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EFFECT OF NANO-PRECIPITATED CALCIUM CARBONATE ON MECHANICAL PROPERTIES OF PVC-U AND PVC-U/ACRYLIC BLEND

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Abstract. Developing nanocomposites based upon polymers and nano-sized fillers has been an attractive approach to achieving good properties. Effects of nano-precipitated calcium carbonate (NPCC) on the mechanical properties of different ductile matrices were investigated. Unplasticised Poly(vinyl chloride) (PVC-U) and PVC-U/acrylic were used as the matrix in this study. To produce the composites, PVC resins, additives, acrylic and NPCC were first dry-blended using a laboratory high-speed mixer before being milled into sheets on a two-roll mill. Test specimens were then hot pressed, after that the mechanical properties and morphology of fracture surface of composites were determined. The flexural modulus and Young modulus of both the composites were enhanced after the addition of NPCC, but the tensile strength was decreased. The NPCC showed good toughening effect and stiffening effect on PVC-U/acrylic and PVC-U matrix, respectively. The flexural strength of both the composites was not significantly affected by the addition of NPCC. The impact strength of both the composites reached the maximum value when 15 phr NPCC was incorporated.

Keywords: Poly(vinyl chloride), nano-precipitated calcium carbonate, mechanical properties, acrylic

Abstrak. Perkembangan nanokomposit berasaskan polimer dan pengisi bersaiz nano telah menjadi pendekatan yang menarik untuk mencapai sifat komposit yang baik. Kesan nano-termendak kalsium karbonat (NPCC) terhadap sifat mekanikal matrik berlainan kemuluran telah dikaji. Poli(vinil klorida) tanpa pemplastik (PVC-U) dan PVC-U/akrilik telah digunakan sebagai matrik pada kajian ini. Untuk menghasilkan komposit, resin PVC, additif, akrilik dan NPCC pada mulanya diadun-kering menggunakan pencampur berkelajuan-tinggi berskala makmal sebelum diadun menjadi kepingan dengan menggunakan pengadun dua penggulíng. Spesimen-spesimen ujian kemudiannya ditekan panas, selepas itu sifat mekanikal komposit dan morfologi permukaan patah komposit ditentukan. Modulus lenturan dan modulus Young meningkat dengan penambahan NPCC, tetapi telah menurunkan kekuatan regangan. NPCC telah menunjukkan kesan pengukuhan yang baik pada matrik PVC-U/akrilik dan kesan kekakuan yang baik pada matrik PVC-U. Kekuatan lenturan kedua-dua komposit tidak dipengaruhi dengan penambahan NPCC. Kekuatan hentaman kedua-dua komposit telah mencapai nilai maksimum apabila 15 phr NPCC ditambah.

Kata kunci: Poli(vinil klorida), nano-termendak kalsium karbonat, sifat-sifat mekanikal, akrilik

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1.0 INTRODUCTION

Poly (vinyl chloride)(PVC) is a low cost commodity polymer that is used in a wide variety of applications, such as pipe, tube, conduit, fittings and a host of others. The ability of PVC to perform such diverse function is due to the ability of PVC to incorporate with various additives to suit the numerous applications [1]. However, PVC-U without impact modifier modification has the disadvantage of being prone to occasional brittleness and is notch sensitive. Impact modifier is therefore used to enhance the impact properties of PVC-U. Acrylic impact modifier is widely used in the PVC-U formulations as it gives consistently high toughness under a wide processing temperature and shear. This is so, because the dispersed rubber particles maintain their particle morphology in the continuous PVC-U phase [2].

Currently, nano-sized fillers have been an attractive approach to enhancing polymers properties. Composites materials based on nano-sized fillers, the so-called nanocomposites, presently studied especially because they may have unusual combinations of properties [3 – 6]. These unusual properties may be a consequence of extremely large specific interfacial area (hundred of m^2/g) [3]. Various nano-sized fillers, including montmorillonite [4], silica [5] and calcium carbonates [6], were reported to be able to greatly increase strength, modulus and toughness. It is generally believed that the main factor affecting toughening and reinforcing effects on thermoplastics-rigid inorganic blends are particles geometry (size, shape and content), dispersive state of fillers in the matrix, the interfacial structure and adhesion, and processing condition [7].

Nano-calcium carbonate (nano-$CaCO_3$) is one of the most common nano-sized fillers used in preparation of nanocomposites. There are two general classes of $CaCO_3$, the ground natural $CaCO_3$ and the synthetic or precipitated $CaCO_3$. The ground natural $CaCO_3$ are generally larger in size and have a much broader particles size distribution than the precipitated $CaCO_3$. All the $CaCO_3$ were surface treated with a fatty acid. Since the fatty acid reacts with the $CaCO_3$ to form a calcium soap on the surface, the resultant filler becomes hydrophobic and easier to disperse in the PVC. This results in substantially improved the impact strength in the filled PVC [7].

In recent years, nanocomposites based on PVC have attracted much attention. PVC/montmorillonite [4], and PVC/clay [8] nanocomposites have been studied. The effect on nano-$CaCO_3$ on mechanical properties on PVC and PVC/Blendex (butadiene-styrene-acrylonitrile copolymer) has also been studied, but few publications concerning the effect of nano-precipitated $CaCO_3$ (NPCC) on the mechanical properties of PVC-U or PVC-U blends have been reported. A study on PVC/nano-$CaCO_3$ and PVC/Blendex/nano-$CaCO_3$ composites revealed that the nano-$CaCO_3$ had a much better toughening effect on PVC/Blendex matrix than that on PVC matrix. The yield strength and elongation at break of pure PVC were increased by the addition of nano-$CaCO_3$, while those PVC/Blendex blend were decreased. The flexural modulus and Vicat softening temperature of PVC and PVC/Blendex blend were increased simultaneously by the presence of nano-$CaCO_3$ [6].

In this paper, the morphology and mechanical properties of PVC-U/NPCC nanocomposites were studied. To evaluate the modification effects of NPCC on different ductile polymer matrix, the PVC-U/acrylic blend were used for comparison.

2.0 MATERIALS AND METHODS

2.1 Materials

Suspension PVC resin used in this study with solution viscosity K-value 66 and trade name MH-66 was produced by Industrial Resin Malaysia (IRM) Sdn.Bhd.Tampoi, Johor, Malaysia. Its specifications are summarized in Table 1. The additives used in the PVC formulations were kindly supplied by IRM Sdn. Bhd. Kureha Chemical Ltd (Singapore) supplied core and shell acrylic impact modifier with a trade name of Paraloid KM355P. It consists of poly (methyl methacrylate) as a shell while poly (butyl acrylate) acts a core. Surface modified NPCC used in this study was supplied by NanoMaterials Technology Pte. Ltd (Singapore). Its specifications are shown in Table 2.

Table 1 Specifications of PVC Suspension Resin MH-66

Specifications	**Resin MH-66**
Appearance	White powder
Degree of polymerization	1000 ± 50
K-value	66
Specific gravity	1.4
Bulk density (g/cm^3)	0.50 ± 0.05
Volatile matter (max) (%)	0.5
Foreign matter (grain/100 g)	15
Particle size (retained on 250 μ) (max)(%)	0.3

Table 2 Specifications of NPCC-200

Specifications	**NPCC-200**
Appearance	White powder
Specific gravity	2.5 – 2.6
Particle size (average), nm	<40
Surface area, m^2/gm	>45
Whiteness %	>95
Particle shape	Cubic
pH	8.5 – 9.5
Water content % (wt)	<0.5
$CaCO_3$ % (wt) (surface modified)	94.5
MgO % (wt)	<0.5
Al_2O_3 + Fe_2O_3 % (wt)	<0.3
SiO_2 % (wt)	<0.3

2.2 Sample Preparation

PVC 100 part per hundred resin (phr), tin stabilizer 2 phr, calcium stearate 0.5 phr, stearic acid 0.6 phr, acrylic processing aid 1.5 phr, titanium dioxide 4 phr were dry blended in a laboratory high-speed mixer for 10 min to give the PVC-U compound [8]. The PVC-U compound and NPCC were melt mixed and sheeted with a two roll mill at 165°C for 10 min to give PVC-U/NPCC binary composites [9]. The NPCC content in the composites was varied from 5 to 20 phr. The PVC compound, NPCC and acrylic impact modifier 9 phr [8] were mixed in the same way to give PVC-U/acrylic/NPCC ternary composites. The composites prepared were molded into sheets of 1 mm in thickness for tensile test specimens and 3 mm in thickness for impact and flexural test specimens by compression molding at 190°C and 1.2 kPa for 5 min. The mold was cooled for 5 min before being removed from the mold cavities.

2.3 Mechanical Tests

Izod impact strength assessment was carried out on notched samples with dimensions of $62.5 \times 13 \times 3$ mm^3 at room temperature using an Izod impact tester from Lotus Scientific Malaysia (LS-22005), according to ASTM D256-88. The specimens were notched with a notch cutting apparatus. The notch depth was fixed at 2.6 ± 0.02 mm with angle 45°. Notched samples were tested at a hammer velocity and mass of 2.8 m/s and 2.79 kg, respectively. The swing angle used was 125°.

Tensile tests were performed at room temperature using the Universal Testing Machine (Instron 5567), according to ASTM D638-82. The samples were tested at a crosshead speed of 20 mm/min and a gauge length of 50 mm. Tensile strength and Young modulus were measured.

Flexural tests were also performed at room temperature using the Universal Testing Machine (Instron 5567), according to ASTM D790. The samples with dimensions of $125 \times 13 \times 3$ mm^3 were tested at crosshead speed of 3 mm/min. The support span for the flexural test was 51 mm. Flexural strength and modulus were measured. All the reported values for the impact, tensile and flexural tests were the means of ten specimens.

2.4 Scanning Electron Microscopy

Studies of the nanocomposite impact-fractured surfaces were performed with a JOEL Model JSM-5600 LV Scanning Electron Microscope (SEM). A small portion of sample was mounted on the copper stub and sputter-coated with a thin layer of gold to avoid electrostatic charging during examination.

3.0 RESULTS AND DISCUSSION

3.1 Notched Impact Strength

The impact strengths of PVC-U/NPCC binary composites and PVC-U/acrylic/NPCC ternary composites are presented in Figure 1. It can be seen that the ternary composites exhibits much better impact performance than binary composites. As reported in our previous paper [8], the acrylic has an ability to compensate the detrimental effect caused by the filler with lowering the yield stress of PVC-U matrix by allowing shear yielding rather than fracture when subjected to the sudden load. As a result, the ability of PVC-ternary composites to absorb energy during facture propagation is increased. Figures 2(a) to 2(d) clearly shows that fracture surfaces changed from rough (Figures 2(a) and 2(c) to smooth (Figures 2(b) and 2(d)) with the addition of 9 phr acrylic. In other words, the failure mode became more ductile.

Figure 1 also shows that the impact strength of PVC-U/NPPC binary composites reaches the maximum value of 32 kJ/m^2 when 15 phr NPCC incorporated, about 52% higher than that of pure PVC-U (21 kJ/m^2), while the higher impact strength of PVC-U/acrylic/NPCC ternary composites is 109 kJ/m^2, which is about 17% higher than that of PVC-U/acrylic blend (93 kJ/m^2). The decrease of both the composites impact strength after the maximum at 15 phr is due to the toughening effect decreases as the interaction between the fillers are closer to each other. This result is in agreement with the result

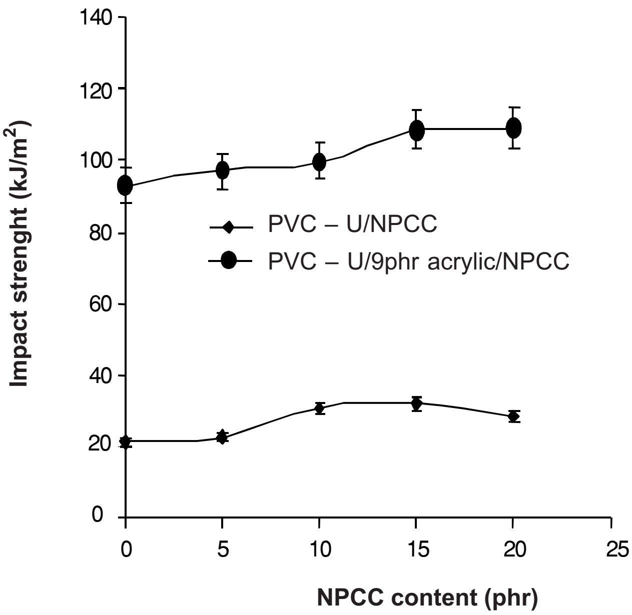

Figure 1 Effect of NPCC content on the impact strength of PVC-U/NPCC binary and PVC-U/acrylic/NPCC ternary composites

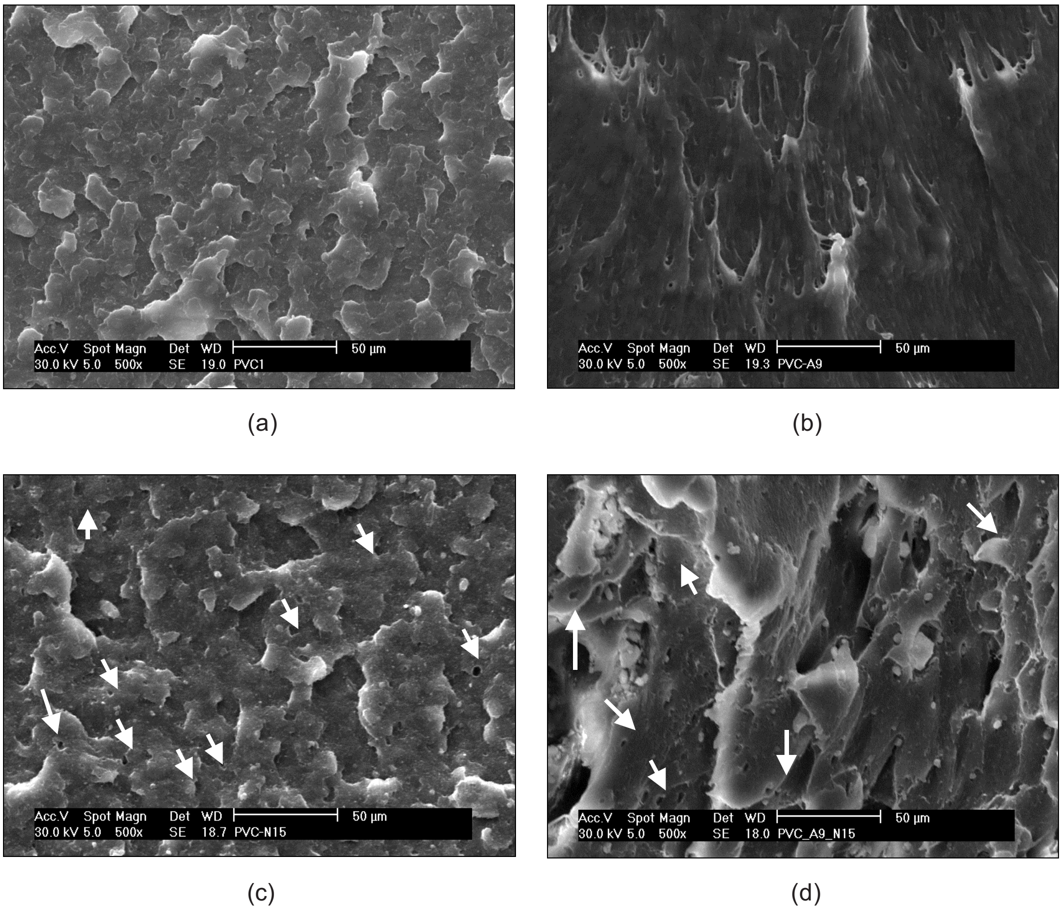

Figure 2 SEM micrographs of impact-fractured surface of (a) PVC-U, (b) PVC-U/9phr acrylic blend, (c) PVC-U/15 phr NPCC binary composite, (d) PVC-U/9 phr acrylic/15 phr NPCC ternary composite

obtained by other researchers working on NPCC [9]. Liang [10] reported that this interaction leads to the decrease of the compressive stress undergone by the matrix around the fillers and then the material becomes damaged in the brittle region. Therefore, the toughening effect decreases when the filler content increases up to a certain extent which is dependent on the types and sizes of filler. As seen in Figure 1, the impact strength results also suggest a much better toughening effect of NPCC on PVC-U/acrylic matrix than that on PVC-U matrix.

SEM micrographs of the impact-fractured surfaces of the composites are shown in Figure 2. As seen in Figures 2(c) and 2(d) cavities (indicated by arrows) can be found on the fracture surface of the composites, some of which are occupied by NPCC particles. Chen [6] also found cavitations on the fracture surface of PVC/nano-$CaCO_3$ composites. These cavities are much larger than the NPCC particles, suggesting cavitation happens during the samples being impacted. Since no cavity is observed on the fracture surface of PVC-U compound and PVC/acrylic blend, as shown in Figures 2(a) and 2(b), the presence of NPCC particles must be responsible for the cavitations. This cavitation could absorb large amount of energy, leading to the improvement of the composites impact strength. The cavitation toughening mechanism takes place when the stress applied exceeds the interfacial adhesion strength between rigid inorganic filler (NPCC) and polymer matrix (PVC-U), debonding at the interface will occur first, leading to the formation of micro-voids [10]. In this case, the deformation restraint of the matrix around the filler is released, resulting in the production of elastic deformation and absorbing energy and the promotion of the brittle-ductile transition. Although the cavitation phenomenon dissipates some energy, this amount remains relatively low compared to what impact modifiers are able to absorb.

3.2 Flexural Properties

Figures 3 and 4 represent the flexural modulus and flexural strength of PVC-U/NPCC binary composites and PVC-U/acrylic/NPCC ternary composites, respectively. The flexural properties of ternary composites are lower compared to that of binary composites. This is due to the softening effect generated by acrylic rubbery phase, which increased the energy absorption, lowered the modulus and strength of PVC-U matrix [8]. Figure 3 shows that the tensile modulus of both composites increases as the

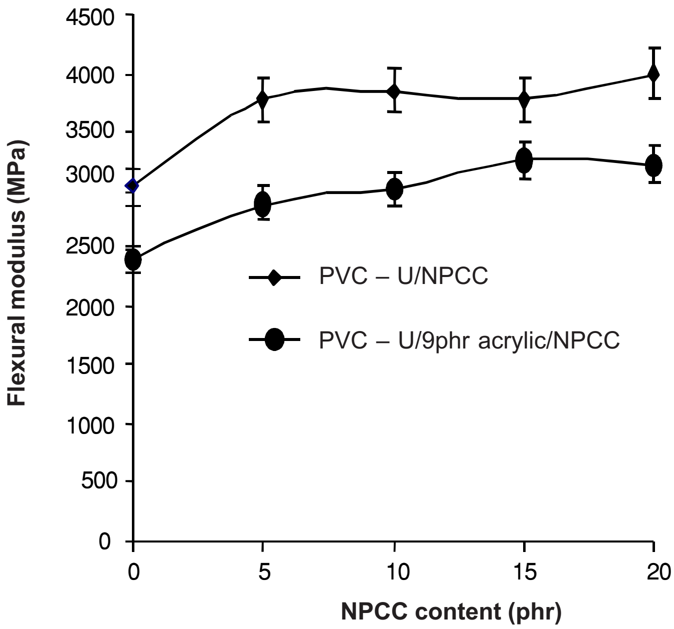

Figure 3 Effect of NPCC content on the flexural modulus of PVC-U/NPCC binary and PVC-U/acrylic/NPCC ternary composites

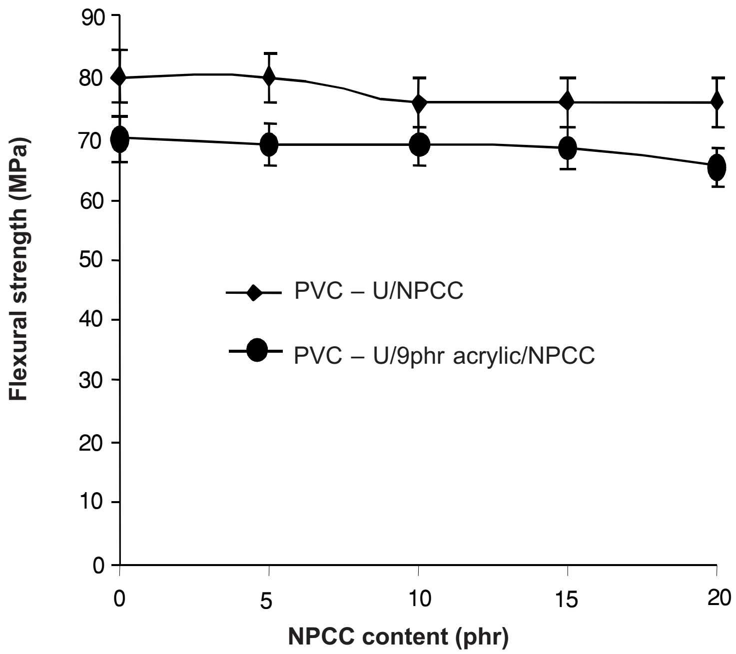

Figure 4 Effect of NPCC content on the flexural strength of PVC-U/NPCC binary and PVC-U/acrylic/NPCC ternary composites

NPCC content increased from 0 to 20 phr. The increment of binary composites flexural modulus is about 31.5% higher than that of pure PVC-U while for ternary composites is about 30% higher than that of PVC-U/acrylic blend. The increase of flexural modulus probably indicates that the rigid NPCC, which is cubic in shape, able to restrict in the mobility of the PVC molecules which resulted in the resistance to elastic deformation of the both composites increases with increasing NPCC content. The increase of flexural modulus also indicates that there is an interaction or interfacial adhesion between NPCC and matrix in both composites. Factors such as the surface modified NPCC as stated in Table 2, the well dispersed in the PVC-U matrix as shown in Figure 2(d), and the finer-sized filler may be contributed to the increase of matrix-filler interfacial adhesion. Liang [10] reported that the use of smaller-sized rigid inorganic particulate, such as $CaCO_3$, in the polymer can improve the interfacial adhesion between the matrix and filler because these fillers have less surface defect and able to disperse in the matrix. Similar result is also found by other researchers who studied the mechanical properties of PP/nano-$CaCO_3$ nanocomposites [11].

Figure 4 shows that the flexural strength of binary composites and ternary composites remains relatively constant when the NPCC content increased from 10 to 20 phr and from 0 to 15 phr, respectively. This result indicates that the flexural strength of both composites have no significant effect with increasing NPCC content. It means that even though NPCC has a lower aspect ratio, the obtainable of interfacial adhesion may be allowed for NPCC to sustain the flexural stress transmitted from the matrix and thus maintained the flexural strength of both composites. Usually, the interfacial adhesion is divided into three types, namely poor adhesion, some adhesion and strong adhesion [10]. Based on the flexural modulus, flexural strength and also impact strength results, therefore, the interfacial adhesion of binary and ternary composites may be fallen into the some adhesion type, which is the interfacial adhesion is between poor and good. It means that the interfacial layer of these composites can transfer a small section of the stress when the deformation of the matrix is very small, and then debonding between the matrix and the filler will be produced with increasing the deformation.

3.3 Tensile Properties

Figures 5 and 6 represent the Young modulus and tensile strength of PVC-U/NPCC binary composites and PVC-U/acrylic/NPCC ternary composites, respectively. Figure 5 shows that the Young modulus of ternary composites increases with increasing NPCC content while the binary composites significantly increases when the NPPC content increased from 10 to 20 phr. The increment of Young modulus of binary composites from 10 to 20 phr is about 10% higher than that of pure PVC-U while for ternary

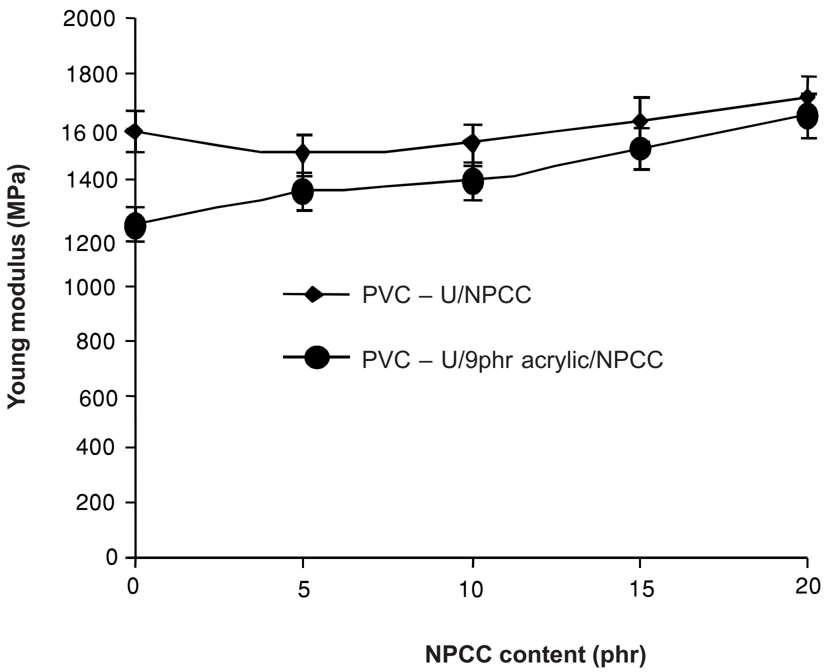

Figure 5 Effect of NPCC content on the tensile modulus of PVC-U/NPCC binary and PVC-U/acrylic/NPCC ternary composites

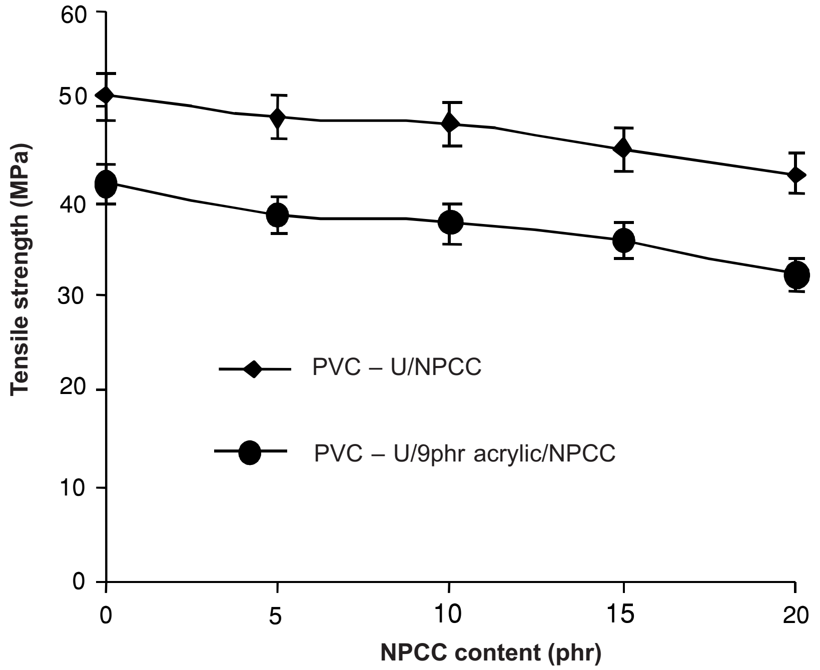

Figure 6 Effect of NPCC content on the tensile strength of PVC-U/NPCC binary and PVC-U/acrylic/NPCC ternary composites

composites from 0 to 20 phr is about 38% higher than that of PVC-U/acrylic blend. This indicates that the addition of NPCC in the binary composites (10 to 20 phr) and the ternary composites (0 to 20 phr) also leads to increase in Young modulus due to the rigidity of NPCC and other reasons as mentioned earlier in flexural modulus section. Similar result also reported by other researchers who studied the tensile modulus of PVC/$CaCO_3$ composite [12]. Figure 6 shows that the tensile strength of both composites decreases as the NPCC content increased from 0 to 20 phr. The decrement of tensile strength of the binary composites is about 15% while for the ternary composites is about 27%. The decrease of tensile strength is due to the weakness of interfacial adhesion between PVC matrix and NPCC. This resulted in the NPCC inability to support the stresses transferred from the matrix.

4.0 CONCLUSIONS

NPCC had much better toughening effect on PVC-U/ acrylic than that on PVC-U matrix. On the other hand, NPCC had shown better stiffening effect on PVC-U matrix. The flexural modulus and Young modulus of both the composites increased with increasing NPCC content, while the flexural strength and tensile strength were remained relatively constant and decreased, respectively. The impact strength of binary and ternary composite increased up to 15 phr NPCC. The flexural modulus, Young modulus and tensile strength of binary composites were higher than ternary composites whereas the impact strength of ternary composites was higher than binary composites.

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