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Research Paper

An Investigation on the Manufacturing Process, Performance and Structure of Micro and Nano Thermoplastic Based Composite with Zeolite Filler

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Abstract

In this work, new nano and micro thermoplastic-based composites are prepared with zeolite filler, the method involves using zeolite in powder form, the preparation of zeolite powder from ores by crushing it into small-sized granules. The characteristics of the zeolite powder are determined. The physical properties and chemical composition (XRD) are evaluated before impeding it into the thermoplastic. Thermoplastics powder is added to the zeolite powder as granules in different sizes, the particles sizes ranging from the size of a millimeter to a nanometer. The manufacturing quality parameters are optimized at volume percentages of filler in the range of 20 to 25%, composite material is formed into molds. New Composite material is characterized by easy deformation into different shapes besides machineability. The characteristics of new composites such as SEM, EDX, and FTIR in absorption and transmission mode are evaluated and compared with the standard characteristics of Zeolite ores. The performance and characteristics of the new composite are completely different. The new composite is hard, solid, and does not absorb water.

Keywords

Zeolite, Thermoplastic, Composite, Filler, Micro-nano, Manufacturing process

1. Introduction

Compared to thermoset resins, there are two major advantages of thermoplastics in composites. The first is that many thermoplastic resins have an increased impact resistance compared to comparable thermoset materials [1]. In some instances, the difference is as high as 10 times the impact resistance. The other major advantage of thermoplastic composites is the ability to reform. When heat and pressure impregnate reinforcing fiber with a thermoplastic resin, physical rather than chemical change occurs. This allows the thermoplastic composites to be reformed and reshaped. Thus, the thermoplastic composite can be recycled at the end of its life. The polymer/filler interface plays an important role in determining the overall performance of thermoplastic composites [2].

Demands for these materials in a high-temperature service environment are constantly evolving (use of new polymers, weight reduction in automotive and building applications. Maximize the performance/cost ratio of your thermoplastics formulations by getting structured knowledge on fillers and the impact of their particle size/shape, and distribution on final performance [3,4]. Figure 1 shows the characteristics of thermoplastic-based composite.

Thermoplastic composite materials that were initially developed primarily for use in the aerospace industry are now attracting interest in new applications [5]. Structural & performance advantages and the continuous emergence of new & unique applications are some of the factors leading to an increased interest in nano and micro thermoplastic-based composite materials [6, 7].

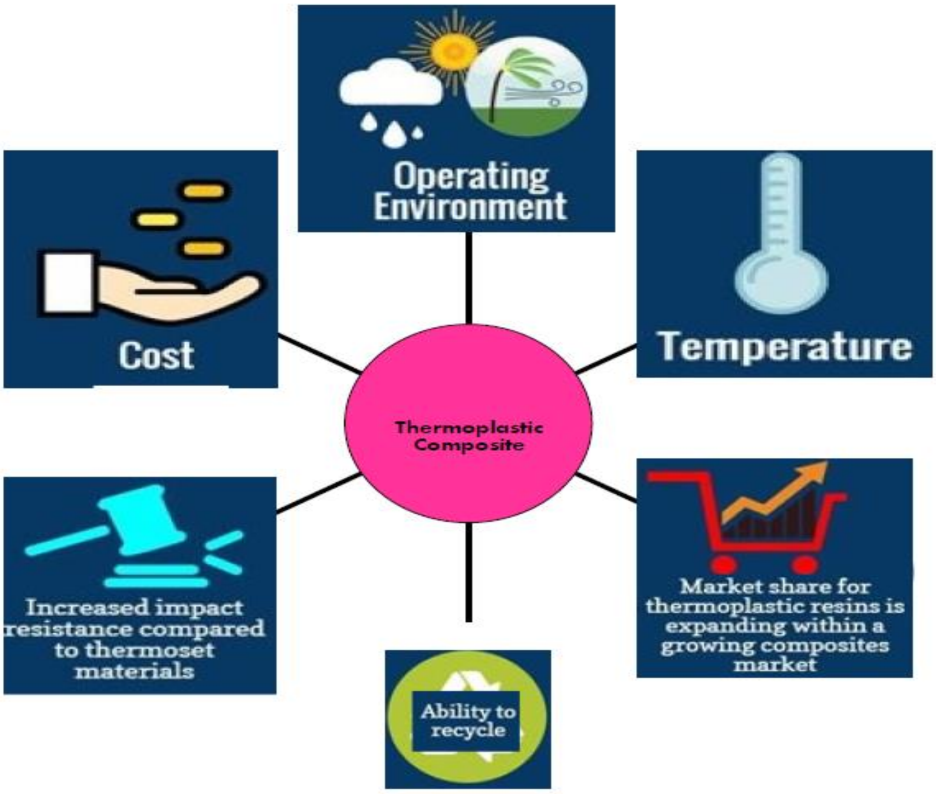


Figure 1. The characteristics of thermoplastic-based composite

Hence, applications such as energy, transportation, and construction that take advantage of more than one feature of carbon fiber are expected to be seen shortly. Utilizing a different unique feature that the composite materials provide [8].

The market share for thermoplastic resins is expanding within a growing composites market. For example, the automotive market is seeking new solutions for lighter vehicles and high-volume production [9]. Some applications of thermoplastic composites in the automotive industry include seat frames, battery trays, bumper beams, load floors, front ends, valve covers, rocker panels, and under-engine covers [10]. In many cases, thermoset resins, such as epoxies, are not satisfactory for these applications and, thus, there is an increased interest in the use of thermoplastic materials [11, 12].

The market of transportation components and parts is challenged by the growing requirement for high performance and lightweight elements, driven in large part by regulatory, sustainability pressure, and fuel efficiency demands [13].

However, the reduced weight should not come with a compromise on other properties like stiffness or processability. Today exists a wide range of solutions is likely to replace metal while ensuring an acceptable level of strength [14].

One pioneering self-reinforced material proposes a new combination of lightweight and strength while insuring impact resistance and aesthetic possibilities. It also offers the advantage of complete recyclability [15].

High heat plastics have been among the fastest-growing plastics products entering new & challenging applications (military/aerospace, automotive, electronics, down-hole oil & gas) traditionally served by metal, ceramics, or thermoplastics [16].

The automotive industry is a continuously growing market with challenges coming from end-users needs, environmental pressure, and innovations thanks to high technology. This combination leads to breakthroughs: vehicles powered by electrical energy and the next generation of vehicles will go even further with autonomous vehicles. The transformation from current structures to fully autonomous vehicles will be supported by new technologies to enhance driver support and also the unrestricted selection of lightweight components for better fuel efficiency [17].

Investments in lighter-weight technologies and sustainability of material recycling have never been this important but the reduced weight should not come with a compromise on other properties like stiffness or processability. Solutions like this self-reinforced composite fabric are standing out thanks to an efficient balance between lightweight and strength with the unique structure composed of highly oriented polypropylene-based fibers, weaved into a high-strength thermoformable fabric. The reinforced fabric technology can support innovations in electrical and autonomous vehicles [18, 19].

2. Experimental work

2.1 Materials (matrix)

The matrix is polymethyl metha acrylate (PMMA). Figure 2 shows the preparation of Polymethyl metha acrylate. It is thermoplastic prepared from monomer (methyl methacrylate) by additional polymerization; polymer was in the granule form with a 5 mm diameter. The main properties of PMMA are explained in Table 1.

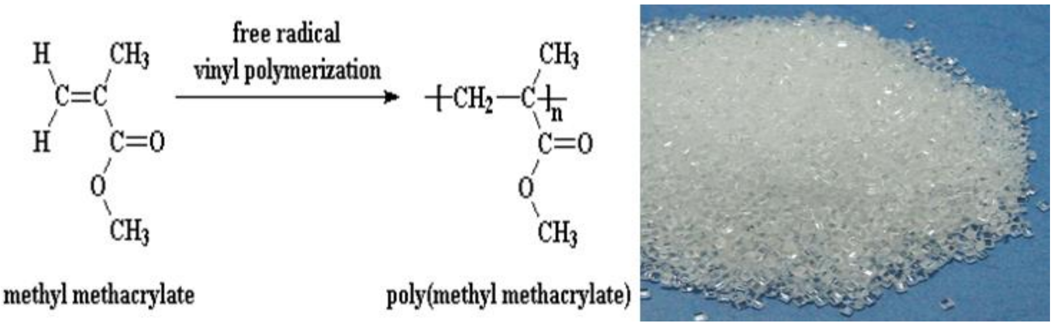


Figure 2. Preparation of Polymethyl metha acrylate

Table1. Physical properties of PMMA

Physical Properties	Value
Density	1.15-1.19 g/cm^3
Water Absorption	0.3-2%
Moisture Absorption at Equilibrium	0.3-0.33%
Linear Mould Shrinkage	0.003-0.0065 cm/cm
Melt Flow	0.9-27 g/10 min

2.2 Filler (Zeolite)

Hydrated aluminosilicate minerals that contain alkali and alkaline-earth metals. Figures 3 and 4 show the structure of zeolite powder used in this work while Tables 2 and 3 show its chemical composition and physical properties respectively

General properties of natural zeolite in powder form:

1. non-dusting
2. hard and resistance to attrition
3. non-clouding in liquid due to the absence of clays
4. good permeability
5. high density
6. high water retention

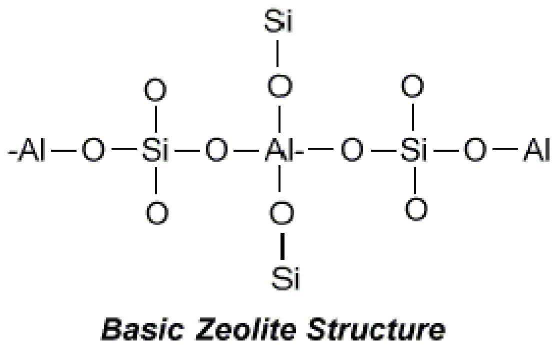


Figure 3. Structure of natural zeolite

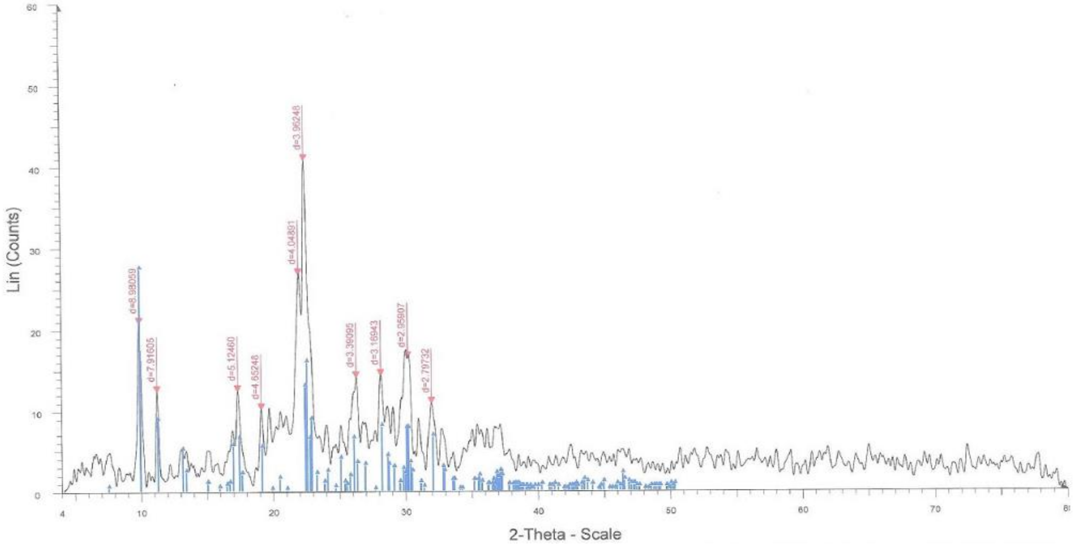


Figure 4. X.ray analysis of the natural zeolite

Table 2. Chemical composition of natural zeolite

Compound	Type	Percent%
K_2O	Cations	3.266
CaO		3.583
Na_2O		0.78
SiO_2	Major Elements (oxides)	62.22
Al_2O_3		11.096
Na_2O		0.78
MgO		0.599
CaO		3.583
Fe_2O_3		4.033
K_2O		3.266
TiO_2		0.339
ZrO_2		0.112
C1	Other elements (trace)	0.025
BaO		0.085
P_2O_5		0.033
ZnO		0.025
SrO		0.047
PbO		0.002
MnO		0.12
SO_3		0.035

Table 3. Physical properties of natural zeolite in powder form

Properties	Value	Unit
Bulk (particle) density	1.83	gr/Cm^3
Apparent (skeletal) density	2.377	gr/Cm^3
Over all surface area	89.82	m^2/gr
Porosity	27.8	%
Total pore area	35.836	m^2/gr
Average pore diameter	0.0181	μm
Solubility	7.38	%
Swelling index	2.52	
PH	6.8	
Humidity	6.75	%
L.O.I	13.6	%
Hardness	4	Moh scale
Grain size	6 mm <	
Non-toxid		
Non-combustible		
Loss on ignition		
Appearance color	Greyish-white	

2.3 Mixing & Sieving

The outcome of the two materials zeolite and PMMA after grinding are collected in the automatic sieve. Automatic mixing for thermoplastic in the powder form with different aspects ratio was done.

The amount of material required was calculated. The mixture moves to the final drying and mixing phase by laser irradiation. This is for guaranteeing the final drying of the two mixtures.

2.4 Manufacturing process

Plastic powders and natural zeolite were mixed in the solid-state. The mixture is heated at the required temperature, according to its components. Heating, compression, and cooling were done for the heated mixture. The heating rate depends on the type of the joining material, the heating rate depends on the type of the joining material.

Nanocomposite material is fabricated, the new composite material is distinguished with the lightweight and the ability to endure scratch and damping capacity compared with the natural zeolite it is also liable for the easy formation and distinctive with different colors and shapes. Figure 5 shows the manufacturing steps.

2.5 The manufacturing quality parameters

The manufacturing parameters were adjusted and the effect of temperature, pressure, and cooling rates were recorded. The design and test of the new system were evaluated. The nano-composite material consists of polymethyl metha acrylate as matrix reinforced with natural zeolite filler in powder form the manufacturing steps may be summarized in the following steps:

- Grinding of PMMA by electrical blinder-and control the grinding time to be less than 1.5 min to avoid temperature rise and agglomeration of particles after that use mesh < 300µm diameter for sieving.
- Zeolite have used in powder form.
- The two powders are mixed in a multi-speed mixture with continuous cooling to avoid agglomeration of particles.
- Heating the empty mold which is lubricated with heavy oil.
- The mixture is added to the hot mold.
- Compress the mixture with a hydraulic system with continuous heating and pressing.
- Holding the compress and heating until the heat is distributed uniformly
- Cooling the mold with water JET.
- Extract the final product by pressing.

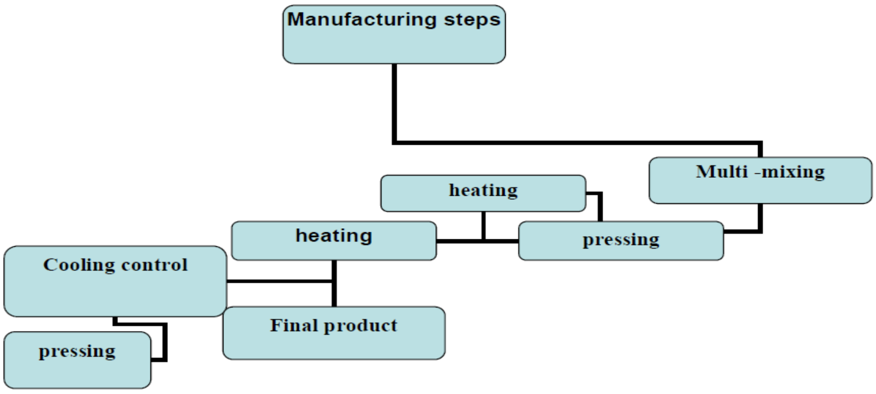


Figure 5. The manufacturing steps

2.6 Scanning Electron Microscope (SEM)

The specimens were examined by scanning electron microscope (SEM) operating at a nominal accelerating voltage of 30kv. Specimen preparation is very simply accomplished by cutting a thin slice of the specimen containing the surface of interest, chemical and electro etching were done at standard conditions, and the samples were inserted into the specimen chamber for direct examination of the structure.

2.7 Energy-dispersive X-ray "EDX"

The quantitative method of elemental analysis of the samples has been examined by SEM JSM-T200 at 25KV acceleration voltage, 20mm working distance, and magnification of 200x, (1peak omitted 0.02 KeV). Each value is at least an average of 2 or3 readings at least.

2.8 FTIR spectroscopic Analysis

The Fourier Transform Infrared (FTIR) analysis was carried out for samples Using FTIR Model Cary 630 FTIR spectrometer for both Qualitative and Quantitative for solid samples analysis produced by Agilent technologies Company, Samples were investigated in spectral range (wave number cm^{-1}) from $4000cm^{-1}$ to $400cm^{-1}$ without any treatment

2.9 XRD

The XRD technique is used to determine the mineralogical phases of the investigated limestone and clay as well as the prepared clinker. The limestone samples were prepared by fine grounding to 20 μm using HERZOG (Herzog Co., Germany) grinder, to minimize the effect of absorption and extinction of the x-ray beam. A rectangular type sample holder was used to pack about 0.2 gm of the examined sample. The sample holder is then fed into the PAN-Analytical X' Pert Pro MPD PW 3050/60 X-ray diffract meter, provided with a proportional digital counter and Nickel-filtered Cu-kα radiation at 40 kV and 30 mA, and scanned throughout 5 to 50° of 2θ at a scanning speed of 5°/min. The obtained XRD patterns were converted to a series of lattice spacing (Å) and identified by computer software "X'pert High Score" using ASTM cards of the International Center of Diffraction Data (ICDD 2006).

3. Results and discussion

The new green composite material with natural zeolite filler has morphology and properties completely different from natural zeolite. Table 4 shows the comparison between the properties of the new composite material and natural zeolite, while Figure 6 shows the shape of the new composite material and its appearances difference from the natural zeolite.

Figure 6. The final products of the new composite material

Table 4. Comparison between the new composite material and natural zeolite

No	Properties	Natural zeolite	Composite with zeolite filler
1	Hardness	4 Mohs scale	65 barcoul
2	Water absorption	High water absorption	No water absorption
3	Porosity	High	Very low
4	Water content	High moisture content	Free of water content
5	Wear rate	Very low	High
6	Dimension stability	Irregular shape	Dimensional stable
7	Resistance to compact (compression)	Low resistance	High resistance
8	Reaction with water	High water retention	Does not interact with water
9	Particle size	6 mm	150-300 μm

The structure and performance of the new composite material were analyzed by SEM, Figure 7 shows the structure of the new composite. In comparison with SEM images of natural zeolite powder in the literature and references (Appendix A). The random distribution of the zeolite particles in the PMMA matrix is clear, the very fine particles of zeolite powder are agglomerated as spots in the structure. This random distribution of the natural zeolite powder plays a significant role in the elimination of crack propagation. The matrix characteristics and manufacturing parameters eliminate micro-voids and water content, the change in the properties of composite in comparison with natural zeolite due to the change in the structure of composite and distribution of particles inside the thermoplastic matrix.

Green composite with zeolite filler is analyzed by Scanning Electron Microscopy coupled with Energy Dispersive X-Ray apparatus. The surface morphology and mineral contents of the zeolites were obtained, respectively. Figure 8 and Table 5 show the elemental analysis of the composite.

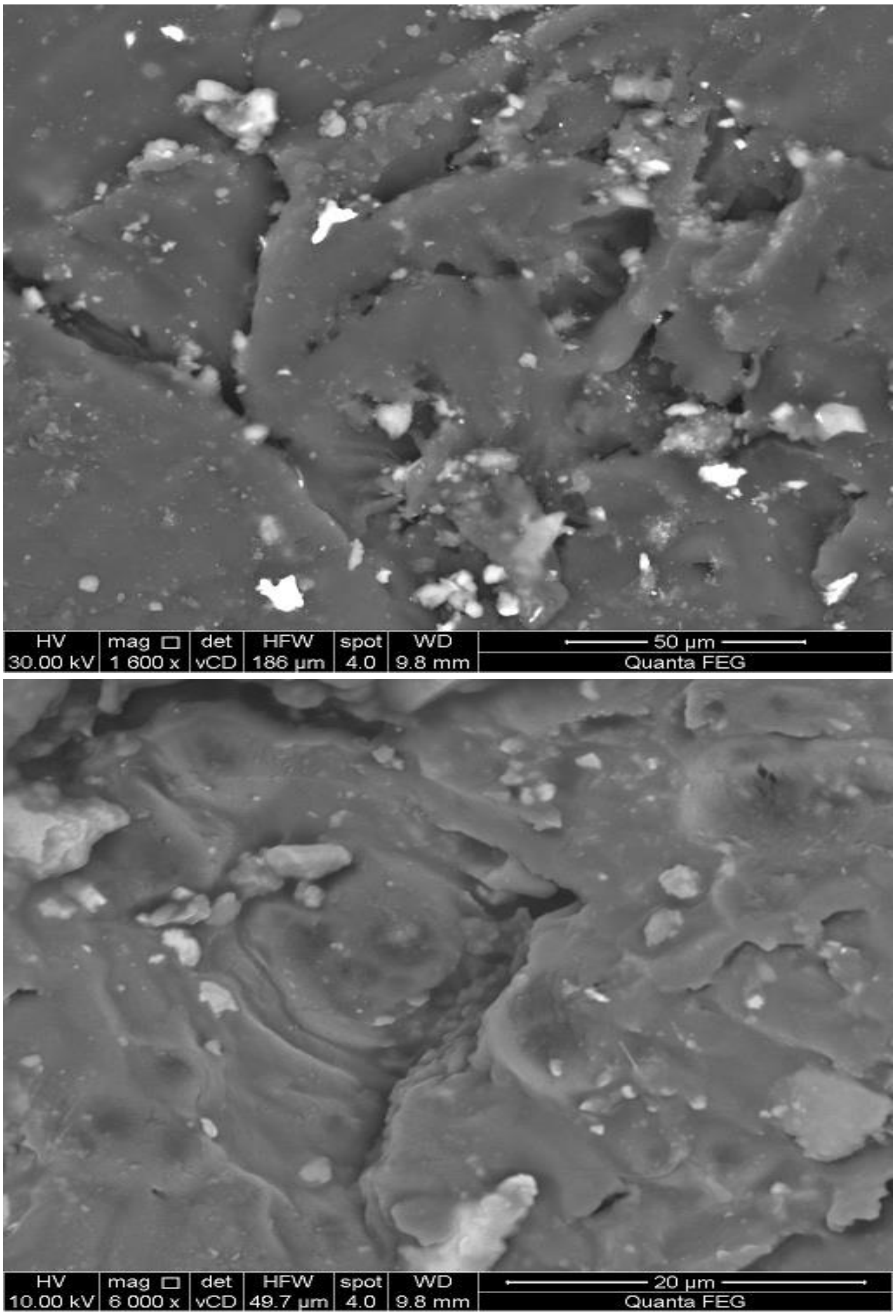


Figure 7. SEM of the new composite material with zeolite filler

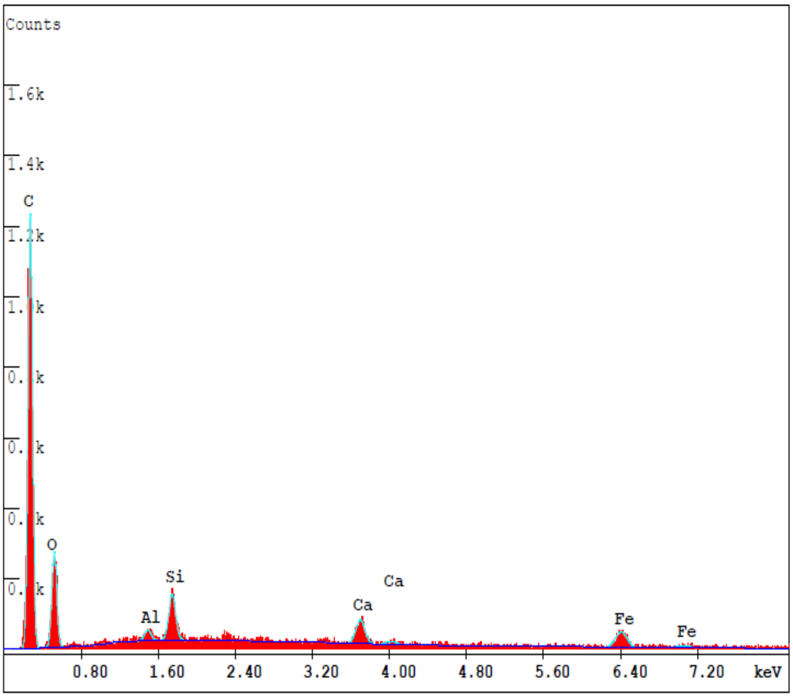
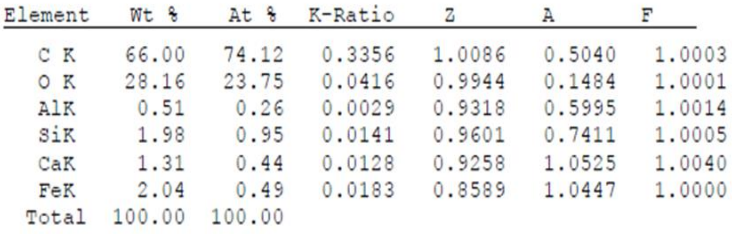


Figure 8. EDX analysis of the new composite material with zeolite filler

Table5. EDX analysis of the new composite material with zeolite filler



Element	Wt %	At %	K-Ratio	Z	A	F
C K	66.00	74.12	0.3356	1.0086	0.5040	1.0003
O K	28.16	23.75	0.0416	0.9944	0.1484	1.0001
AlK	0.51	0.26	0.0029	0.9318	0.5995	1.0014
SiK	1.98	0.95	0.0141	0.9601	0.7411	1.0005
CaK	1.31	0.44	0.0128	0.9258	1.0525	1.0040
FeK	2.04	0.49	0.0183	0.8589	1.0447	1.0000
Total	100.00	100.00				

When comparing the weight percent of the composite material with the natural zeolite samples in the references(appendix A), the carbon percentage is dropped in the composite to 66% weight percentages, while the oxygen weight percentage increased to 28%, while the silicon weight percentage almost unchanged. The main reason for this difference is related to the percentage of carbon and oxygen in the matrix (PMMA) as shown in Figure 2. The reactions during manufacturing at elevated temperatures lead to the formation of gases such as CO, CO_2, and other hydrocarbon gases which leads to the change in weight percentages of Carbon and oxygen in the final product.

When IR radiation is passed through the composite material with zeolite filler, some radiation is absorbed by the sample, and some passes through (transmitted) due to the properties of the PMMA matrix composite which is semitransparent material. In the origin, the gloss grade of PMMA (polymethyl metha acrylate) is used as a matrix due to the random distribution of opaque zeolite filler. So the new composite material is semi-translucent to opaque. The resulting signal at the detector is a spectrum representing a molecular ‘fingerprint’ of the sample. The usefulness of infrared spectroscopy arises because different chemical structures (molecules) produce different spectral fingerprints.

Zeolites are a class of microporous crystalline materials that have been widely used as adsorbents and ion exchangers. Zeolites contain uniformly sized pores and can display molecular recognition, discrimination, and organization properties. Zeolite characteristics depend on the nature of their pore openings and their hydrophobic or hydrophilic properties Figures 8 and 10 show the absorbance and transmission mode of the natural zeolite powder respectively.

Figures 9 and 11 show FT-IR the absorbance and transmission mode spectra of the new composite. In comparison with FT-IR spectra of natural zeolite in powder form, sharp peaks with strong absorptions were observed in the 1000 cm^{-1} region and these peaks are not similar to the FT-IR spectra of composite with zeolite filler which have more absorption bands observed at 1700 cm^{-1}, 1150 cm^{-1} and 1400 cm^{-1} these absorptions bands indicate the change occurs in the structure.

The micro void and porous structure of natural zeolite are changed to solid and confirmed the formation of strong bonds between the zeolite particles and matrix.

The broadband of zeolite also can be seen in both absorbance and transmission mode where the main bands associated with vibration transitions of PMMA matrix can be observed, However, it is possible to see some of them present attributed to C-C and C-H stretch vibrations of the matrix. Some peaks related to vibrations in bonds between matrix and filler were observed.

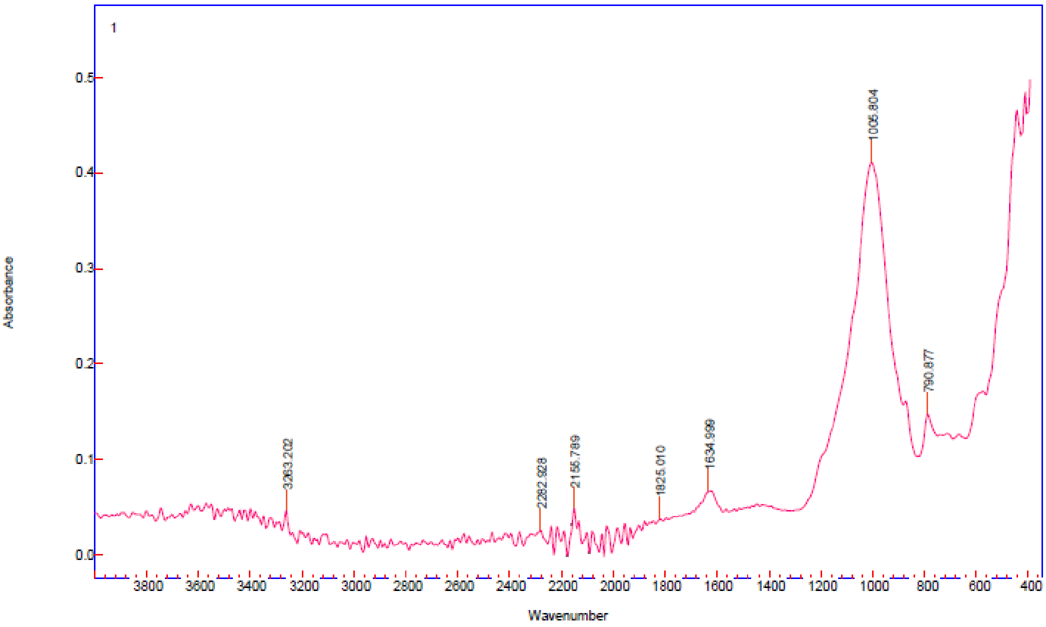


Figure 8. FTIR absorption spectrum of the natural zeolite (powder)

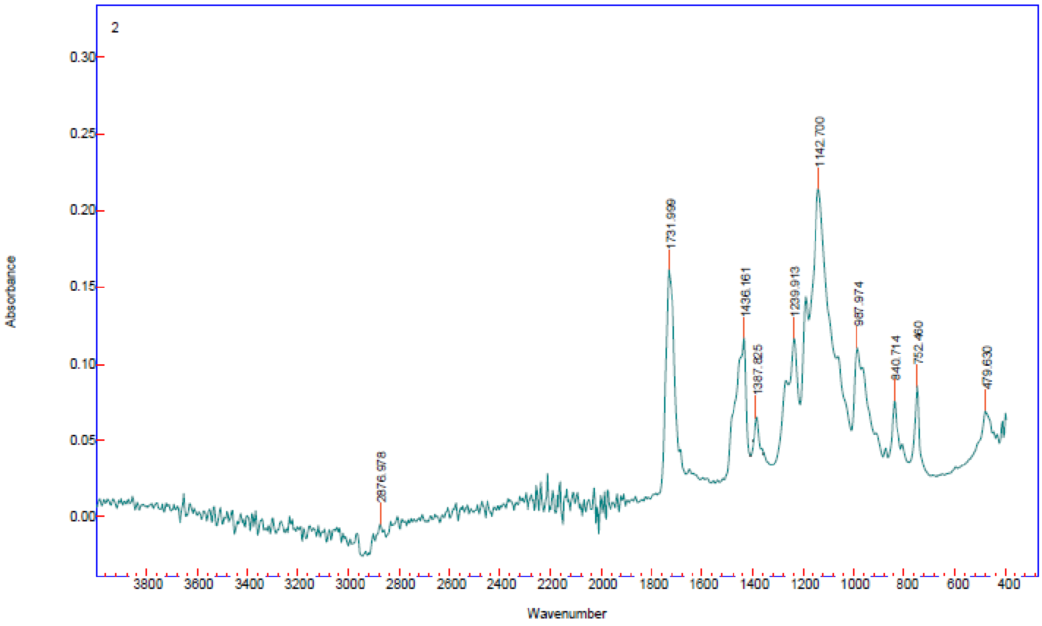


Figure 9. FTIR absorption spectrum of the composite with zeolite filler

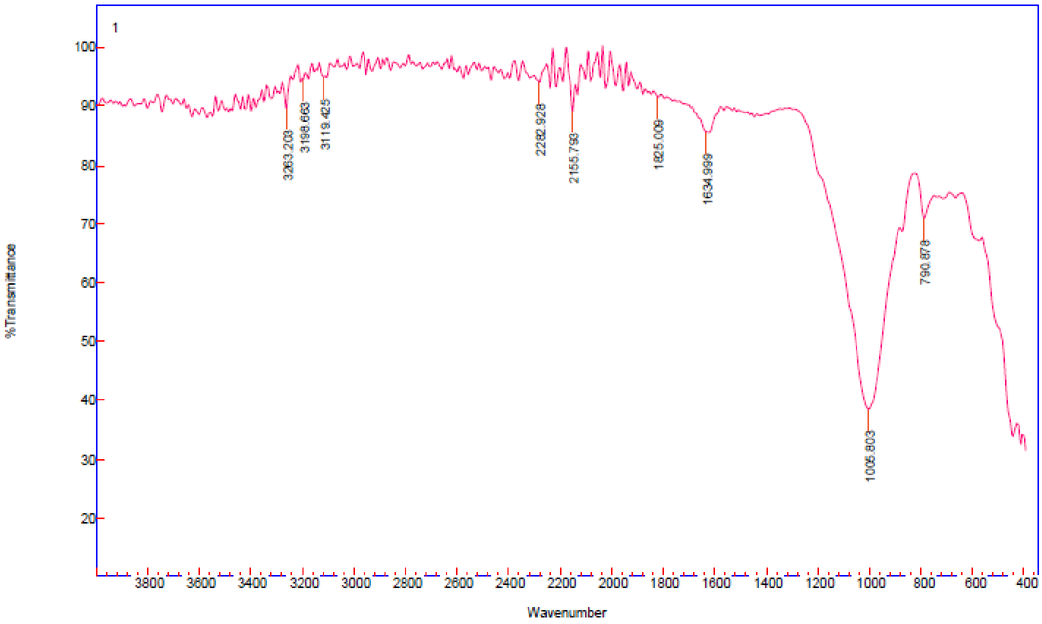


Figure 10. FTIR transmission spectrum of the natural zeolite (powder)

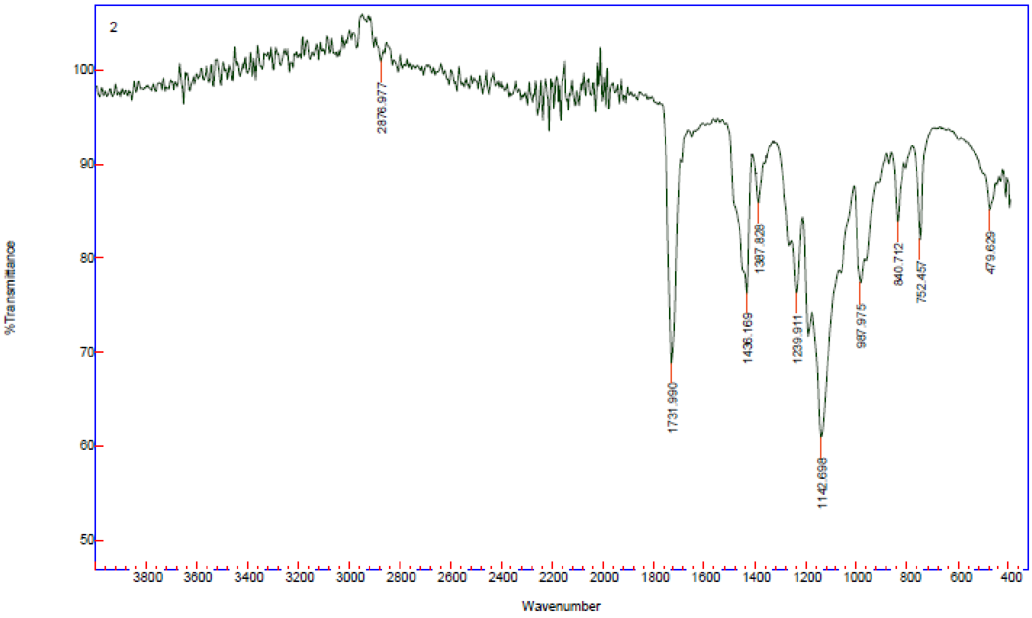


Figure 11. FTIR absorption spectrum of the composite with zeolite filler

4. Conclusion

1. The rising concern towards environmental issues and, on the other hand, the need for more versatile polymer-based materials has led to increasing interest in polymer composites filled with natural-organic fillers.
2. The new composite material has properties completely different from natural zeolite, it does not interact or absorb water, is compact, dimensionally stable with high resistance to wear and compression.
3. The manufacturing parameters such as temperature, pressure, heating, and cooling rates play a significant role in the new characteristics created in thermoplastic-based composite reinforced with natural zeolite filler.
4. The new composite can be further environment-friendly when the polymer matrix is biodegradable and comes from renewable sources as well
5. Several natural substances are not degradable and renewable, such as zeolites which are the right solution to environmental remediation.
6. Prospects are wide-ranging, especially in the field of functionalized nano-green composite materials for environmental remediation using very economical systems.
7. The development of a new economic manufacturing method for the manufacturing of green composite material creates new materials with superior characteristics.

5. References

[1] Koronis, G.,Silva, A. and Fontul, M. 2013. Green composites: A review of adequate materials for automotive applications. Composites Part B: Engineering.44 (1):120-127.

[2] Cai, Y., Zhao, L., and Zhang, Y. Composites Based Green Poly (L-Lactic Acid) and Dioctyl Phthalate: Preparation and Performance. Advances in Materials Science and Engineering: Green Composite Materials. Article ID 289725.

[3] Lee, S. M. 1989. Reference Book for Composites Technology, Volume I. CRC Press.

[4] Moliner, M., Martínez, C. and Corma, A. 2015. Multipore Zeolites: Synthesis and Catalytic Applications. Angewandte Chemie. 54(12):3560-3579.

[5] Liu, J. W., Chen, L. F., Cui, H., Zhang, J. Y., Zhang, L., Y. and Su, C. Y. 2014. Applications of metal-organic frameworks in heterogeneous supramolecular catalysis. Chemical Society Reviews. 43:6011–6061.

[6] Chughtai, A. H., Ahmad, N., Younus, H. A., Laypkovc, A. and Verpoort, F. 2015. Metal–organic frameworks: versatile heterogeneous catalysts for efficient catalytic organic transformations. Chemical Society Reviews. 44:6804-6849.

[7] He, H., Perman, J. A., Zhu, G. and Ma. S. 2016. Small. Metal-Organic Frameworks for CO_2 Chemical Transformations. 12(46): 6309-6324.

[8] Rimoldi, M., Howarth, A. J., DeStefano, M. R., Lin, L., Goswami, S., Li, P., Hupp, J. T. and O. K. Farha. 2017. Catalytic Zirconium/Hafnium-Based Metal–Organic Frameworks. ACS Catalysis, 7(2): 997–1014.

[9] Huang, Y-B., Liang, J., Wang, X-S. and R. Cao. 2017. Multifunctional metal–organic framework catalysts: synergistic catalysis and tandem reactions. Chemical Society Reviews. 46: 126-157.

[10] Guo, X., Feng, Y., Ma, L., Gao, D., Jing, J., Yu, J., Sun, H., Gong, H. and Zhang. Y. 2017. Phosphoryl functionalized mesoporous silica for uranium adsorption. Applied Surface Science. 402: 53-60.

[11] Falcaro, P., Ricco, R., Yazdi, A., Imaz, I., Furukawa, S., Maspoch, D., Ameloot, R., Evans, J. D., and Doonan, C. J. 2016. Application of metal and metal oxide nanoparticles at MOFs. Coordination Chemistry Reviews.307 (Part 2):237-254.

[12] Chen, Y-Z., Wang, Z. U., Wang, H., Lu, J., Yu, S-H., Jiang. H-L. 2017. Singlet Oxygen-Engaged Selective Photo-Oxidation over Pt Nanocrystals/Porphyrinic MOF: The Roles of Photothermal Effect and Pt Electronic State. Journal of the American Chemical Society. 139(5):2035–2044.

[13] Guisnet, M. and Gilson, J. 2003. Zeolites for Cleaner Technologies, Imperial College Press, London.

[14] Maxwell, I. E., Minderhoud, J. K., Stork, W. H. J. and van Veen, J. A. R. 1997. Handbook of Heterogeneous Catalysis. Wiley-VCH, Weinheim, Germany.

[15] Baerlocher, Ch., McCusker, L. B. and Olson, D.H. 2007. Atlas of Zeolite Framework Types. Elsevier Science; 6th edition.

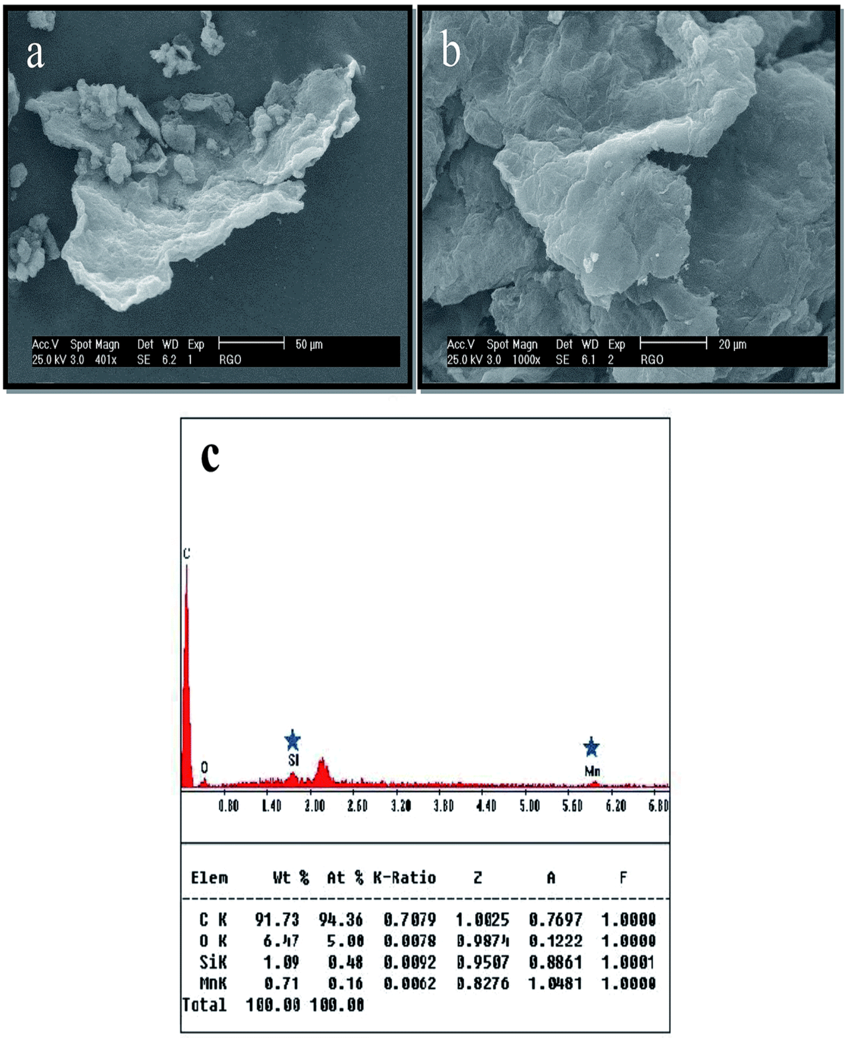
[16] Ferraz, E., Andrejkovicová, S., Velosa, A., Santos Silva, A. and Rocha, F. 2014 Synthetic zeolite pellets incorporated to air lime–metakaolin mortars: mechanical properties. Construction & Building Materials. 69: 243–252.

[17] Auerbach, S. M., Carrado, K. A. and Dutta, P. K. 2003. Handbook of zeolite science and technology. CRC Press, Boca Raton.

[18]First, E. L., Gounaris, C. E., Wei, J. and Floudas, C. A. 2011. Computational characterization of zeolite porous networks: An automated approach. Physical Chemistry Chemical Physics. 13(38): 17339–17358.

[19] Koningsveld, H. 2007. Compendium of Zeolite Framework Types (Building Schemes and Type Characteristics). Elsevier, Amsterdam.

Appendix -A-



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Elem      Wt %  At % K-Ratio    Z       A       F
-------------------------------------------------------
 C K     91.73  94.36  0.7079  1.0025  0.7697  1.0000
 O K      6.47   5.00  0.0078  0.9874  0.1222  1.0000
 SiK      1.09   0.48  0.0092  0.9507  0.8861  1.0001
 MnK      0.71   0.16  0.0062  0.8276  1.0481  1.0000
Total   100.00 100.00
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