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GMA-Based Emulsion Templated Macroporous Foams: Tailoring the Mechanical Properties by Nanoclay Loading

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Abstract

Glycidyl methacrylate (GMA) based low density macroporous foams (polyHIPE foams) were synthesized by high internal phase emulsion (HIPE) templating. Strengthen foams were produced by polymerizing the continuous phase of HIPEs consisting of GMA, 1,3-butanediol dimethacrylate (BDDMA) and nanoclay. In order to ensure the compatibility between the nanoclay particles and monomers, surface modified nanoclay containing 25-30 wt. % of methyl dihydroxyethyl hydrogenated tallow ammonium was used. The composite foams were prepared by incorporating up to 5 wt. % of nanoclay particles. Compressive modulus of the composite foams was improved by ca. 55 % as compared to neat polyHIPE foam. The specific compressive modulus and specific compressive strength were also significantly improved by increasing the amount of nanoclay loading.

Keywords: GMA, emulsion templating, polyHIPE, macroporous polymer, nanoclay, mechanical properties.

1. Introduction

Macroporous polymer monoliths are versatile materials for many different applications due to their tunable morphological and physical properties. Since they offer high porosity accompanied with low density and relatively enough mechanical strength, they can be used in the fields including adsorption, filtration, catalysis, tissue engineering, and etc [1]. Consequently, not only tuning the pore sizes or surface areas but also altering the chemical composition and the functionality has a great importance. In this respect, scientists have been exploring the variety of synthetic approaches for the preparation of macroporous polymer matrices for many years. There are several approaches being effectively used for this purpose including templating and non-templating approaches. However, emulsion templating which is based on using high internal phase emulsion (HIPE) as a template for the creation of porosity is coming front between the all other methods [2-4].

A HIPE is a concentrated emulsion prepared by dispersing high volume of internal phase within a continuous phase. The volume fraction (Ø) of the internal phase is greater than 0.74 and can be reached up to 0.99. If the continuous phase of a HIPE is prepared by using monomer(s) polymerization of this phase gives a continuous polymeric film surrounding the adjacent emulsion droplets. After the removal of the internal phase and drying of the polymerized HIPEs, open porous cellular polymeric foams (polyHIPEs) are obtained [5-7].

The most important advantage of using emulsion templating for the creation of macroporosity is the easy control of the porous structure [2-6]. This approach provides the opportunity of preparing polymers with well-defined morphologies. However, the applicability of this approach is dependent of the polarity of the monomers [8, 9]. The most studied and conventional emulsion templated polymers are based on styrene, which is a highly hydrophobic monomer [5, 7]. Polystyrene polyHIPEs were first prepared by free radical copolymerization of styrene (St) and divinilybenzen (DVB) in water-in-oil (w/o) type HIPEs and patented by Unilever researchers Barby and Haq in

1982 [10]. Afterwards, scientists have succeeded in many attempts for the synthesis of polyHIPEs with the use of polar monomers which enables further functionalization of the resulting foams. In this respect, not only acrylates [11] and methacrylates [8, 9, 12, 13], but also unsaturated resins [9,14], dicyclopentadiene (DCPD) [15-19], and etc. [20] were also used for this purpose. Moreover, due to the interest of adapting different monomeric kinds, various polymerization techniques such as condensation polymerization, ring opening metathesis polymerization (ROMP), atom transfer radical polymerization, click chemistry, and etc. were also applied for the polymerization of the continuous phase of the HIPE templates [20].

Due to the advantages of polyHIPEs, mostly arises from their unique morphology and low-density, scientists are focused not only on altering the chemistry but also improving the other properties such as mechanical strength over the last decade. For this respect, using stress reducer and/or impact modifier monomers [11, 13, 21], monomers that produces high strength polymers [15-19], addition of nanoparticles [14, 18, 19, 22], and lowering the nominal porosity [14, 23] are the most preferred approaches.

In this study, we aimed preparing polyHIPEs exhibiting relatively high mechanical strength and having suitable sides on the main chain for post-functionalisation. With this respect, GMA, an epoxy functional monomer, was crosslinked with 1,3-butanediol dimethacrylate (BDDMA) which is a stress reducer comonomer providing additional free volume to the polymer chains. Moreover, surface modified montmorillonite clay was also incorporated to the continuous phase of the HIPEs not only for improve mechanical properties but also add additional functionality to the resulting polyHIPE foams [14, 24].

2. Materials and Methods

2.1 Materials

Glycidyl methacrylate (GMA, %97, Aldrich), 1,3-butanediol dimethacrylate (BDDMA, contains 150-250 ppm MEHQ as inhibitor, 95%, Aldrich), poly(ethylene oxide-*block*-propylene oxide-*block*-ethylene oxide) (PEO-*b*-PPO-*b*-PEO, M_w: 4400 g/mol) (Pluronic®L-121, Aldrich), and surface modified nanoclay contains 25-30 wt. % methyl dihydroxyethyl hydrogenated tallow ammonium (NC-T, Nanomer® I.34MN, Aldrich) were used without purification. 2,2'-Azobisisobutyronitrile (AIBN) was used after re-crystallization from ethanol.

2.2 Synthesis of PolyHIPEs

In all experiments polyHIPEs were synthesized with 75 vol. % of nominal porosity. In a typical experiment GMA (85 mmol), BDDMA (8.8 mmol), surfactant (Pluronic®L-121, 0.7 mmol) and polymerization initiator (AIBN, 0.9 mmol) were mixed in a round-bottom glass reactor to prepare the continuous phase. Afterwards, deionised water (37.5 mL) was added dropwise under constant stirring (300 rpm). Once the addition of deionised water is completed stirring was continued for further 15 min to obtain a homogeneous emulsion. Then the emulsion was transferred into a polyethylene tube and cured in an air circulated oven (24 h, @70 °C). After the curing stage resulting monoliths were washed with ethanol and dried in a vacuum oven (@50 °C) under constant weigh was reached.

NC-T incorporated polyHIPE composites (polyHIPE/NC-T) were synthesized with the same experimental approach explained above. The only difference was the addition of 1, 3 or 5 wt. % of nanoclay into the continuous phase when preparing the emulsions (Figure 1).

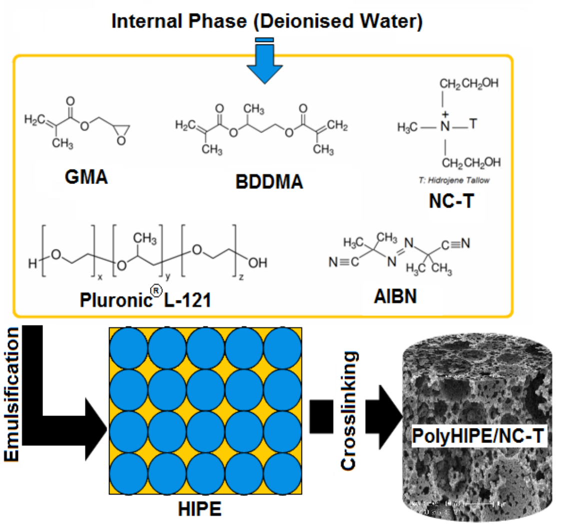

Figure 1. Schematic representation of polyHIPE/NC-T synthesis.

2.3 Characterization

The morphology of the materials was investigated by scanning electron microscope (SEM, FEI-Philips XL30 ESEM-FEG SEM). SEM imagining was conducted with samples 1 mm x 1mm in size which were mounted on a copper stub and coated with gold. SEM images were used for the calculation of cavity sizes ($[C]_{SEM}$, μm) of the foams. For this aim, at least 50 measurements were taken from each SEM image and corrected by a factor ($2/3^{1/2}$) to eliminate the influence of irregular cutting [25].

Surface areas (δ_{BET}, m^2/g) were determined by applying Brunauer-Emmet-Teller (BET) equation on the N_2

adsorption/desorption isotherms of the samples. Isotherms were recorded on a Micromeritics Gemini VII surface are and porosity analyzer (Micromeritics Instrument Corporation, USA). Before the measurement all samples were degassed on a Micromeritics Flow Prep 060 sample degas system (Micromeritics Instrument Corporation, USA) at 70ºC for 24 h. Interconnected pore diameters ($[IP]_{BJH}$, µm) were also calculated from the N_2 adsorption/desorption isotherms by applying Barrett-Joyner-Halenda (BJH) analysis.

Foam densities (ρ_f) of the resulting foams were measured according to Archimed′s principle by using an analytical balance equipped with a density determination kit (Sartorius YDK01).

Mechanical strength of the foams was characterized in terms of compressive properties. Compression tests were performed under 10 kN load at a compression rate of 1.3 mm/min by using Zwick/Roell Z020 Universal Testing Machine (Zwick GmbH &Co.KG). All measurements were performed by using non-treated and undivided cylindrical samples with specific dimensions of 15 mm in diameter and 10 mm in height. For each sample, compression tests were repeated with three different specimens. Stress-strain plots were drawn by using the original data obtained from the software. Compressive modulus (ε_c) of each sample was calculated from the initial slope of the stress-strain plots. The maximum strength at the end of the initial linear elastic region was defined as the compressive strength (σ_c). Specific compressive moduli and specific compressive strengths were obtained by normalizing the stress values by the individual foam densities

3. Results and Discussion

GMA based polyHIPE foams were prepared by the free radical copolymerization of surfactant stabilized w/o HIPE templates. In order to enable the post-functionalization of resulting materials and increase the ratio of the epoxy groups that are suitable for possible further reactions in the polymer composition, GMA: BDDMA ratio was kept constant at 90:10. To make meaningful comparison, neat polyHIPE foams were also synthesized without adding nanoclay particles. This led to stable HIPE templates, which maintain stability more than 24 h at room temperature. Moreover, it was also observed that neat HIPE templates did not breakdown at polymerization temperature and gave monolithic polyHIPE foams.

The morphological structure of the neat polyHIPE sample (PHP) was investigated by SEM. It was observed from the SEM image given in Figure 2 that cavities of polyHIPEs were formed by stacking of agglomerated microgels. As well as this morphology is different from the known morphology of conventional polystyrene polyHIPEs, it is an expected result depending on the monomer polarity [13]. In conventional polyHIPEs, the cavities are interconnected through smaller pore throats, and the size of the pore throats also varies in microns. However, resulting polyHIPE foam exhibited smaller pores. While average cavity size ($[C]_{SEM}$) of the neat polyHIPE was calculated as 29.21 ± 2.86 µm from SEM image, its interconnected pore size ($[IP]_{BJH}$) was measured as 17.51 Å from N_2 adsorption/desorption study (Table 1).

The influence of nanoclay addition was studied by varying the amount of nanoclay within the continuous phase. For this purpose, composite polyHIPE foams were synthesized by dispersing 1, 3 or 5 wt. % of NC-T in the continuous phase during emulsification. It was concluded from the SEM images given in Figure 3 that addition of nanoclay particles significantly improves the pore morphology. Cavity sizes were also found to be significantly increased with the addition of nanoclay particles (Table 1). However, with the increase of nanocaly loading, cavity sizes were found to be decreased from 104.49 µm to 88.57 µm. The similar behaviour was also observed for the interconnected pore sizes. While addition of 1 wt. % of nanoclay increased the interconnected pore size from 17.51 to 35.04 Å as compared to neat polyHIPE sample; interconnected pore size decreased to 13.34 Å with the addition of 5 wt. % of nanoclay. Moreover, it was found that, with the addition of nanoclay, cavity size distributions were broadened as compared to the neat polyHIPE sample (PHP) (Figure 4).

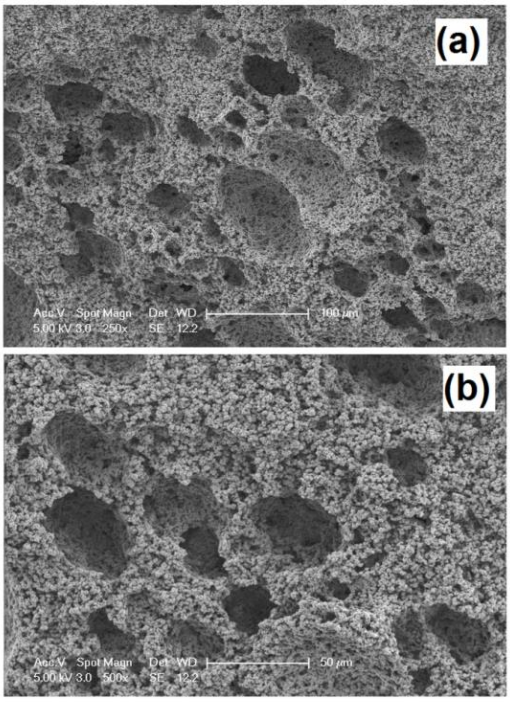

Figure 2. SEM images of neat polyHIPE (PHP) sample.

The variation of cavity sizes observed due to the inclusion of nanoclay particles can be explained by the change of cavity size distribution. According to Figure 4, while 22 % of all cavities of the neat polyHIPE foam (PHP) were between 10-15 µm, the percentage of cavities between 15-20 µm and 20-25 µm was found to be 15 % and 13 %, respectively. On the other hand, the percentage of cavities larger than 150 µm for the composite foams containing 1, 3, and 5 wt. % of nanoclay was determined as 22 %, 24 % and 22 % respectively. The sizes of other cavities were found to be distributed over a wide range for the foams containing 1 and 3 wt. % of nanoclay. In addition, the composite foam prepared by adding 5 wt. % of nanoclay, was found to exhibit narrower cavity size distribution as compared to other composite foams. For this sample 13 % of all cavities were found to be changed between 30-35 µm. These results showed that the neat polyHIPE foam (PHP) has the narrower cavity size distribution, while most of its cavities were in the range between 10 to 25 µm. On the other hand, addition of nanoclay particles was found to be significantly broadened the cavity size distribution. This alteration of average cavity size and cavity size distribution might be attributed to the influence of nanoclay particles on the emulsion stability.

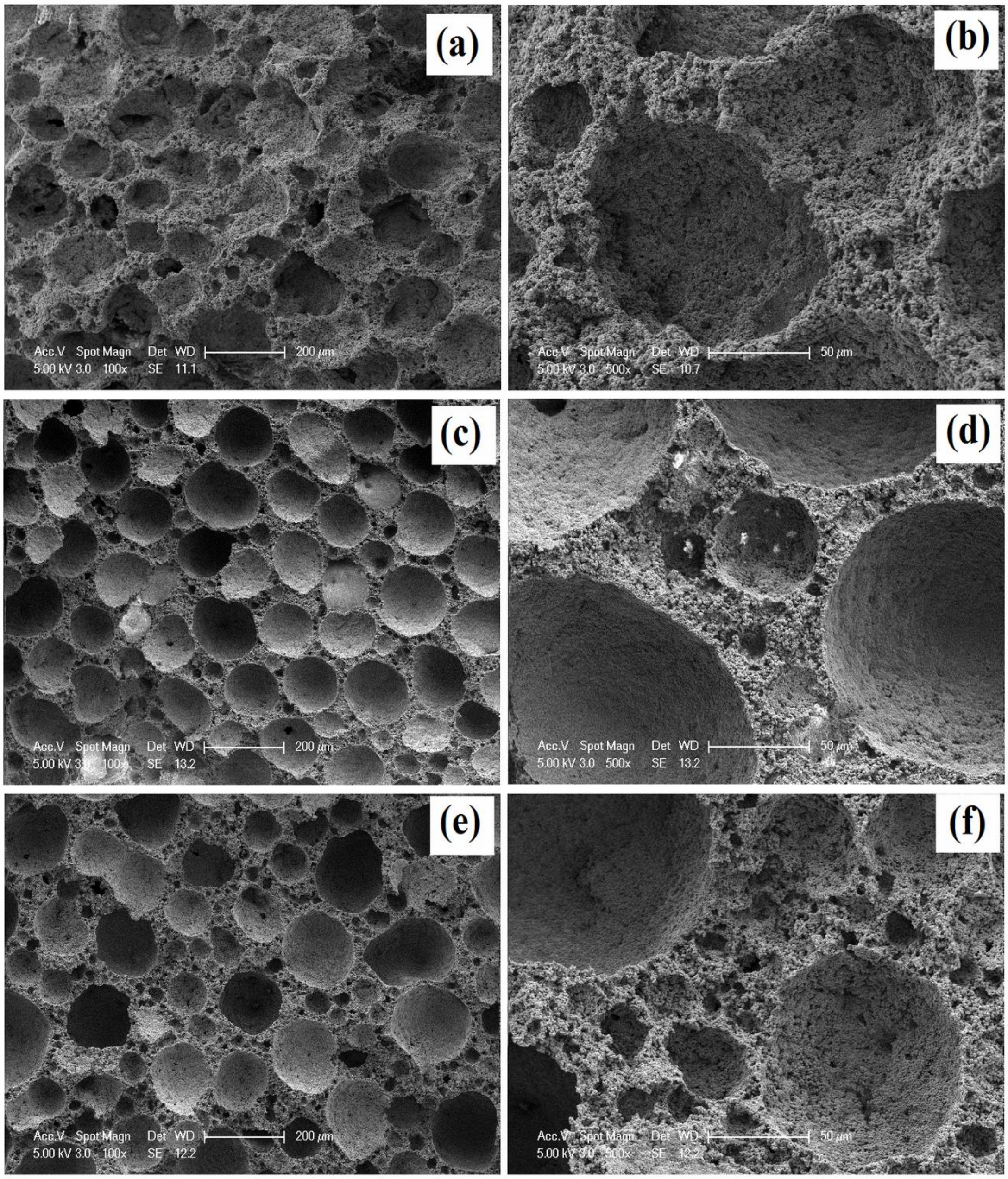

Figure 3. SEM images of polyHIPE/NC-T composites containing 1 wt. % of NC-T (a) and (b); 3 wt. % of NC-T (c) and (d); 5 wt. % of NC-T (e) and (f).

When comparing Figure 2 with Figure 3, one can be easily concluded that the presence of nanoclay particles was improved the emulsion stability: The increasing amount of nanoclay loading lead to formation of more uniform and spherical cavities, which is an indicator of the increased emulsion stability. Accordingly, at 5 wt. % of nanoclay loading, the resulting composite foam has the smallest average cavity size and narrower cavity size distribution, within all composite foams. This situation might be attributed to the increased amount of surface modifying groups which are responsible of establishing the compatibility between the emulsion phases and nanoparticles. In addition to all, the observable change of the pore sizes depending on the amount of nanoclay loading is also attributable to the emulsion stability as explained above.

Moreover, due to the increased porosity in the presence of nanoclay, density of the resulting composite foams was found to be lower than the neat foam (PHP) (Table 1). By reinforcing with nanoclay particles, the specific surface area was found to be increased by approximately 2 times as compared to the neat polyHIPE foam (PHP) for all samples (Table 1). The reasons for using clay nanomaterials are their high aspect ratio which enables large surface areas to interact with the polymers. Therefore, the increase in the specific surface area of the resulting polyHIPE foams can be attributed to the contribution of the nanoclay particles.

Table 1. Properties of neat polyHIPE and polyHIPE/NC-T composites.

Sample	NC-T (wt.%)	δ_{BET} (m^2/g)	$[C]_{SEM}$ (μm)	$[IP]_{BJH}$ (Å)	ρ_f (g/cm^{-3})
PHP	-	3.96	29.21 ± 2.86	17.51	0.79
PHP/NC-1	1	6.81	104.49 ± 6.49	35.04	0.29
PHP/NC-3	3	6.90	100.82 ± 6.44	31.37	0.24
PHP/NC-5	5	6.01	88.57 ± 6.79	13.34	0.21

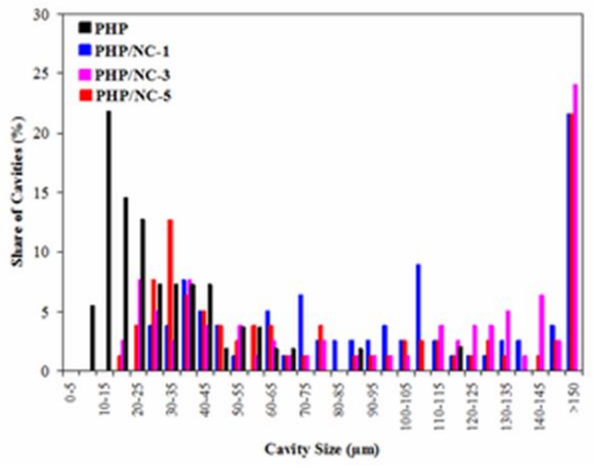

Figure 4. Distribution of cavities for neat polyHIPE (PHP) and polyHIPE/NC-T composites.

Stress-strain curves of the resulting foams are demonstrated in Figure 5 and compressive modulus and strength of each sample was summarized in Table 2. The similar curves obtained from compression tests exhibiting initial linear elasticity demonstrated classical foam behaviour. According to Figure 5, polyHIPE foams showed linear elastic behaviour at small strains, with a slope equal to the compressive modulus (ε_c). However, at higher loads the cavities of the foams begin to collapse. The characteristic maximum at the end of the linear elasticity region was used to determine the compressive strength (σ_c). The addition nanoclay improved compressive modulus as compared to neat polyHIPE foam (PHP) (Table 2). It was found that with the addition of 5 wt. % of nanoclay the compressive modulus increased the by ca. 55 %. In accordance with the compressive modulus, this sample has shown the maximum compressive strength (Table 2). Compressive strength increased by ca. 8 % with the addition of 5 wt. % of nanoclay. Moreover, increasing the nanoclay loading from 1 to 5 wt. % resulted in a significant increase of specific compressive modulus and specific compressive strength. This result can be accepted as the evidence of successful integration of the nanoclay particles in the polymer network due to the existence of surface modifier groups.

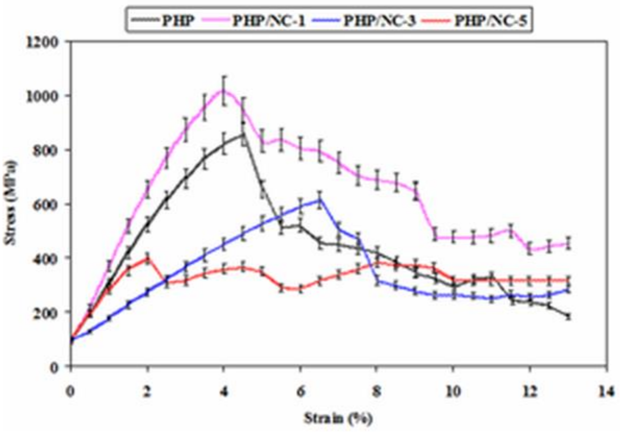

Figure 5. Stress-strain curves for the neat polyHIPE (PHP) and polyHIPE/NC-T composites.

Table 2. Mechanical properties of neat polyHIPE (PHP) and polyHIPE/NC-T composites.

Sample	Compressive modulus (ε_c, MPa)	Specific compressive modulus (MPa g^{-1} cm^3)	Compressive strength (σ_c, MPa)	Specific compressive strength (MPa g^{-1} cm^3)
PHP	18.2	23.04	0.38	0.48
PHP/NC-1	22.4	77.24	0.33	1.14
PHP/NC-3	25.0	104.17	0.38	1.58
PHP/NC-5	28.2	134.29	0.41	1.95

4. Conclusion

Emulsion templating is a versatile approach for the preparation of low-density macroporous foams. However, due to the highly porous structure resulting materials are usually suffered from low mechanical strength. On the other hand, in terms of emulsion stability it is not an easy process to prepare versatile foams by polymerizing functional monomers in emulsion templates due to the disadvantage arises from their polarity. However, most applications require functionality and high mechanical strength. In this respect, GMA is a versatile monomer due to its reactive epoxy ring which enables further functionalization reactions. But GMA-based foams produced by emulsion templating require the improvement of mechanical strength. Herein, by incorporating reinforcement nanoclay particles we were able to improve mechanical properties. The obtained composite foams possessed interconnected porous structure with average cavity sizes ranging between 104 μm and 88 μm. Due to the increased porosity, density of the composite foams were significantly lower than the neat foam sample. Thereby, we were able to increase specific compressive modulus and specific compressive strength ca. 483 % and 306 % by incorporating 5 wt. % of nanoclay as compared to neat polyHIPE foam.

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Author's Contributions

E. Hilal Mert: Drafted and wrote the manuscript. Supervised the experiment's progress, performed the analysis and interpreted the results.

Elif Berber Balta: Performed the experiments and analysis.

Ethics

There are no ethical issues after the publication of this manuscript.

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