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STRUCTURAL AND PERFORMANCE OF THERMOPLASTIC BASED COMPOSITE WITH ZEOLITE FILLER

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ABSTRACT

In this work, new nano and micro thermoplastic based composite is 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 powders are added to the zeolite powder as granules in different sizes, the particles sizes ranging from the size of a millimeter to nanometer. The manufacturing quality parameters are optimized at volume percentages of filler in the range 20 to 25 %, composite material is formed into molds. New Composite material is characterized by easy deformation into different shapes beside machine ability. The characteristics of new composite such as SEM, EDX, 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. The work ends with list of recommendation about the new field and expected application of Zeolite when using it as filler in thermoplastic based micro and nano composites.

KEYWORDS

Zeolite, thermoplastic, composite, filler, micro -nano, characteristics

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INTRODUCTION

Advantages of Thermoplastics over Thermosets in Composites

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. Polymer/filler interface plays an important role in determining the overall performance of thermoplastic composites [2-3].

Demands of these materials in high temperature service environment are constantly evolving (use of new polymers, weight reduction in automotive and building applications [4-5]. Maximize the performance/cost ratio of your thermoplastics formulations by getting structured knowledge on fillers and the impact of their particle size/shape, distribution on final performance [6-7]. Figure 1 shows the characteristics of thermoplastic based composite [3].

Thermoplastic composite materials that were initially developed primarily for use in the aerospace industry are now attracting interest in new applications [8-9]. Structural and performance advantages, continuous emergence of new & unique applications are some of the factors leading to an increased interest in nano and micro thermoplastic based composite materials [10-11].

Hence, applications such as energy, transportation, and construction that take advantage of more than one feature of the carbon fiber are expected to be seen in the near future. Utilize a different unique feature that the composite materials provide [13-14].

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 [15-16]. 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 [17]. 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 [18-19].

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 [20-21].

However, the reduced weight should not come with a compromise on other properties like stiffness or processability. Today, it exists a wide range of solutions likely to replace metal while insuring an acceptable level of strength [22-23].

One pioneering self-reinforced material proposes a new combination of lightweight

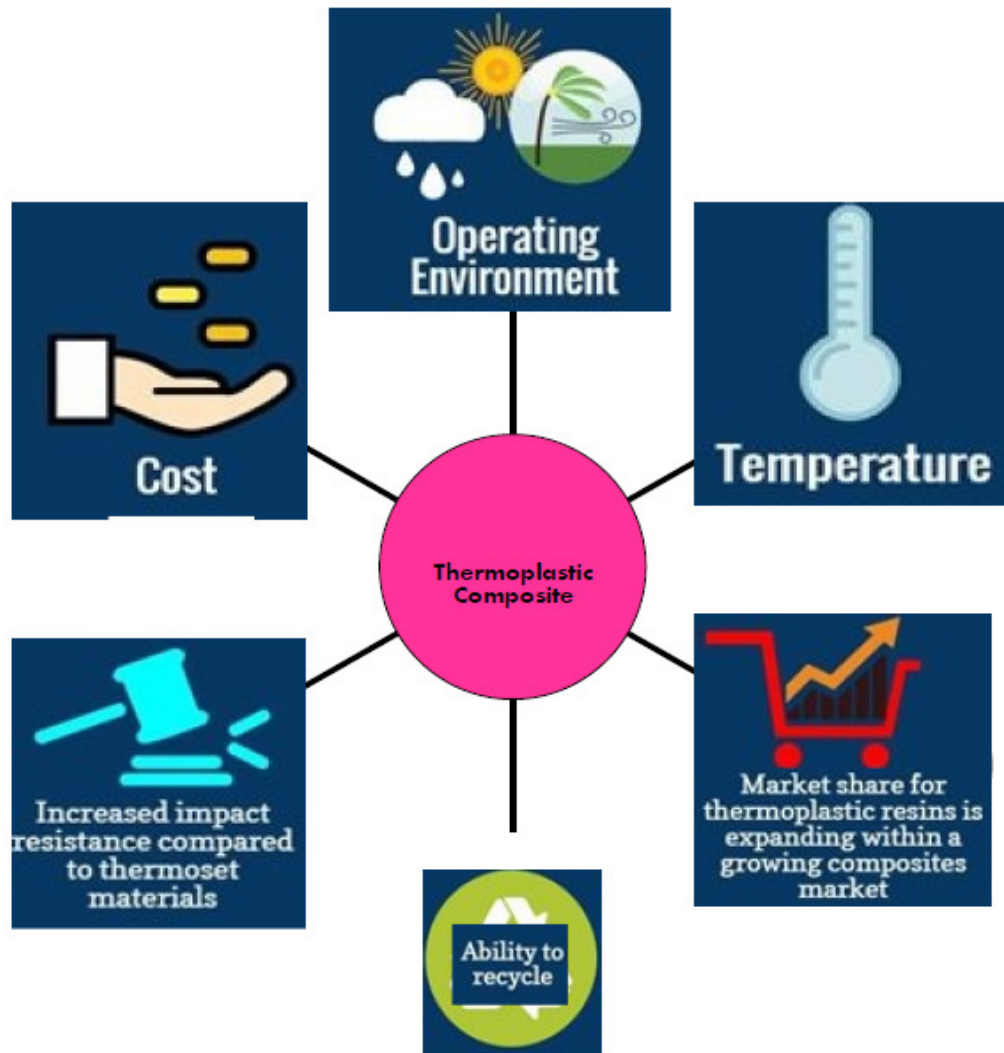


Fig.1. The characteristics of thermoplastic based composite [12].

and strength, while insuring impact resistance and aesthetic possibilities. It also offers the advantage of complete recyclability [24].

High heat plastics have been among the fastest growing plastics products entering new and challenging applications (military/aerospace, automotive, electronics, down-hole oil and gas) traditionally served by metal, ceramics or thermoplastics [25].

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 unrestricted selection of light-weight components for better fuel efficiency [26].

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 thermo formable fabric. The reinforced fabric technology is able to support innovations towards electrical and autonomous vehicles [27].

EXPERIMENTAL WORK

Materials (matrix)

The matrix is polymethyl metha acrylate (PMMA. Figure 4 shows preparation of Polymethyl metha acrylate. It is thermoplastic prepared from monomer (methyl methacrylate) by additional polymerization; polymer was in the granule form with 5mm diameter. The main properties of PMMA are explained in Table 1.

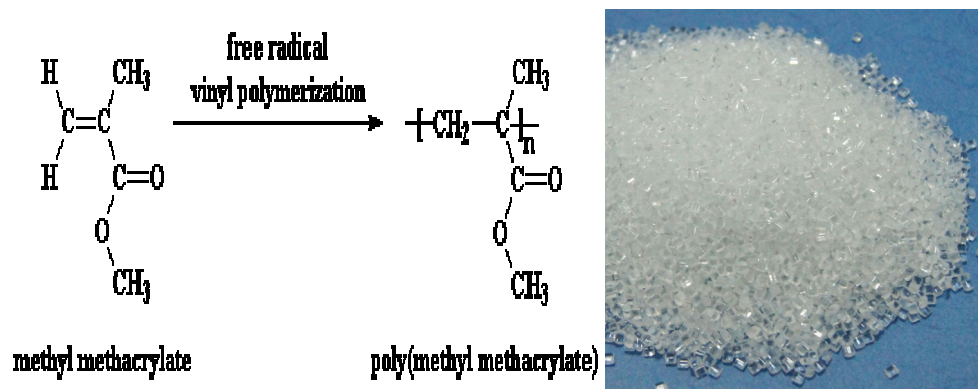


Fig.2. preparation of Polymethyl metha acrylate.

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

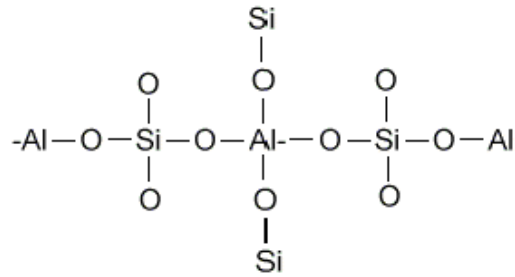
Filler (Zeolite)

Hydrated aluminosilicate minerals that contain alkali and alkaline-earth metals. Figure (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 absence of clays
4. good permeability
5. high density
6. high water retention



Basic Zeolite Structure

Fig. 3. Structure of natural zeolite.

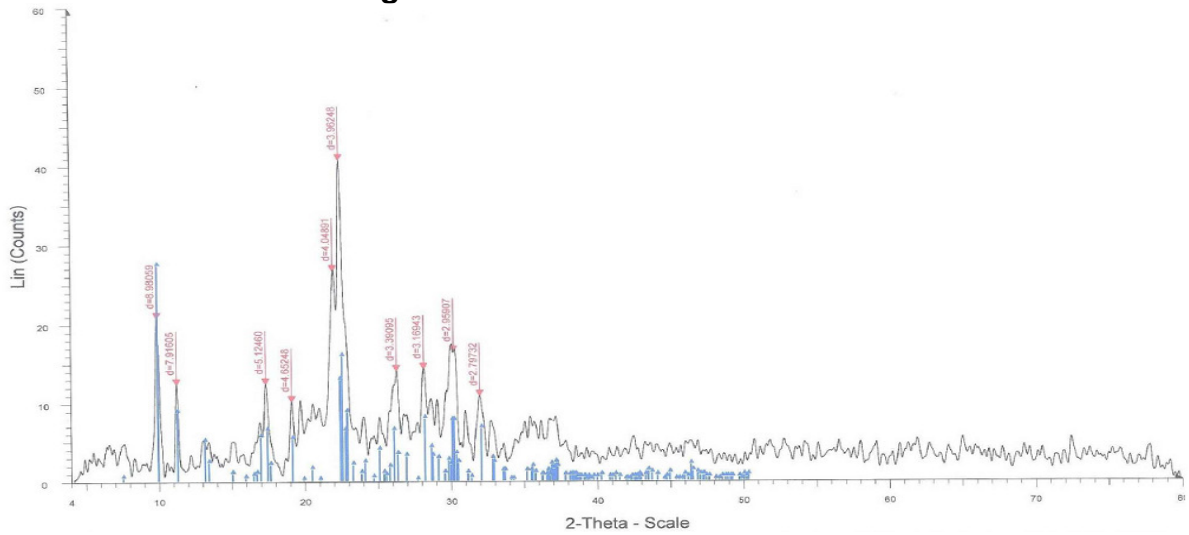


Fig. 4. X-ray analysis of the natural zeolite.

Table 2. Chemical composition of natural zeolite.

Compound	Type	Percents %
K₂O	Cations	3.266
CaO		3.583
Na₂O		0.780
SiO₂	Major Elements (oxides)	62.22
Al₂O₃		11.096
Na₂O		0.78
MgO		0.599
CaO		3.583
Fe₂O₃		4.033
K₂O		3.266
TiO₂		0.339
ZrO₂		0.112
Cl		Other elements (trace)
BaO	0.085	
P₂O₅	0.033	
ZnO	0.025	
SrO	0.047	
PbO	0.002	
MnO	0.120	
SO₃	0.035	

Table 3. Physical properties of natural zeolite in powder form.

Properties	Value	Unit
Bulk (particle) density	1.83	gm/cm ³
Apparent (skeletal) density	2.377	gm/cm ³
Over all surface area	89.82	m ² /gm
porosity	27.80	%
Total pore area	35.836	m ² /gm
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	6mm <	
Non toxic		
Non combustible		
Loss on ignition		
Appearance color	Greyish-white	

Mixing and sieving

The outcome of the two materials zeolite and PMMA after grinding are collected 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.

Manufacturing Process

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

Nano composite material is fabricated, the new composite material is distinguished with the light weight and the ability to endure scratch and damping capacity comparing 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.

The manufacturing quality parameters

The manufacturing parameters were adjusted and the effect of temperature, pressure and cooling rates were recorded. Design and test of the new system were evaluated. The nano-composite material consists of poly methyl 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.

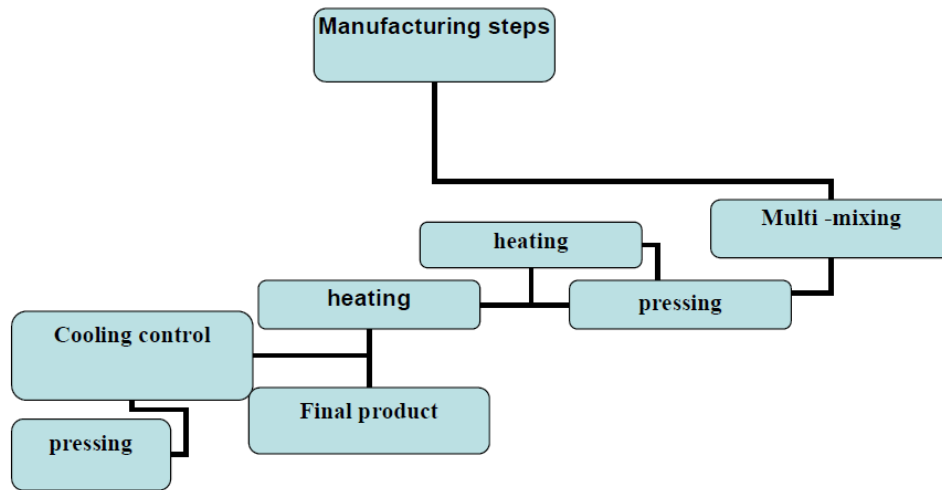


Fig. 5. The manufacturing steps.

- Mixing of the two powders in multi speed mixture with continuous cooling to avoid agglomeration of particles.
- Heating the empty mold which is lubricated by heavy oil.
- The mixture added to the hot mold
- Compress the mixture with (5:10 ton) hydraulic system with continuous heating and pressing.
- Holding the compress and heating until the heat distributed uniformly
- Cooling the mold with water JET.
- Extract the final product by pressing.

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, the samples were inserting into the specimen chamber for direct examination of the structure.

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 200X, (1peak omitted 0.02 KeV). Each value is at least an average of 2 or 3 readings at least.

FTIR spectroscopic Analysis

The Fourier Transform Infrared (FTIR) Analysis were 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

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 grinding to 20 μm using HERZOG (Herzog Co., Germany) grinder, to minimize the effect of absorption and extinction of the x-ray beam. 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 diffractometer, provided with a proportional digital counter and Nickel-filtered Cu- α radiation at 40 kV and 30 mA, and scanned over an interval of 5 - 50° 2 θ 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 HighScore" using ASTM cards of International Center of Diffraction Data (ICDD 2006).

RESULTS AND DISCUSSION

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



Fig. 6. The final products of new composite material.

Table 4. Comparison between 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	Particles size	6mm	150-300μm

The structure and performance of the new composite material were analyzed by SEM, Figure 7 shows the structure of new composite in comparison with SEM images of natural zeolite powder in the literatures 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 the significant role in the elimination of the 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.

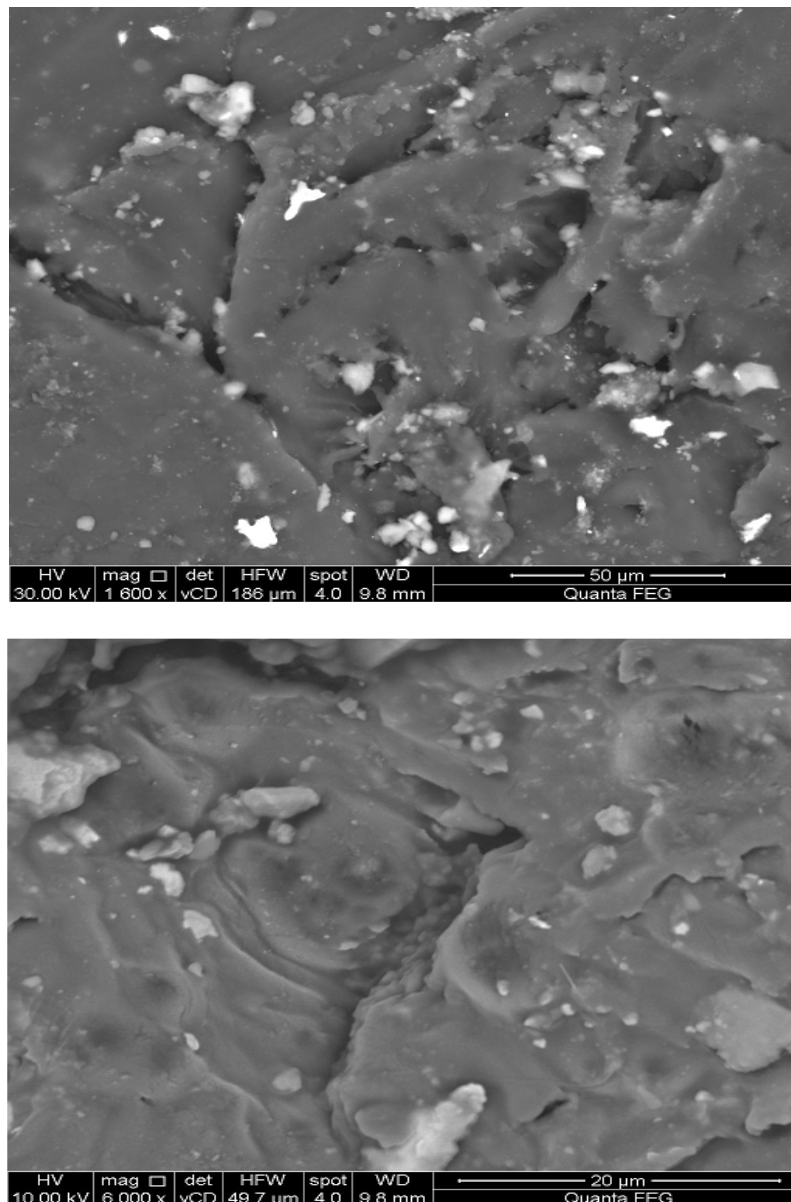


Fig. 7. SEM of the new composite material with zeolite filler.

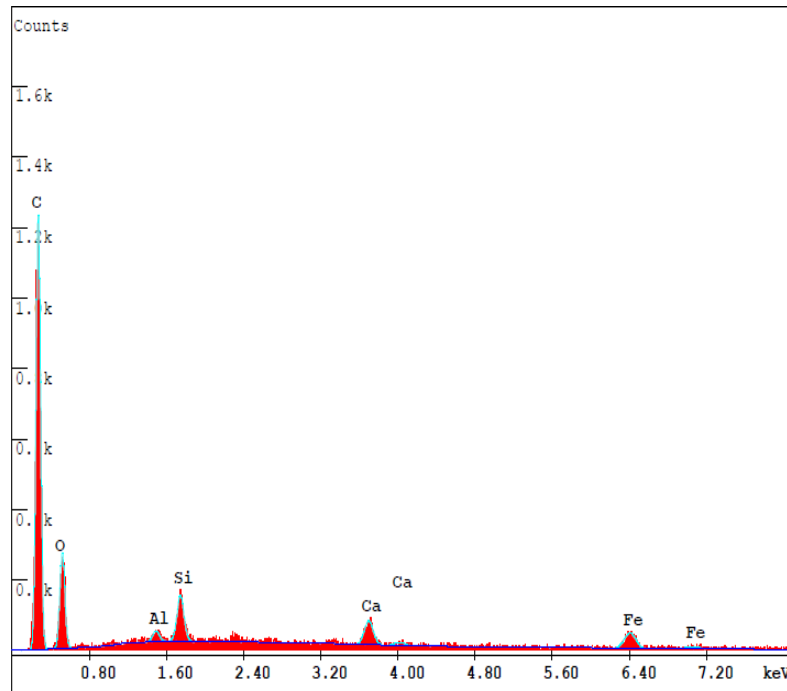


Fig. 8. EDX analysis of the new composite material with zeolite filler.

Table 5. 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 percentages is dropped in the composite to 66% weight percentages, while the oxygen weight percentage increase to 28%, while the silicon weight percentage almost unchanged. The main reason of this difference related to the percentage of carbon and oxygen in the matrix (PMMA) as shown in Fig. 2. The reactions during manufacturing at elevated temperature leads to the formation of gases such as Co, Co₂ 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 semi transparent material. In the origin the gloss grade of PMMA (polymethyl metha acrylate) is used as matrix due to 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 micro-porous 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 9 and 11 show the absorbance and transmission mode of the natural zeolite powder, respectively.

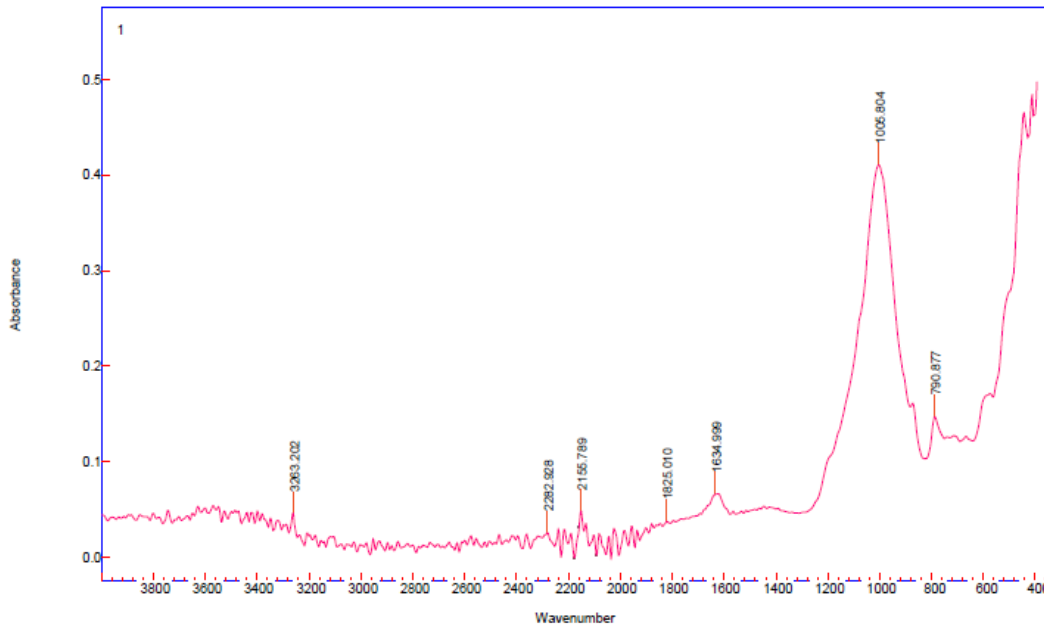


Fig. 9. FTIR absorbance spectrum of the natural zeolite (powder).

Figures 10 and 12 show FT-IR the absorbance and transmission mode spectra of new composite. In comparison with FT-IR spectra of natural zeolite in powder form, sharp peaks with strong absorptions were observed at 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 give indication about the change occur 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.

Broad band 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.

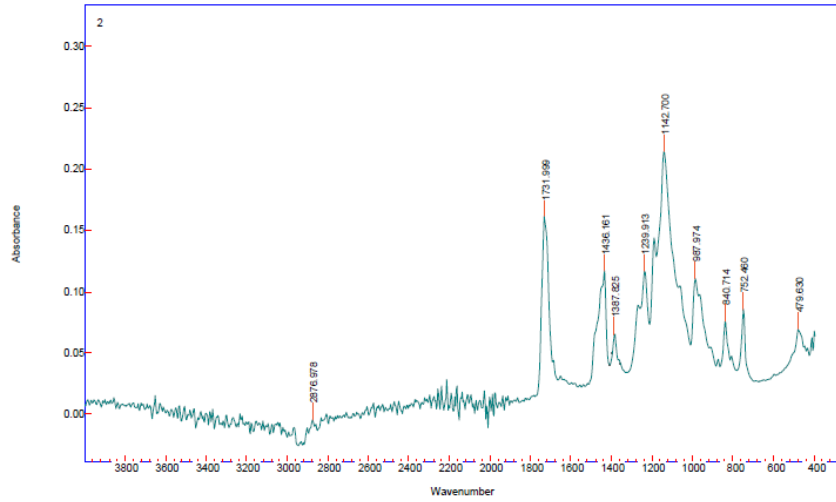


Fig. 10. FTIR absorption spectrum of the composite with zeolite filler.

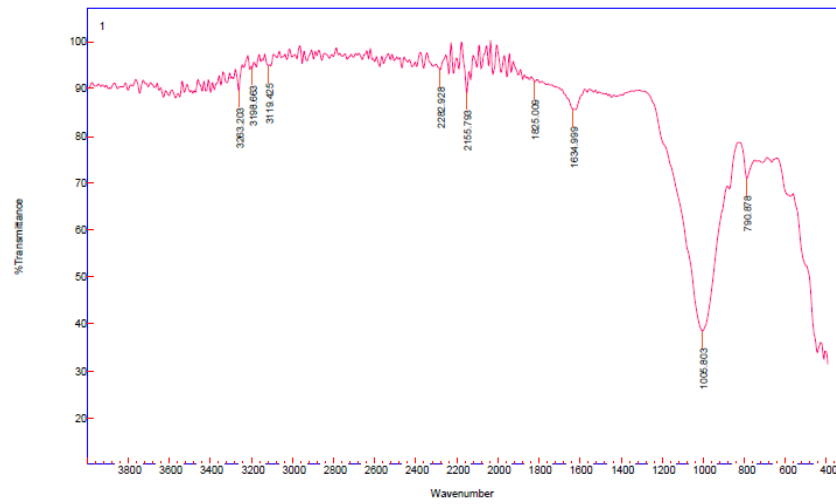


Fig. 11. FTIR transmission spectrum of the natural zeolite (powder).

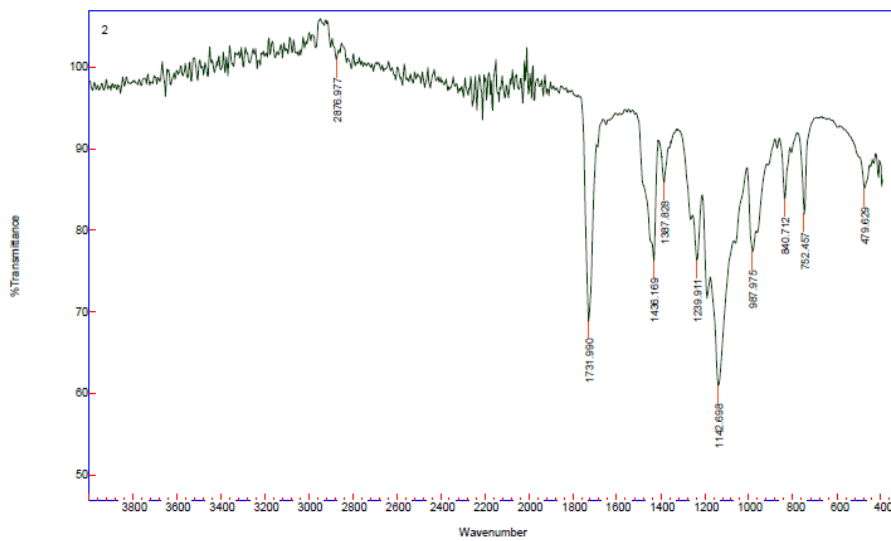


Fig. 12. FTIR absorption spectrum of the composite with zeolite filler.

CONCLUSIONS

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 about 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, compact, dimensionally stable with high resistance to wear and compression.
3. The manufacturing parameters such as temperature, pressure, heating and cooling rates play 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. There are several natural substances which are not degradable and renewable, such as zeolites that are the right solution to environmental remediation.
6. Future 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 new economic manufacturing method for manufacturing of green composite material creates new materials with superior characteristics.

RECOMMENDATION

The mechanical, chemical and electrical characteristics of the new composite material with zeolite filler should be studied to identify all possible applications of the new green composite.

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Appendix –A:

