EPOXY RESIN, VINYL COPOLYMER, AND RICE HUSK SILICA BASED TERNARY NANOCOMPOSITES: FABRICATION, MECHANICAL CHARACTERISTICS, AND THERMAL AGING

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Abstract

In this research, the bio-composites based on epoxy resin filled with nano-silica and vinyl copolymer were fabricated using diethylene triamine as a curing agent and casting method. The vinyl copolymer was synthesized from Hydroxyethyl Acrylate and Methacrylic acid using ammonium persulfate as an initiator. The bio-silica was extracted from rice husk via a simple technique of acid treatment and calcination. The chemical structure of poly(HEA-Co-MAA), silica was confirmed with help of the FTIR, and NMR-1H. The high-speed mechanical stirrer was used to obtain the good dispersion of silica and poly(HEA-Co-MAA) in epoxy resin before mixing and curing with Diethylenetriamine (DETA) hardener. The thermal stability of cured epoxy resin was enhanced with the presence of rice husk silica and poly(HEA-Co-MAA). The composite sample with 1 wt.% of bio-silica and 3 wt.% of poly(HEA-Co-MAA) showed the best mechanical properties with an improvement of up to 28.82%; and 35.36% of impact strength and tensile strength, respectively when compared with a pristine sample. The aging testing was also performed to investigate the effect of additive added on the thermal resistance of epoxy resin.

Keywords: *Epoxy resin; rice husk silica; bio-silica; bio-composite; poly(HEA-Co-MAA); mechanical properties; vinyl copolymer.*

1. Introduction

A rising number of publications relating to polymer nanocomposites has been realized in recent years as a result of its advantages such as high performance, and good toughness [1, 2]. Epoxy resin is the common matrix for the fabrication of nanocomposites due to its high bonding strength, easy fabrication, and high mechanical properties [3, 4]. However, due to the high crosslinking density, the cured epoxy resin seems to be brittle and easy to break by a low impact [5, 6]. So we need to improve the fracture toughness of epoxy resin to expand its applications. The use of liquid rubber to

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improve the fracture toughness of epoxy resin has been realized for a long time [7, 8]. However, along with enhanced fracture toughness, and ductility, the liquid rubber also induced a reduction in thermal properties and tensile strength [9, 10]. The finding of alternative reinforcements for liquid rubber has been focused on for recent years. Among them, both thermoplastic and inorganic nanoparticles have shown their role in the simultaneous improvement of fracture toughness, tensile strength, and thermal stability [11, 12].

In this work, both vinyl thermoplastic and rice husk silica were applied to modify the epoxy resin to enhance the impact strength, tensile strength, and thermal stability. The vinyl thermoplastic was directly synthesized from Hydroxyethyl Acrylate and Methacrylic acid using ammonia persulfate as an initiator. The name of the copolymer was also assigned as poly(HEA-Co-MAA). While, the silica was extracted from rice husk via acid pretreatment and calcination, and assigned as R-SiO_2. To the best of our knowledge, the simultaneous use of poly(HEA-Co-MAA) and R- SiO_2 for epoxy resin seem to be new. The effects of these additives on mechanical properties and thermal stability were investigated in detail. The thermal aging of the nanocomposite was also examined at a certain temperature and time.

2. Experiment

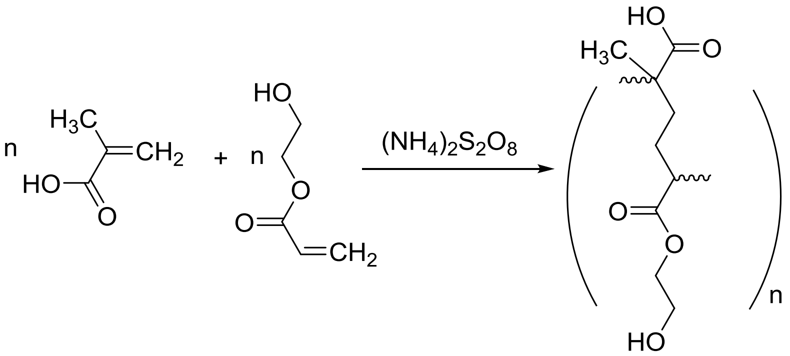
2.1. Materials

Epoxy resin (DER331, $\bar{M}_W$ = 760 g/mole) was supplied by DOW chemical company. Rice husk was supplied by the Vietnamese domestic-based industry. Hydroxyethyl Acrylate, Methacrylic acid, diethylene triamine (DETA), and concentrated HNO_3 were provided by Xilong Scientific Co., Ltd. (China).

2.2. Synthesis of the Vinyl copolymer

The polymerization reaction was performed in the three-neck round glass equipped with a thermometer using a magnetic stirrer bar. Firstly, 5.8 g of HEA was weighted, and stirred with 20 mL of distilled water before charging into the reaction media. Then, the solution of 4.3 g Methacrylic acid in 20 mL of distilled water was also slowly dropped. The mole ratio between two monomers is 1/1. While the solution of 1 g $NH_4S_2O_8$ in 20 mL distilled water was also slowly dropped into the three necks round glasses. The temperature was kept at 70°C for 5 h, and 300 rpm. Finally, the product was collected and washed again with distilled water three times to remove the residues before drying in a lab oven at 50°C for 3 h. The vinyl copolymer was assigned to poly(HEA-Co-MAA). The average molecular weight ($\bar{M}_W$) of the copolymer was determined by using an Ostwald viscometer at room temperature is 3056 g/mole [13].

The polymerization of the copolymer was established in the Scheme 1 as follows:



Scheme 1. Steps of Copolymer synthesization.

2.3. Rice husk silica fabrication

The nano silica was fabricated as same as our previous work [14]. Firstly, 200 g of rice husk was weighed and washed with distilled water three times to remove dust. Then the rice husk was immersed into one neck round glass containing 500 mL of HNO_3 2N solution and stirred at 50°C for 3 h. Then, the rice husk was washed with distilled water until pH = 7 before calcinating in a lab furnace at 800°C for 5 h to obtain the white power of silica. The silica was assigned as R-SiO_2. The size of R-SiO_2 is in the range of 40 to 80 nm [14].

2.4. Epoxy resin based Composite fabrication

100 g of epoxy resin was weighted, and charged into a 100 mL glass beaker. Then 1 g of R-SiO_2 and 1 g of poly(HEA-Co-MAA) were added into the epoxy before pre-mixing by hand using a glass stirring rod. The homogeneous mixture was obtained with help of a high mechanical stirrer at 2000 rpm for 4 h. This mixture was heated in a lab oven at 80°C for 2 h to remove all the formed bubbles. This mixture was then cooled to room temperature before mixing with the DETA curing agent. Finally, the nanocomposite was received by casting method in a steel mold at room temperature for one day before removing it for another test.

This method was applied to prepare another nanocomposite with different ratios of R-SiO_2 and poly(HEA-Co-MAA) as shown in Table 1.

Table 1. Detail of compositions of epoxy nanocomposite

Samples	**Epoxy resin (g)**	**RSiO$_2$ (g)**	**Poly(HEA-Co-MAA) (g)**	**DETA (g)**	**Curing temperature (ºC)**	**Curing time (h)**
M0	100	0	0	10	rt	24
M1	100	1	1	10	rt	24
M2	100	1	3	10	rt	24
M3	100	1	5	10	rt	24
M4	100	1	7	10	rt	24

2.5. Chemical structure confirmation

The chemical structure of poly(HEA-Co-MAA), and R-SiO$_2$ were analyzed by using a Spectrum Two FT-IR Spectrometer (PerkinElmer) with a wavenumber in the range of 400 to 4000 cm^{-1}.

The NMR-1H of poly(HEA-Co-MAA) was examined in the Nuclear magnetic resonance spectroscopy (NMR) 500 MHz (Bruker, Germany) using CDCl$_3$ as a solvent.

2.6. Mechanical analysis

The tensile property of nanocomposites was received in a universal testing machine in accordance with ISO 527-1993. The testing speed was set at 0.5 mm/min. The average values were calculated from three real values.

2.7. Thermal aging testing

The thermal aging testing was performed at 175°C for 48 h. After that, the aged samples were mechanically tested to determine the changes in mechanical properties. Moreover, the FTIR analysis was also applied to determine the changes in functional groups.

3. Results and discussion

The chemical structure of R-SiO$_2$ and poly(HEA-Co-MAA) were determined by the FTIR technique as seen in Fig. 1.

The characteristics of the Si-O-Si linkage of silica were realized at the peaks of 1069.07; 798; 448 cm^{-1}. There is no evidence of water trace in the FTIR spectrum of R-SiO$_2$ due to the calcination processing being processed at a very high temperature.

For the poly(HEA-Co-MAA), the peak OH stretching, and OH bending were realized at 3,424.06 cm^{-}1, and 1,296.85 cm^{-1}, respectively. The sharp peak at 1,296.85 cm^{-1} indicated the high density of hydrogen bonding. The peak at 1,704.96 cm^{-1} was assigned for C=O stretching. The characteristic of aliphatic CH stretching was at 2,959.71 cm^{-1}. The peaks at 1,638, and 935 cm^{-1} that were assigned for double bonds indicated that the monomers still existed in the copolymer.

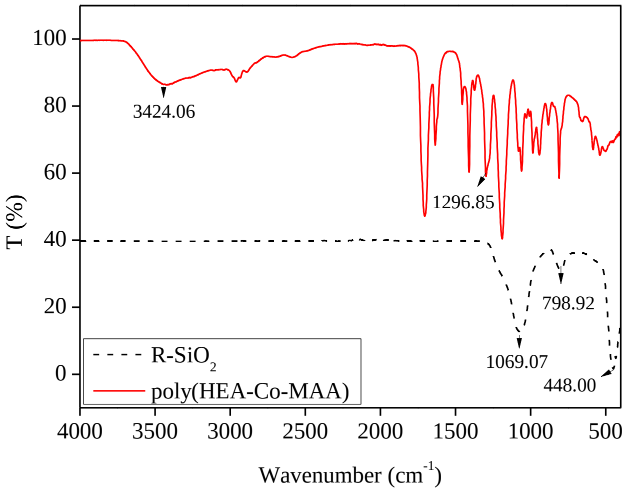


Fig. 1. FTIR of R-SiO$_2$, and poly(HEA-Co-MAA)

The NMR-H1 of poly(HEA-Co-MAA) was also analyzed as seen in Fig. 2. The peaks at 3.65; 3.85; and 4.3 ppm were assigned for the proton of a; b; and c position as seen in both Hydroxyethyl Acrylate and Methacrylic acid.

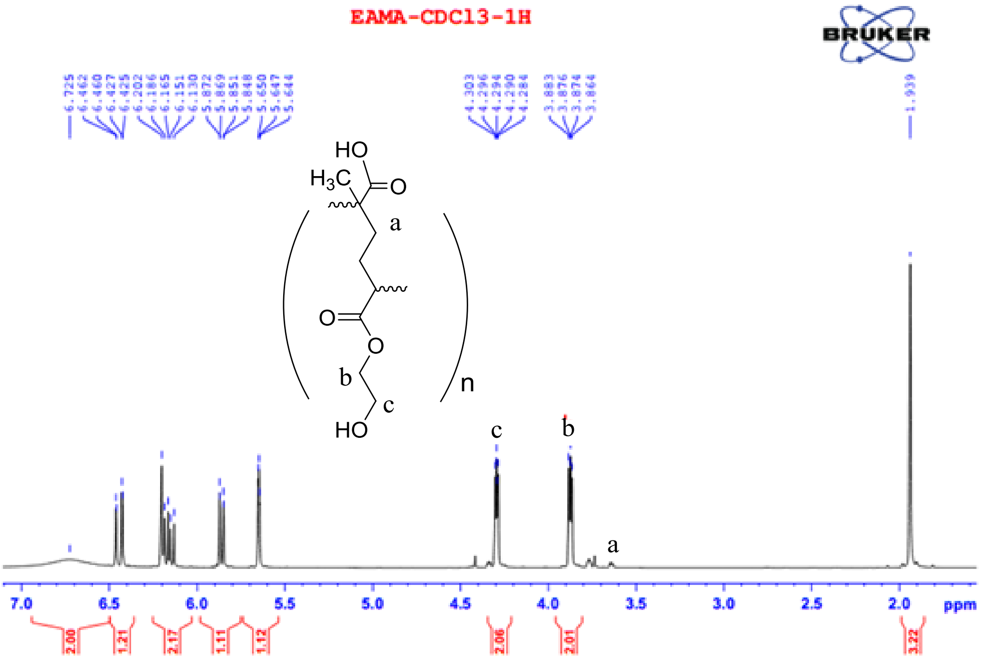


Fig. 2. NMR-1H of poly(HEA-Co-MAA).

The effect of additives added on the tensile strength and impact strength was shown in Table 2.

The cured pristine epoxy exhibited a low tensile strength of 35.43 MPa. The presence of additives added made the rising value of tensile strength. The maximum tensile strength of nanocomposite was asigned for the M3 sample with 1 phr of R-SiO_2 and 5 phr of poly(HEA-Co-MAA).

Table 2. Tensile and impact strenght of various epoxy samples

Samples	**Maximum stress (MPa)**	**Impact strength (kJ.m^{-2})**
M0	35.43 ± 0.12	70.25 ± 0.23
M1	36.53 ± 0.37	83.02 ± 0.31
M2	42.18 ± 0.31	90.49 ± 0.25
M3	47.96 ± 0.24	89.33 ± 0.17
M4	43.60 ± 0.18	1.78 ± 0.09

In the case of impact strength, the virgin epoxy sample showed a value of 70.25 kJ.m^{-2}. The impact strength also was improved by adding nanoparticles and thermoplastic. The maximum impact strength was realized for the M2 sample with increasing of 28.82% in comparison with the pristine sample. The improvement mechanism was counted by preventing the crack propagation of nanoparticles. While, the hydrogen bond and intermolecular force between thermoplastic resin and epoxy main chains was considered as main reason for producing plastic deformation [15]. These results also indicated that the influence of nanoparticles and thermoplastics on different mechanical properties was different.

To explain the obtained results above the fracture surfaces of various samples were analyzed as seen in Fig. 3.

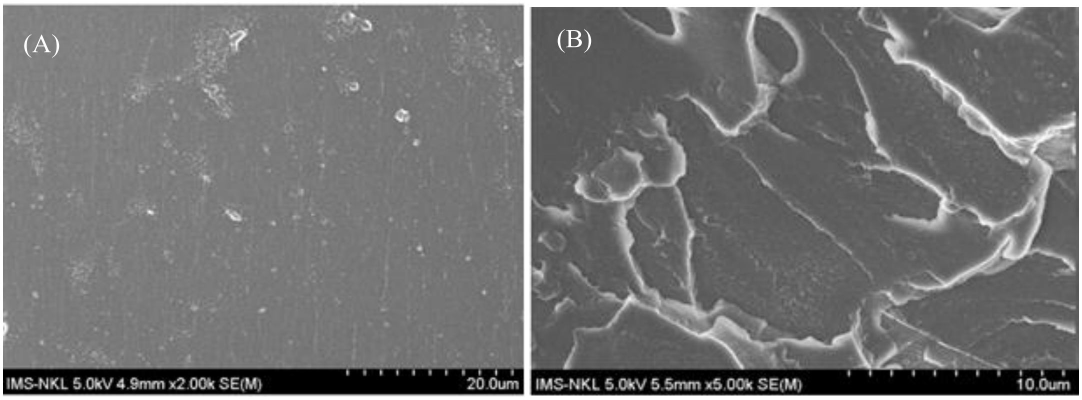


Fig. 3. SEM fracture surface of M0 and M3 samples.

The pristine sample exhibited its smooth surface while the surface of the M3 sample was rougher and rugger. The distribution of poly(HEA-Co-MAA) inside of nanocomposite was quite uniform. The nano silica inside the nanocomposite also contributed to the improvement of the mechanical properties of epoxy resin. The co-effect of these additives induced the plastic deformation of nanocomposite under external stress as an explanation of the improvement above.

The effect of additives on the thermal degradation of epoxy resin was shown in Fig. 4, and Fig. 5.

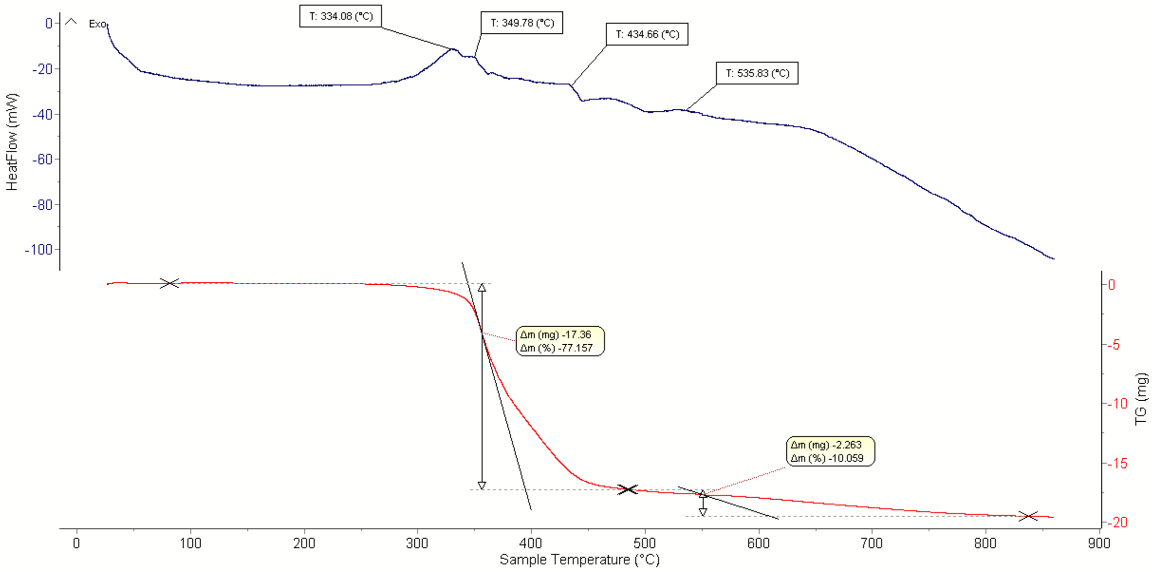


Fig. 4. TG-DTA/DSC of M0 sample.

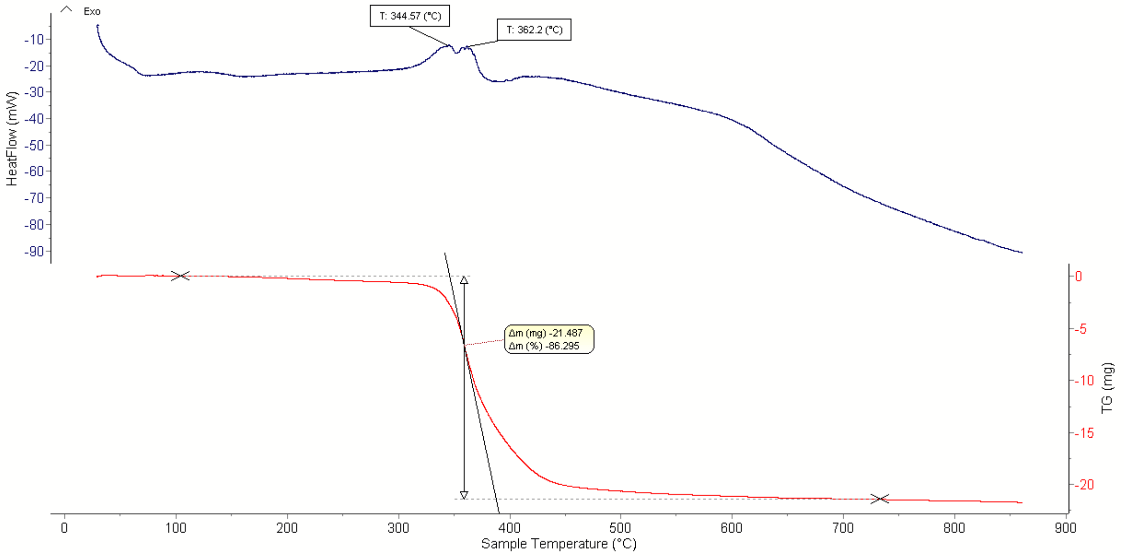


Fig. 5. TG-DTA/DSC of M3 sample.

The glass transition temperature of the M0 and M3 samples were 349.78°C and 362.24°C, respectively. The improvement of T_g indicated that the presence of additives added has a strong effect on the mobility of the epoxy chain. It also means that the movement of the epoxy main chain was restricted.

The influence of thermal aging on the tensile strength of the epoxy samples was presented in Table 3.

Table 3. Influence of thermal aging on tensile strength of epoxy sample

Samples	**Maximum stress (MPa)**
M0	26.03 ± 0.15
M3	36.56 ± 0.21

After processing of thermal aging the tensile strength exhibited a decreasing trend with a percent of 26.53% for the M0 sample and 23.76% for the M3 sample. The changes in the functional groups of epoxy samples after thermal aging were tested with help of the FTIR technique as seen in Fig. 6.

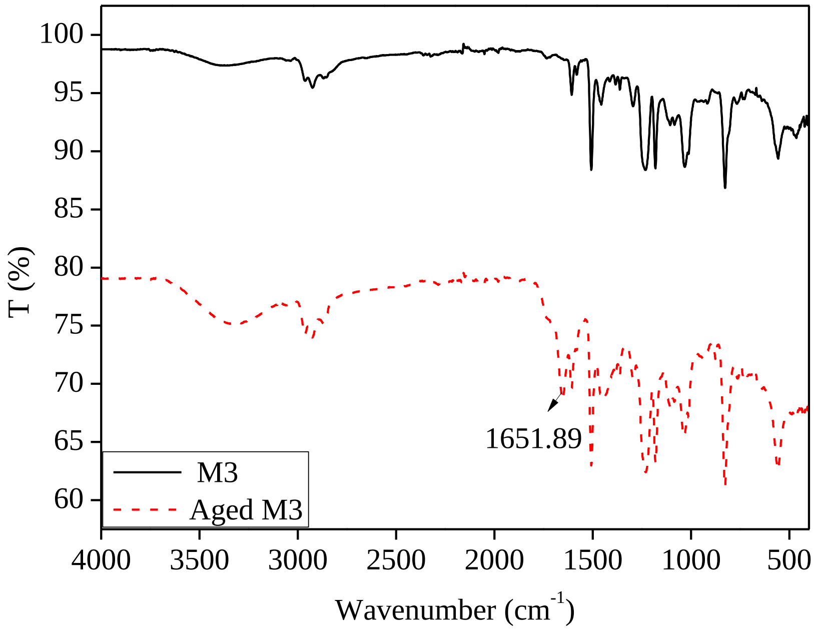


Fig. 6. FTIR of M3 and aged M3 samples.

The formation of quinone structure after thermal aging was realized at the peak of 1,651.89 cm^{-1} [16] when comparing the FTIR of aged M3 and M3 sample. The degradation of the main chain to form a quinone structure was considered as the main reason for reducing of the tensile strength above.

4. Conclusions

The ternary nanocomposites were fabricated from epoxy resin, rice husk silica, and thermoplastic resin. Simultaneous using of nanoparticle and thermoplastic induced the improvement in mechanical properties and thermal resistance. The broken surfaces of epoxy samples were investigated for the explaination of obtained results. The thermal aging induced the reduction in tensile strength and the formation of quinone structure after aging was considered as the main reason for this reduction.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

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VẬT LIỆU NANOCOMPOSITE BA THÀNH PHẦN TRÊN CƠ SỞ NHỰA EPOXY, COPOLYMER HỌ VINYL, VÀ SILICA TỪ VỎ TRẤU: PHƯƠNG PHÁP CHẾ TẠO, CÁC ĐẶC TRƯNG CƠ HỌC, VÀ LÃO HÓA NHIỆT

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Tóm tắt: Trong công trình này, vật liệu biocomposite trên cơ sở nhựa epoxy gia cường bằng nanosilica và copolymer họ vinyl đã được chế tạo sử dụng DETA làm chất đóng rắn bằng phương pháp đổ khuôn. Copolymer họ vinyl được tổng hợp từ Hydroxyethyl Acrylate và Methacrylic acid sử dụng $(NH_4)_2S_2O_8$ làm chất khơi mào. Nanosilica được tách từ vỏ trấu bằng phương pháp đơn giản kết hợp của xử lí bằng acid và nung. Cấu trúc hóa học của poly(HEA-Co-MAA), và nanosilica được xác định bằng phổ FTIR, và NMR-1H. Poly(HEA-Co-MAA), và nanosilica được phân tán vào nhựa epoxy bằng cách sử dụng máy khuấy tốc độ cao trước khi trộn hợp và đóng rắn với DETA. Sự có mặt của poly(HEA-Co-MAA), và nanosilica giúp cải thiện tính chất nhiệt của nhựa epoxy. Vật liệu nanocomposite với sự có mặt của 1 wt.% bio-silica và 3 wt.% poly(HEA-Co-MAA) thể hiện tính chất cơ lý tốt nhất với mức tăng độ bền va đập và độ bền kéo lên tới 28,82%; và 35,36%. Thử nghiệm lão hóa nhiệt được tiến hành nhằm nghiên cứu ảnh hưởng của chất biến tính tới khả năng chịu nhiệt của nhựa epoxy.

Từ khóa: *Nhựa epoxy; silica từ vỏ trấu; bio-silica; bio-composite; poly(HEA-Co-MAA); các tính chất cơ lý; copolymer họ vinyl.*

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