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# The Effect of Synthesis Parameter On HKUST-1 Nanocomposites Studied by FTIR Characterisation and Mechanical Testing

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**ABSTRACT**

In the present work, Hong Kong University of Science and Technology (HKUST-1) has been synthesised at room temperature with 1:0, 1:1 and 0:1 ratio of ethanol and water and reinforced into polyurethane. In order to understand the impact of synthesis parameters on HKUST-1 nanocomposites, an investigation was conducted using FTIR characterisation and mechanical testing. The objective was to examine the potential improvement of the reinforced polymer. The mechanical testing results were shown to be significantly influenced by the presence of HKUST-1 with 1:0 ratio of ethanol and water (sample A) into polyurethane (PU). The samples underwent Fourier Transform Infrared Spectroscopy (FTIR) analysis to determine the types of bonds within the polymer-MOF nanocomposites. It was observed that the reinforced nanoparticles did not undergo any chemical changes, as indicated by the recorded spectra, which can be related to the overlapping characteristics of HKUST-1 and PU. The findings indicate that the A/PU exhibited a notable impact in comparison to other materials, as evidenced by the results of the tensile test and nanoindentation study.

**Keywords:** *FTIR, HKUST-1, Nanoindentation, Physicochemical characteristics, Tensile testing*

## 1. INTRODUCTION

Polymer composites have emerged as hybrid materials with superior properties compared to their individual components, offering a high strength-to-weight ratio that makes them ideal for structural applications. Their resistance to corrosion and wear ensures durability in harsh environments, while excellent thermal and electrical conductivities enhance their suitability for electronic and thermal management applications. With ongoing research aimed at improving the dispersion and alignment of nanomaterials within polymer matrices, the integration of advanced materials like metal-organic frameworks (MOFs) presents an exciting avenue. Researchers are now exploring the potential of MOFs, traditionally used as catalysts and adsorbents for gas filtration, to reinforce polymer composites and enhance their mechanical performance [1-2].

Metal-Organic Frameworks (MOFs) are highly porous crystalline materials with sponge-like structures. They have the ability to capture, retain, and disperse various gases effectively. Their structures consist of metal ions and organic molecules known as "linkers," as represented in Figure 1. The advantageous characteristics, specifically selectivity and capacity, can be modified by carefully choosing the suitable metal and linker for the MOF [3-4].

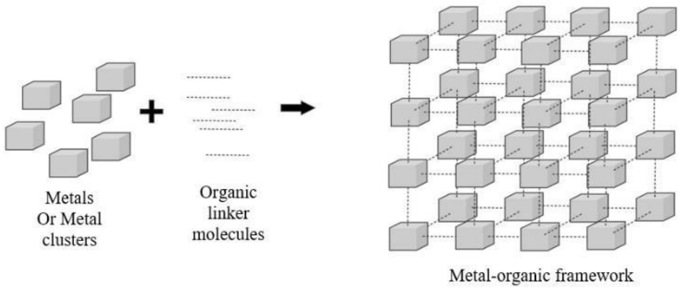



**Figure 1.** Schematic structure of MOFs.

MOFs are coordination compounds consisting of metal ions bound to organic molecules, which are often stiff, resulting in the formation of one-, two-, or three-dimensional structures that possess porosity [5-6]. These metals have diverse geometries in their metallic coordination settings, as observed. The formation of coordination bonds between metal ions and organic linkers can also be reversible, facilitated by the inherent instability of metal complexes.

HKUST-1, with the chemical formula $Cu_3(BTC)_2(H_2O)$, is widely regarded as one of the most promising MOFs [7-8]. Due to the strong attraction between its metallic group and $NH_3$ and $CO_2$ molecules, HKUST-1 has the ability to effectively eliminate hazardous gases, such as ammonia and carbon dioxide, from polluted air and flue gases. HKUST-1 possesses the ability to selectively isolate carbon dioxide from various gases like hydrogen, methane, nitrogen, and oxygen. Furthermore, it can effectively cleanse these gases and mitigate the release of greenhouse gases. The HKUST-1 has favourable adsorption properties as a result of this separation process [9].

As previously mentioned, MOFs' intrinsic crystalline and brittle nature makes them suitable for fabricating MOF/polymer composites. Several methods can be used to fabricate MOF into polymers. The nano hybridisation technique involves encapsulating polymer chains within controlled and modifiable nanoparticles, enabling them to exhibit enhanced performance in polymer composites compared to bulk-state MOF entanglement. Nevertheless, the application of this approach on an industrial scale is hindered by its inherent complexity. Solution casting is a commonly employed fabrication technique in various industries. The MOF particles are initially dispersed in the solvent using either stirring or sonication. They are combined with the polymer solution to create the final MOF/polymer solution. Subsequently, the solution is heated to a specified temperature to eliminate any leftover solvent effectively. The solution casting approach is employed in this work due to its ability to avoid elevated temperatures, which may impede alterations in the features of MOFs. Consequently, with the fabrication of composites consisting of metal-organic frameworks (MOFs) and polymers at different scales, it becomes feasible to fulfil the requirements of diverse characteristics and applications [10].

Thus, this is a vital approach to determine the impact of varying solvent ratios on the properties of the synthesized HKUST-1 nanocomposite, whereby less effort has been carried out in the past concerning these issues. The material characterization of the synthesized HKUST-1, which has been discussed our in that HKUST-1 synthesized using a solvent ratio of 1:0 (ethanol: water), had noteworthy significance in material characterization [11]. Therefore, this will result in the definitive choice of HKUST-1 produced using varying proportions of solvents.

## 2. MATERIAL AND METHODS

### 2.1. Synthesis of HKSUT-1 with Difference Solvent Ratio

Firstly, 1 g of Cu $(NO_3)_2.3H_2O$, 1.5 g of sodium bicarbonate, and 1g of 1,3,5-benzene tricarboxylic acid was added in a solution of distilled water and stirred for 24 hours at room temperature (~25°C). The solution will turn turbid, indicating HKUST-1 particle formation. To purify the product, ethanol is then introduced, and the mixture is centrifuged. The resulting precipitate is re-dispersed in tetrahydrofuran for storage. This washing process is repeated using both a 1:1 water-ethanol mixture and water alone for the HKUST-1 synthesis.[12]. Table 1 shows the summarised parameter of synthesised HKUST-1.

**Table 1** Summarised synthesis parameter of synthesized HKUST-1

| Sample | MOF | Parameters | |
|---|---|---|---|
| A | HKUST-1 | Solvent ratio (Ethanol: Water) | 1:0 |
| B | | | 1:1 |
| C | | | 0:1 |

### 2.2. Fabrication of Nanocomposites

Nanocomposites were fabricated using the solution casting method. A polyurethane (PU) polymer solution was prepared by dissolving approximately 1 g of Poly [4,4'- methylenebis (phenyl isocyanate)-alt-1,4-butanediol/di (propylene glycol)/polycaprolactone] beads in tetrahydrofuran (THF), allowing the solution to sit for 24– 48 hours until the beads were fully dissolved, as visually confirmed. The previously synthesised HKUST-1 nanoparticles, dispersed as colloidal particles, were then added to the PU solution, following the weight percentage equation provided below.:

$$\text{MOFs wt.\%} = \frac{m(MOFs)}{(m(MOFs) + m(PU))} \times 100\% \quad (1)$$

Here, m(MOFs) refers to the mass of the HKUST-1 nanoparticles dispersed in THF, while m(PU) denotes the mass of the PU beads dissolved in THF. This method results in the preparation of three distinct nanocomposite solutions, each containing 30 wt.% of synthesized HKUST-1 nanoparticles, using ethanol-to-water ratios of 1:0, 1:1, and 0:1, respectively. Song et al. demonstrated that this colloidal mixing approach can significantly minimize the risk of nanoparticle agglomeration, a common issue in nanocomposites formed by re-dispersing dried HKUST-1 nanoparticles [13]. After 24 hours of drying, the nanocomposites were detached from the glass mold by submerging them in water and stored for further analysis.

### 2.3. Chemical Bonds of MOF-Reinforced Polymer Nanocomposites

The Fourier-transform infrared spectroscopy (FTIR) instrument was utilised to determine the types of bonds within the polymer-MOF nanocomposites. Test samples will be sectioned (~5 $mm^2$) from larger specimens and analysed in the FTIR apparatus. The FTIR spectra consist of vibration peaks representing specific types of bonds. Due to the speculation that the organic ligands within the MOF nanoparticles form weak interactions with the polymer matrix (PU), vibrational peaks representing both constituents are expected to appear in the spectra.

### 2.4. Mechanical Testing (Tensile Testing and Nanoindentation)

The (quantitative) quasi-static properties of the polymer-MOF nanocomposites can be determined via the tensile test. The stress-strain ("σ-ε)" plots of the polymer-MOF nanocomposites will be generated using data collected from the Instron universal testing machine (UTM) equipped with a 100-N load cell (ASTM D882). The samples with the geometry of specimen of 100mm x 15mm will be clamped to the rig and subjected to a tensile load applied at a displacement rate of ~10 mm/min until sample failure.

A nanoindenter with a Berkovich three-sided pyramid diamond tip was used to conduct nanoindentation studies to evaluate Young's modulus (E)as in Equation (2) and indentation hardness (H). A rectangular grid of 20 indentations was produced for each probed sample (three films were tested per wt.%). A 100N load cell on an Instron universal testing machine measured stress–strain curves. The test coupons had a gauge length of 30 mm and a width of 5 mm. Tensile loads applied at 0.5 millimetres per second were applied to the clamped samples until the sample was fractured. The obtained load-displacement data were turned into nominal stress-strain plots using the samples' initial cross-sectional area and gauge length.

$$\frac{1}{E_r} + \frac{(1-\nu_s^2)}{E_s} + \frac{(1-\nu_i)^2)}{E_i} \quad (2)$$

Where ν is the Poisson's ratio (i = indenter, s = sample). For diamond indenters, E = 1141 GPa and ν = 0.07. Therefore, if the Poisson's ratio of the sample is known, then the reduced modulus can be converted to Young's Modulus.

## 3. RESULT AND DISCUSSION

The study examines HKUST-1 nanocomposites, a partnership between the famous metal-organic framework HKUST-1 and other materials, under different synthesis conditions. An investigation of the effects of these synthesis factors using FTIR characterisation and mechanical tests, including tensile and nanoindentation. This study investigates how synthesis parameters affect these nanocomposites. FTIR analysis and mechanical testing, specifically tensile testing and nanoindentation, to illuminate nanocomposites' significant changes in features and mechanical behaviour.

### 3.1. Material Characterization

Typically, interpreting FTIR spectra starts at the high- frequency end to identify the functional groups present, and the pattern regions are then studied to identify the compound positively. The compatibility between filler and matrix has become an essential factor that must be clarified. Therefore, we performed a series of FT-IR analyses on each filler, matrix, and composite for characterisation. Figure 2 shows the FT-IR spectrums of neat PU, HKUST-1, and HKUST-1/PU composites. For FT-IR spectrum HKUST-1, the absorption band at 3323 $cm^{-1}$ corresponds to N-H stretching, and the absorption band at 1734 $cm^{-1}$ is associated with C=O stretching, corresponding to the PU in the previous study [14]. Interestingly, all spectra recorded almost similar patterns of HKUST-1/PU composite, whereas it attributed to the overlapping characteristic of HKUST-1 and PU.

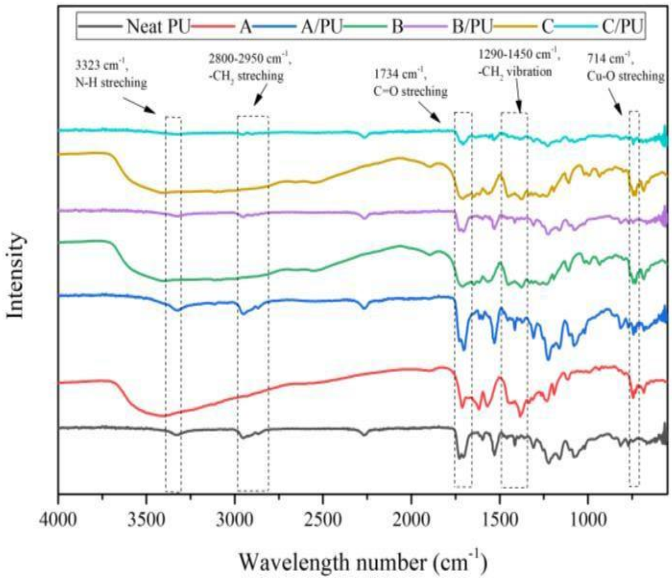



**Figure 2.** FTIR spectra of Neat PU, HKUST-1 and HKUST-1/PU.

### 3.2. Mechanical Testing (Tensile Test and Nanoindentation Analysis)

Stress-strain curves are a significant graphical measure of materials' mechanical properties. The curves will provide a preliminary overview of the material's mechanical proportions, including ductility, fracture energy, ultimate tensile strength, yield strength, and many more. Fixed particle loading of MOFs at 30% makes it easier for the polymer chain to form uniformity in the observation, and the stress-strain curve is valid. Thus, the stress-strain curves of the composite, with different synthesis parameters (solvent ratios), measured under static loading rates of ~10 mm/min, are summarised in Figure 3.

From the recorded data in Figure 3, A/PU showed the highest flow stress increment value than B/PU and C/PU. This phenomenon attributed to sample A enhances the composite molecular structure. The justification of the crystal structure's influence on the composite's molecular structure can be generated through the observation using SEM analysis so that the arrangement of the crystal structure can be.

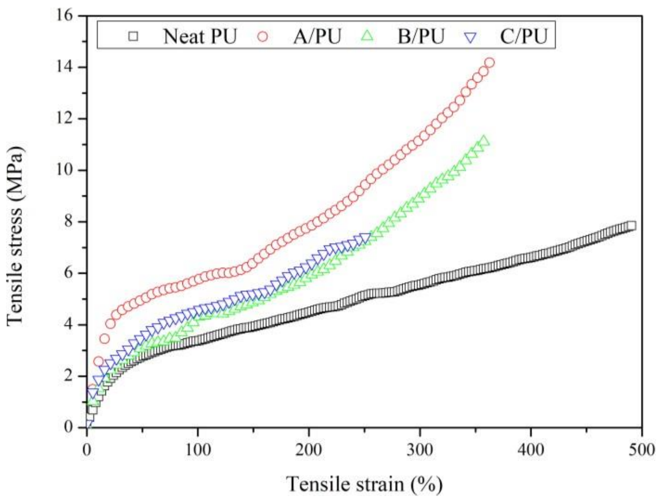
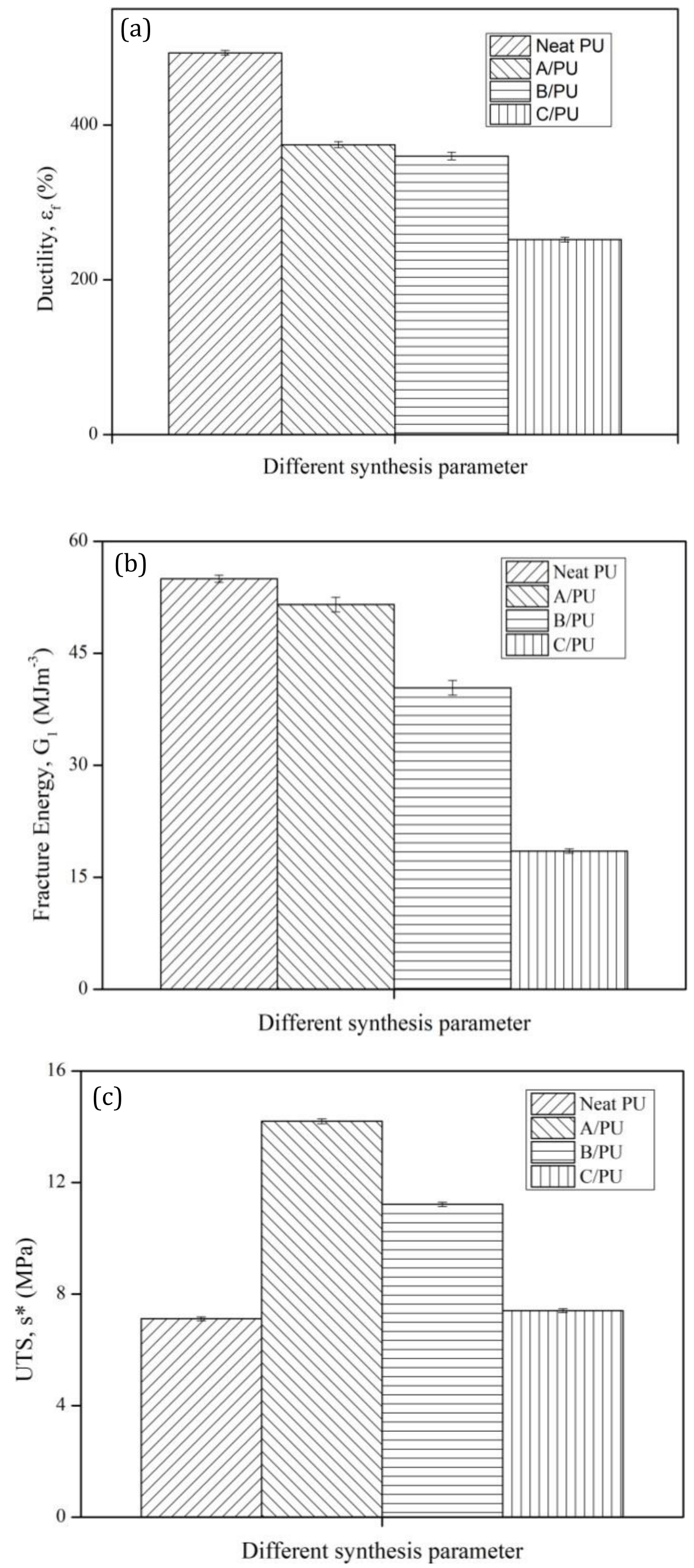



**Figure 3.** Effect of tensile strength on different synthesis parameters of HKUST-1/PU.

In Figure 4, the mechanical properties of HKUST-1/PU nanocomposite derived from the stress-strain plots (Figure 3), with (a) ductility (ef), (b) fracture energy (Gf), (c) ultimate tensile strength (σ*), and (d) yield strength (σy). The average results obtained from three test coupons and the respective standard deviations for each sample are displayed on the error bars.

From the ductility point of view (ductility and fracture energy) in Figure 4, it can be seen that sample A/PU recorded the highest values, which are 374.67 % and 51.54 $MJm^{-3}$. These results are closely related to the structure appearance of synthesised MOFs.



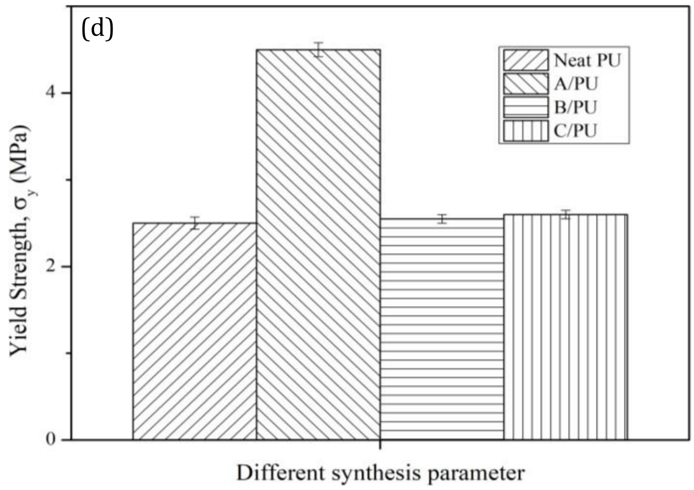



**Figure 4.** The mechanical properties of HKUST-1/PU nanocomposite derived from the stress-strain plots (Figure 3), with (a) ductility ($e_f$), (b) fracture energy ($G_f$), (c) ultimate tensile strength ($\sigma^*$), and (d) yield strength ($\sigma_y$). The calculated values averaged from three test coupons and the corresponding standard deviations for each sample on the error bars.

It is believed that synthesised MOFs with aligned octahedral and cubic structures in sample A/PU enhance PU chain movement during tensile loading [15]. This result is in line with the one that has been reported by Mansouri and his colleagues [15]. They speculated that the particles' shape is an essential factor in improving the resistance of composite materials toward deformation from triangular to circular shapes.[15].

From the strength perspective, it is interesting that HKUST- 1 reinforced PU significantly correlates yield strength and ultimate tensile strength. It can be seen that the filler strengthening mechanism is significantly related to both synthesised MOFs' structure and size. Sample A/PU with octahedral structures promotes the locking effect resulting in free-volume polymeric chains that are not free to deform, thus giving better strength properties. Mahdi and Tan have reported a similar finding with their ZIF-reinforced PU matrix.

Subsequently, nanoindentation calculates the small scale of forces applied to the sample. Nanohardness and indenter modulus are two distinct mechanical properties determined through nanoindentation testing, a technique used to evaluate the mechanical properties of materials at the nanoscale. The relation of nanohardness and indenter modulus provides information about the material's response to indentation. Nanohardness provides information about the material's ability to resist plastic deformation, making it useful for assessing wear resistance, material strength, and susceptibility to deformation. Meanwhile, indenter modulus offers insights into the material's elastic behaviour, helping characterise its stiffness, compliance, and deformation under load. Figure 5 shows the recorded data for the nanoindentation of HKUST- 1/PU, and it can be seen that the increasing in the value of nanohardness from neat PU to HKUST-1/PU. The highest value of A/PU, 21.61 GPa, compared to B/PU and C/PU.

Consequently, the theoretical thought of the particle size and crystal structure may affect the hardness of the sample [15]. Sample B/PU and C/PU tend to agglomerate during fabrication, and synthesising with ethanol can minimize defects and impurities in the MOF structure. Thus, can lead to improve MOF performance and purity [16]. Gabriele and his colleague stated that a defect site might introduce plastic deformation and a possible disordered layer stacking sequence, thus decreasing their rigidity properties [17] [18].

Meanwhile, Figure 6 shows the calculated Young's modulus of the nanoindentation testing. The recorded data shows that A/PU has a higher value of 91.91 MPa, which means that the particle size and dispersion of the particles affect the fabrication of the composite so that it can harden the composite well [19]. The mechanical qualities of composites has improved by the presence and interaction of both interpenetrating networks and bonding sites, called physical pinning and chemical bonding, simultaneously [19]. Hence, A/PU has enhanced the nanocomposites' mechanical stability while introducing accessible porosity and active sites.

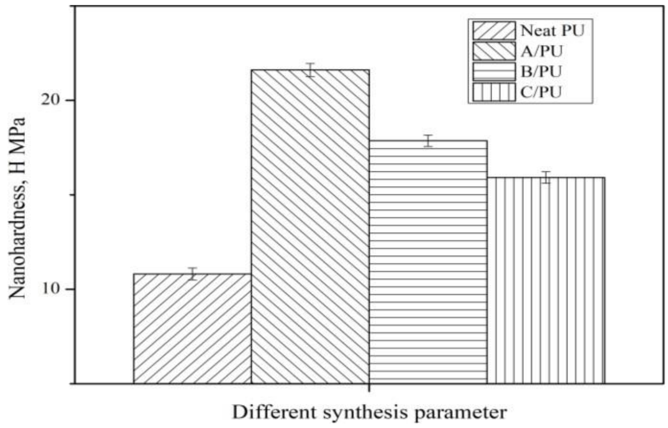



**Figure 5.** Effect of nano hardness test on HKUST-1-reinforced polyurethane with different synthesis parameters.

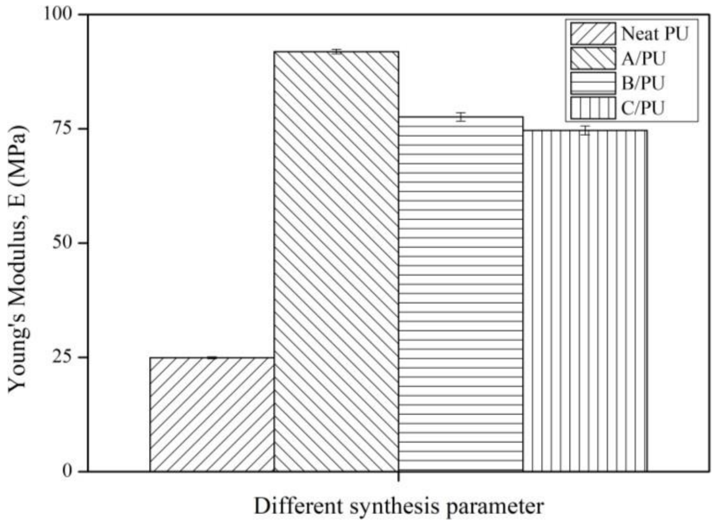



**Figure 6.** Calculated Young's modulus of HKUST-1/PU and neat PU.

## 4. CONCLUSION

In the current study, HKUST-1 was synthesised with different solvent ratios. To comprehend the effect of synthesis parameters on HKUST-1 nanocomposites studied by FTIR characterisation and mechanical testing to explore the enhancement of the reinforced polymer. It was observed that sample A/PU shows a significant effect on the mechanical testing. FTIR and the reinforced nanoparticles analysed in the samples do not have chemical changes occur as all spectra recorded attributed to the overlapping characteristic of HKUST-1 and PU. The result shows that the tensile test and nanoindentation analysis, A/PU, significantly affected the composite.

## ACKNOWLEDGMENTS

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