nanocoating
(a) before and (b) after abrasion test

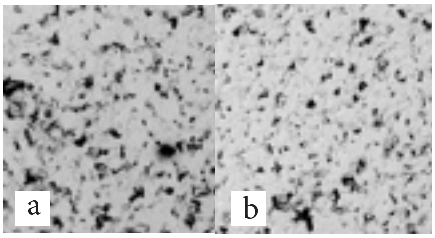

Figure 10 PP-BNC 20 wt% nanocoating
(a) before and (b) after abrasion test

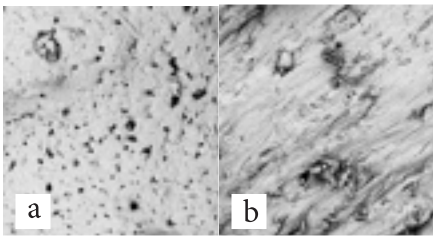

Figure 11 PP-BNC 30 wt% nanocoating
(a) before and (b) after abrasion test

resistance test. However, the surface of PP-BNC 20 wt% nanocoating after mechanical testing is smooth and remains the same as before mechanical testing. Therefore, PP-BNC 20 wt% nanocoating possessed high wear resistance and protection as compared to pure PP, PP-BNC 10 wt% and PP-BNC 30 wt%.

Tensile Test Analysis

After the compression moulding method, tensile test was done on the nanocoating. Based on Table 1 and Figure 12, pure PP has the highest tensile strength, followed by PP-BNC 20 wt%, PP-BNC 10 wt% and lastly, PP-BNC 30 wt% with the value of 20.52 MPa, 13.47 MPa, 12.58 MPa and 1.01 MPa respectively. The tensile test could not be done on PP-BNC 40 wt% and PP-BNC 50 wt% because the nanocoatings were too brittle that they broke before the tensile test could be done. From Table 1, it can be concluded that the thickness of nanocoating did not play an important role to the tensile strength but the percentage of PP. Although PP-BNC 30 wt% was thicker than PP-BNC 20 wt%, the tensile strength of PP-BNC 20 wt% was much greater than PP-BNC 20wt%. Tensile strength reached maximum value at a specific weight percentage [18]. After certain amount of nanofiller was added, the tensile strength will decrease due to bond weakness and nanofiller, BNC will face difficulty to penetrate the matrix material, PP [18]-[19]. As more BNC was added to PP, the tensile strength also decreased because there was a lesser binding agent, which is PP, to hold the atoms together. The BNC will place in between the PP atoms and disrupt the arrangement.

Table 1 Tensile test data

Sample	Length (mm)	Width (mm)	Thickness (mm)	Tensile Strength (MPa)
PP	60	10	3.00	20.52
PP-BNC 10 wt%	60	10	1.24	12.58
PP-BNC 20 wt%	60	10	1.28	13.47
PP-BNC 30 wt%	60	10	1.85	1.01

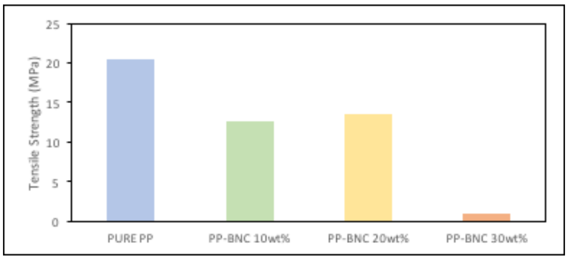

Figure 12 Tensile test graph

Abrasion Resistance Test Analysis

Although PP has the highest tensile strength, as mentioned previously, but after abrasion test was done based on Table 2, PP has the highest weight loss and wear index followed by PP-BNC 30 wt% and PP-BNC 10 wt% which indicates that PP nanocoating will be worn out fast and easily erode over time which defeats the objective of the research; to develop an erosion-resistant nanocoating. Whereas PP-BNC 20 wt% has the least total weight loss and lowest wear index, after the first 10 cycles, the weight remains the same with no further weight loss, making PP-BNC 20 wt% the most promising candidate for erosion-resistant nanocoating. Shahapurkar et al. reported that for fiber-reinforced composites, increasing the amount of nanofiller (BNC) will decrease the nanocomposites' erosion resistance due to the nanofiller's nonuniform distributionith the matrix [20]. Erosion-resistant nanocoating is not required to possess high tensile strength as the nanocoating will just cover the eroded part of petroleum pipeline where no load will be put on top of the nanocoating.

Table 2 Abrasion test data

Sample	Weight (g)				Total Weight Loss (g)	Wear Index (mg/cycles)
	Before Test After Test	After Test				
		10 cycles	20 cycles	30 cycles		
PP	0.430	0.429	0.427	0.425	0.005	0.167
PP-BNC 10 wt%	0.110	0.109	0.108	0.107	0.003	0.100
PP-BNC 20 wt%	0.115	0.114	0.114	0.114	0.001	0.033
PP-BNC 30 wt%	0.124	0.123	0.121	0.120	0.004	0.133

CONCLUSION AND RECOMMENDATION

Conclusion

In conclusion, PP-BNC nanocoating was fabricated via thermal decomposition, coagulation and compression moulding methods and the PP-BNC 20 wt% is the promising candidate for erosion-resistant nanocoating to enhance energy efficiency of petroleum pipelines. The combination of bamboo-based BNC and PP enhanced the mechanical properties such as tensile strength, resist towards erosion and high-temperature conditions which can be tested through tensile test and abrasion resistance test and characterised by DSC, XRD, SEM. However, the optimum percentage of BNC that can be added is only 20 wt%. If more than 20 wt% BNC is added to PP, it makes the nanocoating less crystalline (which can be determined from XRD analysis) and brittle instead of durable. Based on DSC results, PP-BNC nanocoating can withstand high temperature up to 163°C which should be completely fine for real-life applications as the highest temperature for petroleum pipelines underwater is 100°C. Besides that, PP-BNC 20 wt% is the potential erosion-resistant nanocoating because the morphology of the nanocoating remains the same after abrasion resistance test which was observed by SEM instrument. PP-BNC 20 wt% has the lowest weight loss and wear index, indicating that it is not easily eroded and can be worn long-term. By comparing PP-BNC 20 wt% and pure PP, PP-BNC 20 wt% is a more sustainable option as it reduces the usage of plastics as well as biowaste. Therefore, by implementing PP-BNC 20 wt% nanocoating, it hopes to contribute to the petroleum industry, although only for a minor part on petroleum pipelines but it is crucial as pipelines are the main component for oil and gas transportation.

Recommendations

Although the research objectives have been achieved, there is always room for improvement. For future work, among the parameters that can be modified is the percentage of BNC to PP by synthesising the nanocomposites with a percentage less than 20 wt% (5 wt% and 15 wt%). Besides that, adding different nanofillers when fabricating the nanocomposites could help improve the nanocoating's mechanical strength and wear resistance. For mechanical testing, salinity and boiling test could be done as a simulation to evaluate the ability of nanocoating to withstand high temperature and high pressure in conditions similar to petroleum pipelines environment such as seawater or crude oil. The surface of nanocoating will be observed for further analysis. Other than that, erosion test by using a sand blasting machine with different impact velocities and angles could be conducted as a simulation to evaluate the wear resistance. However, extensive research and a literature review need to be done to comprehend the subject matter to proceed with this research.

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