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Mechanical and thermal properties of polyurethane/neoprene/graphene blends

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Abstract. This work investigated the properties of the polyurethane/neoprene/graphene nanocomposites blends specifically in mechanical and thermal aspects for solid ankle cushion heel (SACH) foot in the prosthetic application. The aim of this work was to study the effect of neoprene and graphene contents in mechanical and thermal properties of polyurethane/neoprene/graphene blends. Polyurethane is one of the most frequently used polymers in the medical devices, footwear, automotive and construction industries. Polyurethane which is high mechanical strength, high thermal withstands and flexibility was blended with the additives, neoprene and graphene to reduce the rigidity and enhances the mechanical properties for a prosthetic foot. A solution mixing method was used to prepare the samples with different formulations of polyurethane, neoprene and graphene. The samples were analyzed and characterized in terms of mechanical, thermal and morphology properties. The result shows that the optimum composition blended with 97 wt% polyurethane, 2 wt% neoprene and 1 wt% graphene. The sample possesses high tensile strength (14.38 MPa) and high Young's modulus (1.11 MPa), high thermal stability, elastic and flexible. The use of a low amount of graphene in polyurethane and neoprene blend has been demonstrated to enhance the mechanical and thermal properties of the nanocomposites.

1. Introduction

Polymers based on polyurethane are widely used in many applications such as medical devices and medical parts. Polyurethane, commonly abbreviated as PU is any polymer containing a chain of organic units combined by urethane (carbamate) relations. Polyurethane polymers are shaped through step-growth polymerization by retorting a monomer holding at least two isocyanate functional collections with another monomer covering at least two hydroxyls (alcohol) collections in the incidence of a catalyst. Due to its exceptional properties in tensile modulus, good chemical resistance, low-temperature elasticity processable gained raised in various industries [1-2]. Commonly, PU has been blended with other polymers like rubber, graphene, silica [3-5], organo-clay and etc. through various methods and applications [6].



Neoprene which is also known as chloroprene rubber (CR) is known for its versatility [6]. It provides excellent resistance to moderate exposure to ozone, sunlight, oxidation, weather, oils, gasoline, greases and solvents [7]. Graphene exhibits outstanding chemical stability and remains flexibility over a wide temperature range, good in mechanical, thermal and optical properties. It has been proven that graphene with a single layer is able to withstand up to 42 Nm of stress, with Young's modulus of 1.0 TPa [8]. Furthermore, polyurethane/neoprene/graphene blends through solution method are one of the simplest approach and efficient in dispersing nanoparticles for preparing nanocomposites [9]. This method has enabled a very broad domain of mechanical and thermal characteristics and processing conditions to be explored. Long, flexible parts are contributed by the polyol to provide smooth elastic polymer. Hard or rigid polymers are offered by high crosslinking quantities. In order for the short chains with lots of crosslinks to generate a hard polymer, long chains and low crosslinking provide a polymer that is very stretchy. Despite the fact that long chains and intermediate crosslinking provide a helpful polymer for foam making.

The medical devices and footwear for coatings, adhesives, sealants and elastomers which are used on floors and automotive interiors are considered some of the usage of Polyurethane. Polyurethane is a distinctive material that provides the combination of rubber's elasticity with metal's toughness and durability. Besides that, there are also disadvantages such as poor chemical stability and mechanical properties. Polyurethane is known of its rigidity and durability, in order to provide comfort for the use of prosthetic foot polyurethane is blends with neoprene and graphene to reduce the rigidity and enhance the mechanical properties for prosthetic foot used. The addition polyurethane with neoprene and graphene are expected to improve the mechanical and thermal properties of this resin blends.

2. Experimental section

2.1. Materials and methods

The materials used were ethylene glycol, polyurethane pre-polymer that terminated with toluene diisocyanate, neoprene and graphene. Solution mixing has been introduced for the preparation of samples. To produce polyurethane, the ethylene glycol and polyurethane pre-polymer that terminated with toluene diisocyanate were mixed together by 1:1 mass ratio. The solution was stirred by using magnetic stirred under temperature of 97 °C and nitrogen atmosphere in a fume hood until a homogeneous solution formed. Then, the homogeneous solution poured into moulding cast that contains OHP plastics at both sides. Next, the moulding cast sent to hot and cold moulding press machine to be press under a temperature of 64 °C for an hour. After compression moulding, the samples were cooled for 10 min. Lastly, the sample was prepared and the steps were repeated for other formulations. Table 1 shows the various compositions of the materials for each sample.

Table 1. Composition of materials.

Sample	Percentage by mass (%)		
	Polyurethane	Neoprene	Graphene
PU	100	0	0
PU/CR	97.5	2.5	0
PU/CR/GR 1	97.0	2.0	1.0
PU/CR/GR 1.5	96.0	2.5	1.5
PU/CR/GR 2	95.0	3.0	2.0

2.2. Characterization

Fourier Transformation Infrared Spectroscopy (FTIR) Thermo-Electron Corporation (Waltham, MA, USA) Nicolet 8700 Spectrometer in the Attenuated Total Reflectance (ATR, Gold State II) was used to measure the changes of functional groups in the blend in the range of 500 to 4000 cm^{-1} .

Tensile test was carried out according to ASTM D638 using a universal tensile test machine under ambient conditions. The test was performed at the constant loading speed of 10 mm min^{-1} with the maximum 5 kN load cell at room temperature. At least three specimens of each formulation were tested and the average value is recorded. Tensile modulus, tensile strength and elongation at break were determined.

Impact tests were conducted by using Ray-Ran Advance Universal Pendulum Impact Tester based on ASTM 256 under ambient conditions. The energy required to break or rupture specimen was determined. At least three specimens of each formulation tested and the average value is recorded.

Scanning electron microscope (SEM) was utilized to examine the dispersion and dispersed condition from the surface of nanocomposites. The X-Ray Diffraction Analysis (XRD) has been used to measure the scattering of graphene and polyurethane composites were performed using a Bragg–Brentano X'PERT PHILIPS diffractometer, equipped with a Cu Anode X-ray tube and diffracted beam monochromator (40 kV, 30 mA, λ Cu $K\alpha = 0.1542$ nm). The scanning process of PU, PU/CR and PU/CR/GR nanocomposites samples are in 2θ range from 5° to 35° [10].

Thermogravimetric analysis (TGA) has been utilized to measure the degradation of all the samples. The process of degradation will be performing within nitrogen-atmosphere with gas-flow rate 40 mL per minute in the temperature range starting from room temperature up to 700 $^\circ\text{C}$. The temperature, weight and derivative of the sample and heat flow were identified after heating from the ambient temperature at an increasing rate of 10 $^\circ\text{C}$ per minute [11].

Differential Scanning Calorimetry (DSC) measurements have been carried in a range of the temperature starting from room temperature to 350 $^\circ\text{C}$. About 10 mg of the weight of the sample is analysed within nitrogen-atmosphere with gas-flow 40 mL per minute. The aluminium pan with pierced lids was heated up to 300 $^\circ\text{C}$ at 10 $^\circ\text{C} / \text{min}$ steady rate [11].

3. Results and discussion

3.1. Chemical analysis

Fourier Transform Infrared spectroscopy (FTIR) was used to examine PU, PU/CR and PU/CR/GR nanocomposites which the over a range of wavelengths estimates via intensity transmittance at time. Additionally, it can be used to display and observe if there are any changes in chemical functional group of the polyurethane via added the graphene and neoprene. The FTIR curves of the PU, PU/CR and PU/CR/GR nanocomposites are shown in figure 1. The loading of graphene in the polymer matrix displays that CH stretching change of the blend starting from 2868 to 1726 cm^{-1} , proves that the van der Waals interaction occurred in the polymer matrix. There were no changes in the functional group and therefore suggesting that only noncovalent interaction exists in the blend.

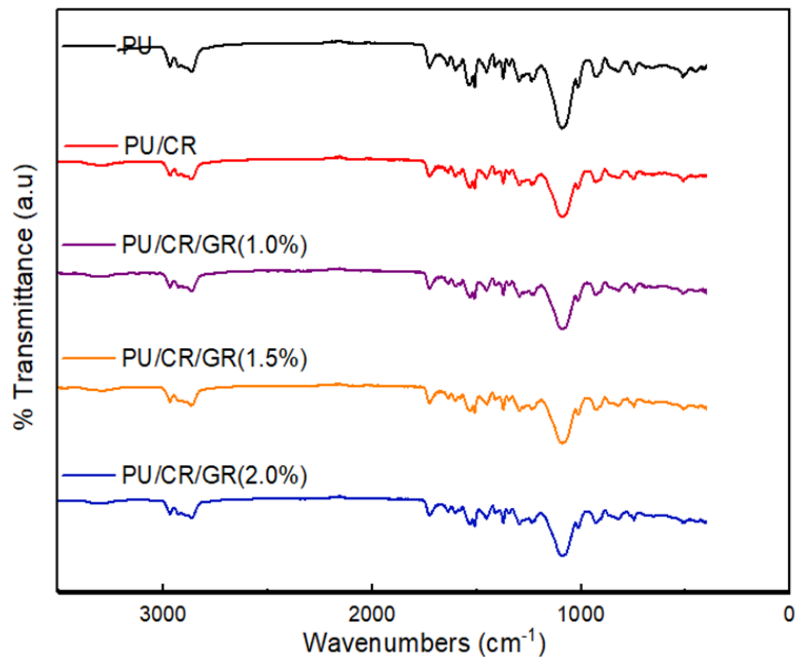


Figure 1. FTIR spectrum of various compositions of PU, PU/CR and PU/CR/GR nanocomposites.

3.2. Mechanical analysis

3.2.1. Tensile test. The effect of reinforcement of graphene (GR) as nanofiller on the mechanical properties of binary blends of polyurethane (PU) and neoprene (CR) (PU/CR) was investigated through the tensile test. The results of the investigations were tabulated in table 2 and illustrated in figure 2. The improvement of the mechanical properties of the blends was attributed to the aspect ratio of GR loading. The addition of 1% of GR into the blends obtained the highest stress value and percentage of strain compared to 1.5% and 2.0%. Generally, the results showed, the addition of 2.5% of CR into blend improved the stress to 29% as compared to the neat PU. However, further addition of GR shows that the stress and Young's modulus values decreased. It indicates that the excessive amount of graphene loaded into blends which lead to agglomeration that exhibits the load transfer from the matrix and cracked easily [12].

Table 2. Mechanical Properties for PU, PU/CR and PU/CR/GR nanocomposites.

Sample	Force (N)	Stress (MPa)	Strain (%)	Modulus (MPa)
PU	89.59	11.19	3.72	3.01
PU/CR	115.43	14.42	3.79	3.80
PU/CR/GR 1	115.07	14.38	12.95	1.11
PU/CR/GR 1.5	91.82	11.48	11.04	1.04
PU/CR/GR 2	104.33	13.04	11.75	1.11

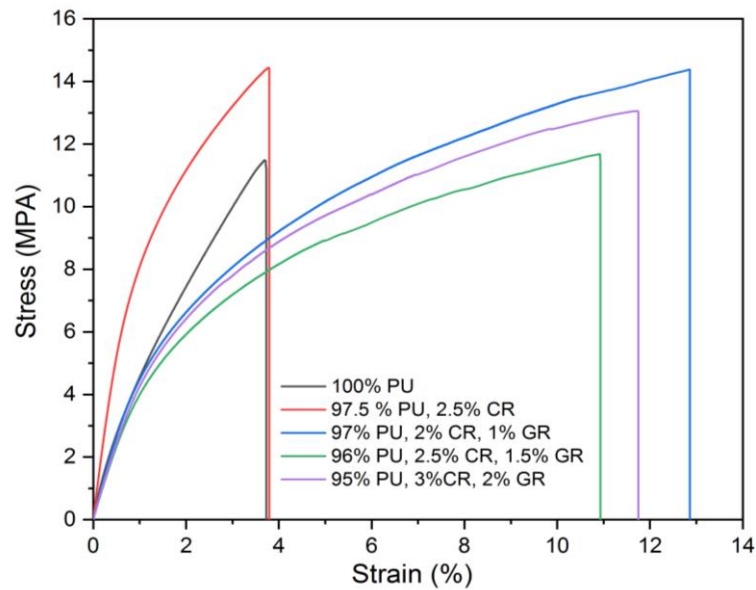


Figure 2. Stress-Strain graph for PU, PU/CR and PU/CR/GR nanocomposites.

3.2.2. Impact test. Toughness is one of vital property that describes the ability of a material to absorb energy and plastically deform without fracturing. The figure 3 shows the relationship between the impact strength values and amount of GR loaded into PU/CR blends.

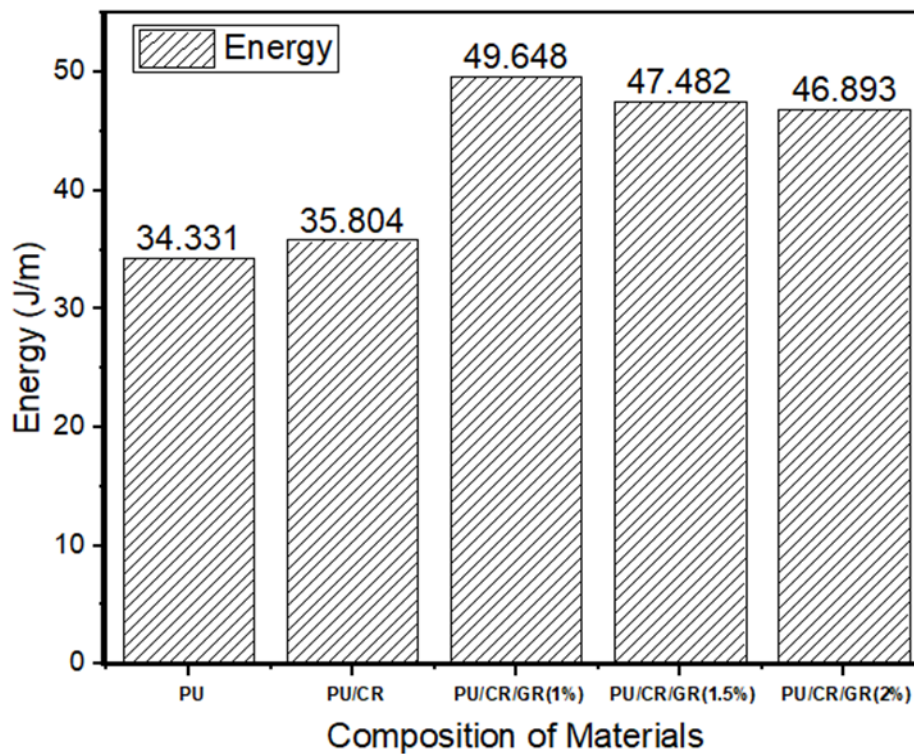
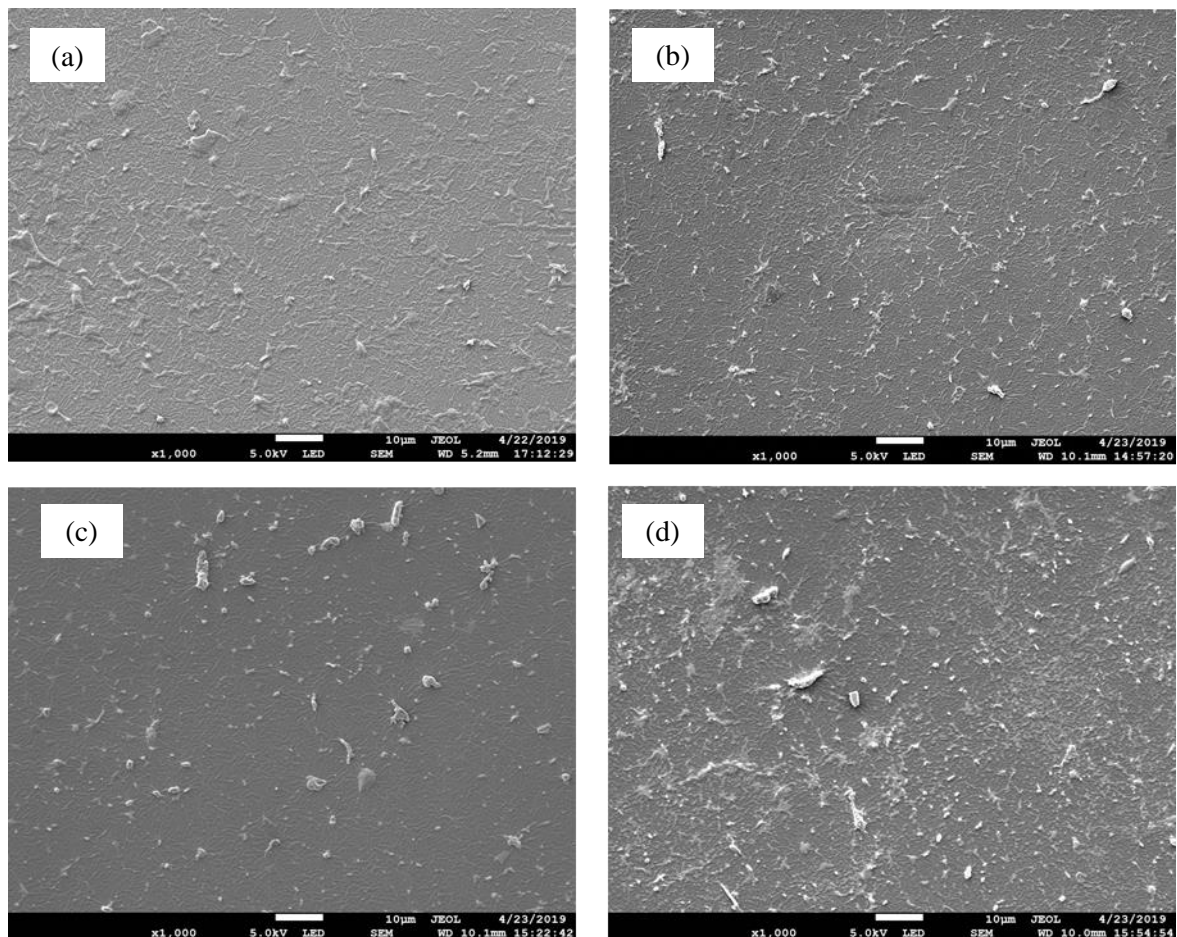


Figure 3. Effect of neoprene and graphene contents to the energy.

3.3. Morphological analysis

3.3.1. Scanning electron microscopy (SEM). The mechanical results of PU/CR/GR ternary blend were also supported by morphological analysis. Scanning electron microscopy (SEM) images of neat PU, PU/CR, and PU/CR/GR were correlated with the mechanical properties. The SEM micrographs in figure 4 resulted from the surfaces of morphology under 1000x magnifications for all compositions. The result shows that the neat PU surface morphological was smooth (Refer figure 4 (a)). However, the dispersion of PU/CR illustrated in figure 4 (b) was poor without GR loaded. Generally, when GR was loaded into PU/CR binary blends, the surface observed to be rougher as the dispersion of nanofiller were improved due to high van der Waals forces to break the layer between GR sheets. Rougher surface of the nanocomposites indicated in the improvement in the general mechanical properties [13]. By comparing the amount of GR loaded into the blend systems, PU/CR/GR 1.0 and PU/CR/GR 1.5 show a better state of dispersion in the polymer matrix compared to PLA/PA6/GNP 2 (Refer figure 4 (c), (d) and (e)). Above 2% GR loading, the materials start to clump together due to the excess amount of nanofiller.



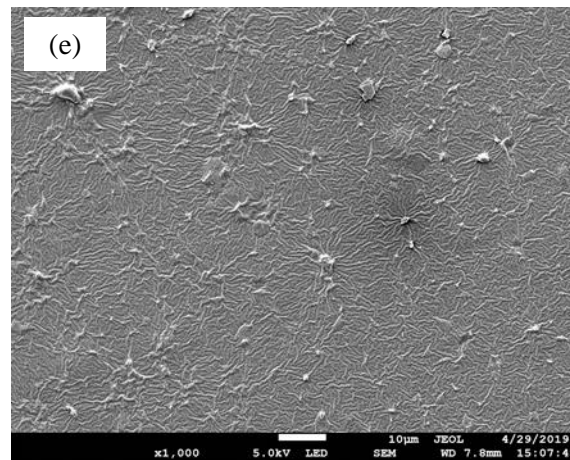


Figure 4. SEM of (a) neat PU (b) PU/CR, (c) PU/CR/GR 1, (d) PU/CR/GR 1.5 and (e) PU/CR/GR 2.

3.4. Crystallinity analysis

3.4.1. X-Ray Diffraction Analysis (XRD). Figure 5 illustrates the X-ray diffraction data for neat PU, PU/CR blends and PU/CR/GR at various CR and GR loadings. The neat PU profile was correlated to its monoclinic modification which demonstrating the main diffraction peak of this crystalline lattice corresponding to the (240) plane. The PU blends diffractogram had visible a strong peak at $2\theta \approx 21.12^\circ$. While, for various contents of CR and GR loaded, the strong peaks were located near the 21.12° for each composition which almost similar as XRD analysis of PU/GO and PU/MgO in Sadasivuni et al. [14]. The strong peak at $2\theta \approx 26.50^\circ$ is attributed to the graphene oxide. There was no effect of GR on another peak. The absence of any additional peak of GR in blends confirmed a very good dispersion of the filler within the polyurethane matrix [14]. The results indicated the morphological behaviour of ternary blends (PU/CR/GR) had complete exfoliation and had better dispersion of graphene and neoprene in the composites especially for 1.5%, 2.0% of GR loaded and PU/CR blends. The intensity of the crystalline peak decreases as GR loaded increased.

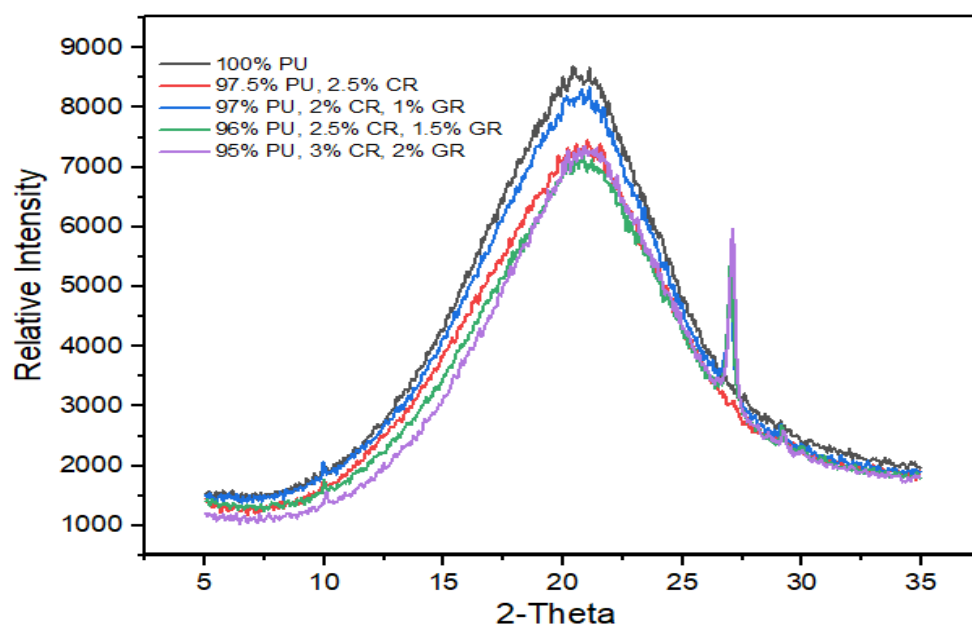


Figure 5: XRD of neat PU, PU/CR and PU/CR/GR at various neoprene and graphene loaded.

3.5. Thermal analysis

3.5.1. *Thermo-gravimetric Analysis (TGA)*. The TGA curves for PU, PU/CR and PU/CR/GR nanocomposites are shown in figure 6. The increment of graphene has contributed to the degradation stability in a polymer matrix. Changes in temperatures at various stages weight reduction are tabulated in table 3.

Table 3. Degradation temperature for PU, PU/CR and PU/CR/GR nanocomposites.

Samples	T _{2%}	T _{20%}	T _{50%}
PU	187.29	287.70	342.45
PU/CR	192.52	289.86	347.11
PU/CR/GR 1	199.33	286.81	346.06
PU/CR/GR 1.5	197.98	292.65	352.18
PU/CR/GR 2	195.28	285.12	330.11

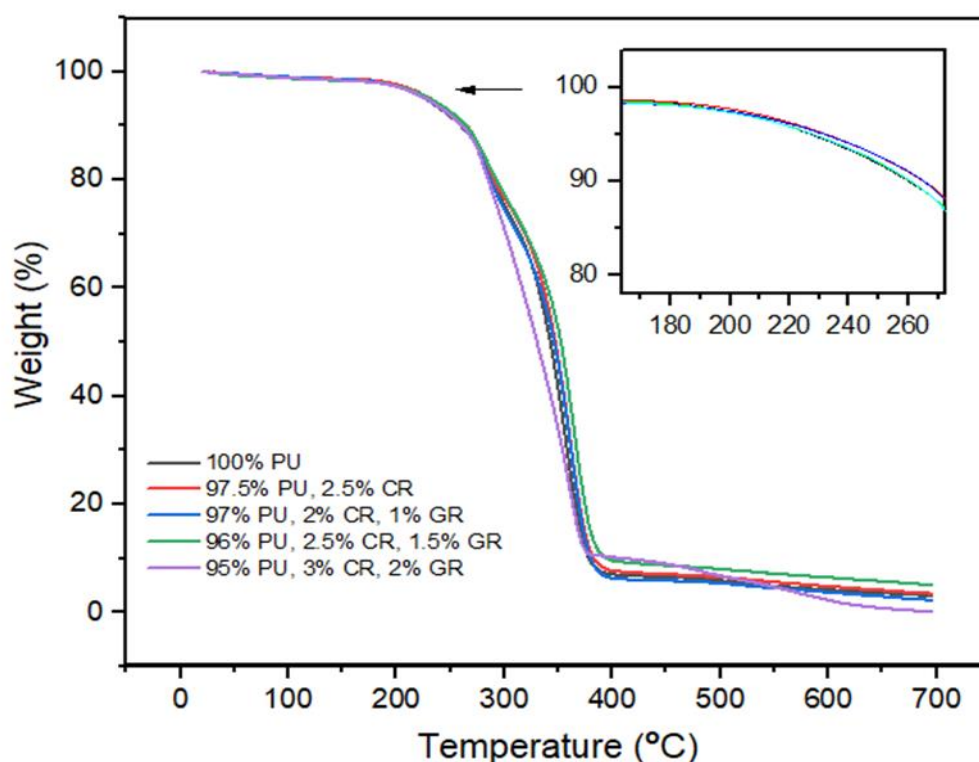


Figure 6. TGA thermograms of PU, PU/CR and PU/CR/GR nanocomposites.

The onset and the mid-point of degradation at T_{2%} and T_{50%} respectively, are the most significant parameters recorded from TGA graph. The weight loss at 2% chosen as the point of evaluation the profile of degradation shows that the net PU polymer began to decompose first at 187.29 °C. However, there is an enhancement in degradation temperature when the PU contained graphene and neoprene. The curves show that PU/CR, PU/CR/GR 1, PU/CR/GR 1.5 and PU/CR/GR 2 having a

degradation temperature at 192.52 °C, 199.33 °C, 197.98 °C and 195.28 °C respectively. The enhancement in the thermal stability of the polymer nano-composites is primarily because of excellent dispersion in which the connection among the polymers and graphene, therefore best dispersion of the sample is PU/CR/GR 1 due to the excellent enhancement in the thermal stability.

TGA curves of PU/CR/GR nanocomposites show that the thermal stability was higher than PU/CR blends. This is most likely because of the dispersion state of GR layers in the polymer matrix. The loading of the graphene-enhanced the thermal stability of the PU/CR matrix because of the intrinsic-characteristic of the graphene prompts the extraordinary improvement of the thermal stability of the polymer matrix. Graphene sheets play a job of thermal barriers and enhance the thermal stability of polymer matrix [15].

3.5.2. Differential Scanning Calorimetric (DSC). TGA curves of PU/CR/GR nanocomposites show that the thermal stability was higher than PU/CR blends. This is likely to be associated with the dispersion state of GR layers in the polymer matrix. The loading of the graphene-enhanced the thermal stability of the PU/CR matrix because of the intrinsic-characteristic of the graphene prompts the extraordinary improvement of the thermal stability of the polymer matrix. Graphene sheets play a function of thermal barriers and enhance the thermal stability of the polymer matrix.

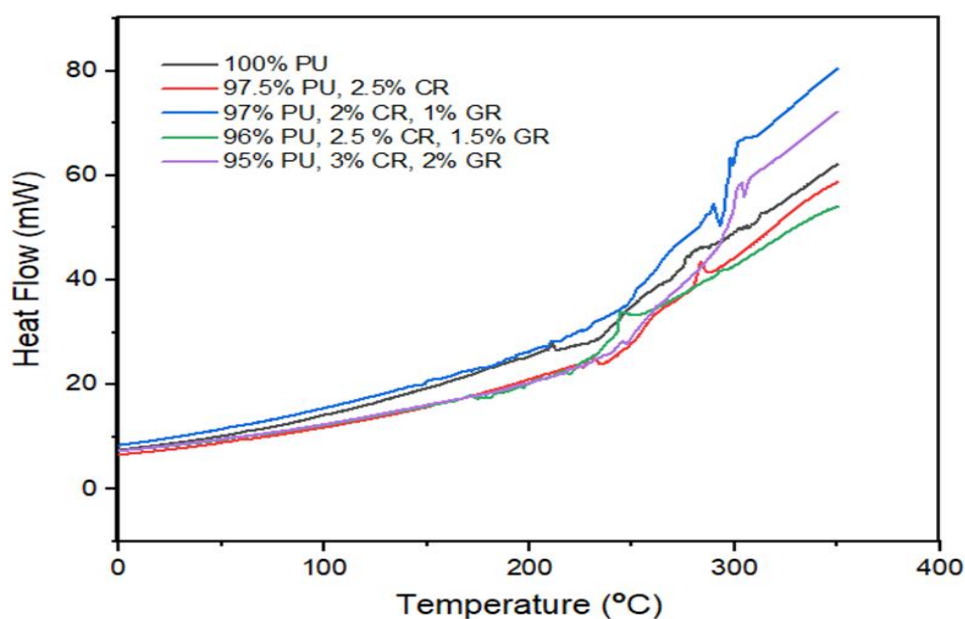


Figure 7. DSC curves of PU, PU/CR and PU/CR/GR nanocomposites.

Table 4. Temperature transitions of PU, PU/CR and PU/CR/GR nanocomposites.

Samples	T_g (°C)	T_m (°C)
PU	60.53	210.50
PU/CR	56.72	282.64
PU/CR/GR 1	58.19	288.90
PU/CR/GR 1.5	58.33	243.57
PU/CR/GR 2	55.27	244.29

4. Conclusion

PU/CR/GR blends were prepared through solution mixing method. In this work, the effect of the various composition of neoprene and graphene loaded were studied in terms of chemical interaction, dispersion of nanofillers in PU matrix, thermal properties, and mechanical properties. It was found that that the PU/CR/GR 1 nanocomposites obtained high tensile strength (14.38 MPa) and high Young's modulus (1.11 MPa) as compared to PU/CR/GR 1.5 and PU/CR/GR 2.5. Degradation temperature, glass transition, and melting temperature also were increased as GR added into PU/CR binary blends. The dispersion of graphene as nanofiller was also increased in the PU matrix as indicated in the morphology.

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References

- [1] Ha Thuc C N, Cao H T, Nguyen D M, Tran M A, Duclaux L, Grillet A C and Ha Thuc H 2014 *J. Nanomater.* 1-11
- [2] Bijarimi M, N Shahadah, Azizan R, Said N, Waleed A, Zakir M M and Jamiluddin J 2019 *Indones. J. Chem.* 1-6
- [3] Tahir M, Heinrich G, Mahmood N, Boldt R, Wiessner S and Stockelhuber K W 2018 *Mater.* (Basel) 11
- [4] Cristofolini L, Guidetti G, Morellato K, Gibertini M, Calvaresi M, Zerbetto F, Montalti M and Falini G 2018 *ACS Omega* **3** 8829-35
- [5] Hamed N, Hassanajili S and Sajedi M T 2017 *Silicon* **10** 1243-55
- [6] Ercan N, Durmus A and Kaşgöz A 2015 *J. Thermopl. Comp. Mater.* **30** 950-70
- [7] Durrieu V, Gandini A, Belgacem M N, Blayo A, Eiselé G and Putaux J-L 2004 *J. Appl. Polym. Sci.* **94** 700-10
- [8] Papageorgiou D G, Kinloch I A and Young R J 2017 *Prog. Mater. Sci.* **90** 75-127
- [9] Ricardo Fischer Brandenburg C M L, Daniela Becker and Luiz Antonio Ferreira Coelho 2017 *Matéria* (Rio de Janeiro) **22** 12
- [10] Strankowski M, Korzeniewski P, Strankowska J, A S A and Thomas S 2018 *Mater.* (Basel) 11
- [11] Bijarimi M, Ahmad S and Alam A K M M 2016 *Polym. Bull.* **74** 3301-17
- [12] Ervina J, Mariatti M and Hamdan S 2016 *Procedia Chem.* **19** 897-905
- [13] Malas A and Das C K 2015 *Compost. Part B: Eng.* **79** 639-48
- [14] Sadasivuni K K, Ponnamma D, Kumar B, Strankowski M, Cardinaels R, Moldenaers P, Thomas S and Grohens Y 2014 *Comp. Sci. Tech.* **104** 18-25
- [15] Bijarimi M, Amirul M, Norazmi M, Ramli A, Desa M S Z, Desa M D A and Abu Samah M A 2019 *Mater. Res. Express.* **6** 055044