



Article Preparation of Melamine Formaldehyde Foam and a Melamine-Formaldehyde-Organo-Clay Nanocomposite and Hybrid Composites

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Abstract: Mineral fillers can be added to thermoset polymers to improve thermal conductivity and deformation behavior, shrinkage, impact strength, dimensional stability and molding cycle time. This study aims to prepare various hybrid composites (MFHCs) using melamine formaldehyde foam (MF), a melamine formaldehyde organo-clay nanocomposite (MFNC) and also pumice as primary filler, and gypsum, kaolinite and a hollow glass sphere as secondary filler. It also focuses on the study of some mechanical properties and thermal conductivities, as well as their microscopic and spectroscopic characterization. For this, firstly, organo-clay was prepared with the solution intercalation method using montmorillonite, a cationic surfactant and long-chain hydrocarbon material, and then was produced using a melamine formaldehyde nanocomposite with in situ synthesis using a melamine formaldehyde pre-polymer and organo-clay. Finally, hybrid composites were prepared by blending various minerals and the produced nanocomposite. For morphological and textural characterization, both FTIR spectroscopy and XRD spectra, as well as SEM and HRTEM images of the raw montmorillonite (MMT), organo-montmorillonite (OMMT), pure polymer (MF) and prepared hybrid composites, were used. Spectroscopic and microscopic analyses have shown that materials with different textural arrangements and properties are obtained depending on effective adhesion interactions between polymer-clay nanocomposite particles and filler grains. Mechanical and thermal conductivity test results showed that melamine-formaldehyde-organo-clay nanocomposite foam (MFCNC) exhibited a very good thermal insulation performance despite its weak mechanical strength (λ : 0.0640 W/m K). On the other hand, among hybrid composites, it has been determined that the hybrid composite containing hollow glass beads (MFCPHHC) is a material with superior properties in terms of thermal insulation and mechanical strength (λ : 0.642 W/m K, bulk density: 0.36 g/cm³, bending strength: 228.41 Mpa, modulus of elasticity: 2.22 Mpa and screw holding resistance: 3.59 N/mm²).

Keywords: mineral-filled composites; nanocomposite; organo-clay; melamine formaldehyde resin; thermal insulation; mechanical strength; hybrid composites

1. Introduction

Composites, which have unique advantages that their components cannot meet, are developed to produce changes according to certain requirements without changing the basic functions of the materials. They are heterogeneous materials with wide application areas such as construction, aviation, automotive, thermal conductivity, electrical and thermal insulation and packaging [1–3]. According to their main matrices, composites are divided into three types as a metal, ceramic and polymer matrix. Due to critical factors such as low density and cost, polymer matrix composites have become increasingly popular, especially in the automotive and aerospace fields. The polymer matrix is also classified as thermoplastic and thermoset matrices, and thermoset polymers have some advantages



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). over thermoplastics such as ease of manufacturing, faster curing, flame retardancy and protection of structural integrity against heating. While nylon, cellulose acetate, polystyrene, polypropylene, polyethylene, polycarbonate, polyvinyl chloride, polyether-ether ketone and acrylonitrile-butadiene-styrene are generally used as a thermoplastic matrix, phenolic, epoxy, polyester, polyimide and polyurethane resins are used as thermosetting matrices [4]. The most important advantage of thermoset matrices is ease of processing and this encourages their use in critical industries. However, the most obvious disadvantages are that they cannot be used to obtain other shapes after curing and that they require high temperature and pressure for molding [5,6]. Many reinforcements can be added to the matrix to improve the properties of brittle thermoset resins. The reinforcements can be long and short fibers, particles and flakes, and the particles can have various geometries, including layered, spherical, tubular and randomly shaped, and the particle sizes can also vary from a few nanometers to 100 μ m [1,3,7,8]. Thermoset polymers with lower curing shrinkage and higher dimensional stability are widely used matrix materials due to their high tensile strength and modulus of elasticity and high-adhesion properties [8]. Many hardening agents such as spherical rubber particles, liquid rubbers, glass beads and branched polymers are often used to increase the ductility of thermoset polymers, but they can adversely alter properties such as glass transition temperature (T_g) , tensile strength and modulus of elasticity [9]. Generally, polymer matrix composites in which thermoset polymers are used as a matrix and at least two different components as additives are called hybrid polymer matrix composites (HPMCs). The use of two different components can give HPMC some superior properties that cannot be achieved with a single component [10]. Hybrid polymer composites play an important role in structural applications due to their multidimensional performance [11].

On the other hand, polymers that need to be modified to improve both their mechanical and tribological performance can be modified through polymer blending, copolymerization and reinforcing fillers and/or fibers. One of the most effective methods for polymer modification and addition of fillers and fibers is polymer blending, with which the strength of polymers and polymer composites can be effectively increased [12].

Fillers can be present in a variety of composite systems commonly used in the packaging, biomedical, cosmetic, pharmaceutical, paper, food, paint and adhesive industries, as they can improve the specific properties of materials such as hardness, durability, clarity, creep resistance and physical appearance [13]. Since the heterogeneous dispersion of a filler in the polymeric matrix may result in the formation of low-performance polymer composites, the desired properties of the polymer composite to be prepared depend on the effective polymer-filler interaction and the homogeneous dispersion of the filler. Fillers, which can be particulate or fibrous, may have their own unique properties and advantages, but modifications or the use of extra compatibilizers may be necessary to meet certain requirements and improve their properties and make them more suitable for particular applications. The high aspect ratio of fibrous fillers such as glass fiber and natural fiber can be effective in increasing the strength and stiffness of polymers. Similarly, particulate fillers such as mineral fillers, usually in powder form and in various shapes and sizes, can effectively increase the strength and toughness of polymer matrices. In particular, the size of the filler has a decisive influence on the properties of the polymer composite, and smaller-sized fillers with a larger surface area are more preferred for more effective interactions between the filler and the polymer matrix. In addition, ultrafine or nano-sized fillers are used because of their homogeneous dispersion throughout polymeric matrices and their high dispersion efficiency, as well as their ability to prevent possible filler aggregation at high loading [14]. On the other hand, compatibility between the filler and the polymer matrix is extremely important, as the high interfacial energy caused by the different surface properties of the filler and polymer molecules can lead to the formation of a low-performance inhomogeneous polymer composite. In addition to chemically or physically modifying the filler to produce a homogeneous polymer composite, the use of effective compatibilizers at the matrix and filler interface and the blending technique can also be considered as

alternative ways of improvement [13,14]. Since the crosslinking density, which causes the brittle structure and low toughness of thermoset-type formaldehyde resins, limits their applications, many studies are carried out to improve the properties of formaldehyde resins such as cracking resistance and dynamic mechanical and thermal stability by adding different types and amounts of nano-fillers [15–18]. The homogeneous dispersion and breakage of possible nanoclusters in the polymer matrix are the main challenges in the preparation of nanocomposites [19]. Cluster size and distribution of nanoparticles in the polymer matrix and the effectiveness of interfacial interactions between the filler and molecular chains are decisive in changing the basic properties of the pure polymer [20,21]. Studies have intensified to find suitable processing techniques to reduce the tendency of particles to agglomerate and non-homogeneously disperse in the polymer matrix through van der Waals interactions and to ensure effective dispersion.

The development of new-generation adhesives with better properties through nanotechnological applications has created a new and great opportunity for the worldwide composite industry. The inclusion of melamine formaldehyde resins in nano-technological applications with nanomaterial reinforcement has enabled the preparation of new highly effective composites that can be used in many industrial areas [22–24]. Micro- or nanofillers, which can be organic or inorganic, can improve the mechanical properties, electrical and thermal conductivity, thermal behavior and fire-retardant properties of melamine formaldehyde resin. For this, formulations using various nanomaterials and additives such as carbon nanofibers, nano-cellulose, nanoclay, nano-SiO₂, nano-TiO₂, zinc oxide and alumina have been developed [25–28]. Nanoparticles, which can generally improve the mechanical and viscoelastic properties of composites, may also tend to agglomerate due to their high surface areas and attractive interactions [29]. Therefore, the degree of dispersion and homogeneity of the nanoparticles in the resin is extremely important in order to ensure an effective interaction between the matrix and the nanoparticles and to obtain the maximum benefit from the high surface areas [30,31].

In particular, uniform dispersion of nanoparticles in the matrix is extremely important in terms of increasing toughness and obtaining other desired material properties [32,33]. Due to the relatively low cost and prevalence, the use of modified clays as nano-fillers is becoming increasingly common. The addition of nanoclay to the polymer matrix can improve thermal degradation resistance, barrier properties and mechanical strength [34–37]. The improvement in mechanical properties is mainly attributed to the excellent particleparticle and particle-matrix interaction in the nanocomposite and the high aspect ratio of the nano-filler [38]. Mineral and fiber-filled polymer nanocomposites have attracted great attention in research as well as in industry, as they can exhibit improved properties and can be easily processed [39]. The improvement in mechanical properties of composites depends mainly on the type of polymer, fiber and filler and preparation technique [39,40]. However, incompatibility between filler and matrix in terms of interfacial properties can have adverse effects on the final properties of the composite, and nanoparticles may need to be incorporated into mineral-filled composites to overcome the incompatibility and prepare hybrid composites. Although there are many types of fillers today, mineral-based fillers such as kaolinite, silica, talc and calcium carbonate are used more because they are cheap and abundant in nature. Various techniques such as solution combination, melt intercalation, mechanical blending [41–43] and ultrasonic irradiation [44–46] are commonly used in composite preparation. The incorporation of nanoparticles can also improve the mechanical properties without causing a significant increase in the weight of the composite [47]. Among various nanoparticles, montmorillonite (MMT), which is relatively cheap and abundantly available, and its modified form, organo-montmorillonite (OMMT), are especially being increasingly used as nano-fillers for polymeric composites [48–52]. Surface modification of montmorillonite is mostly performed with ion exchange using quaternary ammonium salts. Organo-montmorillonite (OMMT) reinforcement can improve the thermal stability, water resistance, barrier properties and mechanical strength of the polymer. This is due to the intercalation of polymer chains into the interlayer space, the

formation of tactoids and even the exfoliation of organo-montmorillonite under appropriate polymer composite preparation conditions [53,54]. It has been reported that the use of 5% MMT as a filler can improve the mechanical and thermal barrier properties of Nylon 6, and similarly, the addition of nano-calcium-carbonate and nanoclay to high-density polyethylene (HDPE) can significantly increase the modulus of elasticity [55,56]. Also, dolomite as filler was able to improve the mechanical and thermal properties of various polymeric materials [57,58].

Nitrogen-rich and stable melamine formaldehyde resin, which has a triazine ring structure, has superior properties such as thermal stability, fire retardancy, low thermal conductivity, low emission and transparency and is waterproof and non-melting. While urea–formaldehyde and epoxy-based nanocomposites are frequently studied in scientific and industrial research, studies on melamine formaldehyde resin are quite limited [29]. Therefore, the presented study focuses on the preparation of hybrid composites in foam form with a new approach, using an organo-clay melamine formaldehyde nanocomposite as a matrix, pumice as primary filler and gypsum, kaolinite and a hollow glass sphere as secondary filler, and examining their morphological and textural properties. For this purpose, some mechanical tests such as bending strength, elasticity modulus, screw holding resistance and thermal conductivity measurements were carried out on the composites prepared and the results were evaluated comparatively.

2. Materials and Methods

2.1. Material

In this study, powder pumice used as the primary filler in the preparation of hybrid nanocomposites was purchased from Blokbims Co. in Nevşehir, Turkey. Kaolinite (Specific surface area: 14.4 m²/g, Lazoğlu Co. in Bursa, Turkey), commercial gypsum and hollow micro-glass spheres (HMGSs, diameter: 100–800 μ m) were used as secondary fillers at 12.5% by weight. Additionally, montmorillonite (specific surface area: 64.2 m²/g) (MMT) obtained from Karakayalar Co. in Çankırı, Turkey was used to prepare organo-montmorillonite (OMMT). XRF chemical compositions of pumice, kaolinite and montmorillonite are given in Table 1.

Table 1. XRF chemical compositions of pumice, kaolinite and montmorillonite.

Component (%)												
	SiO ₂	Al_2O_3	CaO	MgO	Fe ₂ O ₃	K ₂ O	Na ₂ O	TiO ₂	MnO	SrO	SO_3	Other
Pumice	73.35	12.88	0.77	0.08	1.10	4.40	3.82	0.08	0.05	0.01	0.44	3.02
	SiO ₂	Al_2O_3	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	Cr_2O_3	Other		
Kaolinite	71.0	20.0	0.40	0.05	0.15	0.10	0.35	0.50	0.03	7.92		
	SiO ₂	Al_2O_3	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	SO_3	Other		
Montmorillonite	59.32	17.19	5.95	3.63	2.21	1.68	0.97	0.74	0.51	7.81		

For the synthesis of melamine formaldehyde resin to be used as the composite matrix, melamine and formaldehyde (37%), as well as the nonionic surfactant used for encapsulation, Tween 80 and Glycerin of an analytical grade, were obtained from Merck Co., and also gasoline, which is a mixture of isooctane, butane and 3-ethyltoluene, was supplied from a gas station.

2.2. Method

2.2.1. Preparation of Organo-Clay

Organo-clay (OMMT) to be used as nano-filler was prepared with the solution intercalation method using a cationic surfactant, Cetyltrimethyl Ammonium Bromide, CTAB (purchased from Merck Co.), hydrocarbon material (Table 2) and montmorillonite. For this, firstly, an aqueous solution of CTAB was prepared at 40 °C by adding the amount of CTAB corresponding to the concentration of 160 mg/L, and then hydrocarbon material was added at a ratio of 0.3 g/1.0 g. After the resulting dispersion was mixed mechanically for 30 min at a mixing speed of 50 min⁻¹, a sufficient amount of raw montmorillonite (MMT) was added to the hydrocarbon–water dispersion and mixing was continued for 30 min at a mixing speed of 200 min⁻¹. Finally, the mixture was filtered and dried at 110 °C for 2 h, ground and sieved in ASTM standard 200 mesh and stored in a sealed container for further experiments [59,60].

Table 2. Some characteristics of hydrocarbon material.

Density (15 °C), kg/m ³	Calorific Value, MJ/kg	Flash Point, °C	Water Using Distillation, wt. %	С	Н	Ν	S	Ash
990.7	42.74	105.8	0.1	83.4	11.9	0.8	1.5	0.03

2.2.2. Preparation of Melamine Formaldehyde Pre-Polymer (MF), MF-Organo-Clay Nanocomposite and Hybrid Composites

Melamine at a ratio of 1.0/1.1 and 37 wt.% formaldehyde were placed in a three-neck flat-bottom flask with a thermometer and cooling equipment and stirred with a magnetic stirrer, and then heated at about 60 °C for a certain time until the solution became clear. Finally, the pH was adjusted to 8.5 with a NaOH solution of 40% wt. and refluxed for 1 h at approximately 95 °C considering the viscosity of the mixture. Then, a sufficient amount of concentrated acetic acid for neutralization, 1.0% by weight of Glycerin and Tween 80, as well as 6.0% by weight of gasoline were added to the resulting pre-polymer, and vigorously mixed mechanically to ensure a homogeneous mixture. While preparing the MF-organo-clay nanocomposite with in situ synthesis, 0.15% organo-clay by weight was added to the flask. While hybrid composites were being prepared, a certain proportion of pumice and other fillers were added sequentially and mixing was continued. The foaming method was used for the encapsulation and for this, the resulting mixture was exposed to microwave radiation for 2 min in a microwave oven in a suitable container. Finally, it was taken into a modular square aluminum mold with an internal volume of $10 \times 10 \times 1$ cm³, and the mixture was thermally treated for 1 h at 140 °C in a hot-air-heated oven to remove water, residual formaldehyde as well as complete curing [61].

The codes and component ratios corresponding to the pure MF, MF-organo-clay nanocomposite and MF-organo-clay–pumice–gypsum, MF-organo-clay–kaolinite and MF-organo-clay–hallow-glass-sphere hybrid composites are given in Table 3.

Table 3. Codes and component ratios of pure MF, MF-organo-clay nanocomposite and MF-organoclay–pumice, MF-organo-clay–pumice–gypsum, MF-organo-clay–kaolinite and MF-organo-clay– hallow-glass-sphere hybrid composites.

Specimen Code	Nano-Filler	(%wt.)	Primary Filler	(%wt.)	Secondary Filler	(%wt.)
MF (Melamine formaldehyde foam)	-	-	-	-	-	-
MFCNC (MF-organo-clay nanocomposite)	Organo-clay	0.15	-	-	-	-
MFCPHC (MF-organo-clay–pumice hybrid composite) MECPGHC	Organo-clay	0.15	Pumice	44.4	-	-
(MF-organo-clay–pumice–gypsum hybrid composite)	Organo-clay	0.15	Pumice	38.9	Gypsum	5.5
MFCPKHC (MF-organo-clay–kaolinite hybrid composite)	Organo-clay	0.15	Pumice	38.9	Kaolinite	5.5
(MF-organo-clay–hallow-glass-sphere hybrid composite)	Organo-clay	0.15	Pumice	38.9	Hallow glass sphere	5.5

For the characterization of pure MF resin, raw fillers and composites, Fourier transform infrared spectroscopy (FTIR), X-ray powder diffraction spectroscopy (XRD), scanning electron microscopy (SEM) and high-resolution transmittance electron microscopy (HRTEM) analyses as well as mechanical tests such as bending strength, elasticity modulus and screw holding resistance and also thermal conductivity coefficient measurements were performed [62].

2.2.3. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

FTIR spectra of raw clay, organo-clay, mineral fillers and hybrid composites were taken to determine their functional groups, taken using a Vertex 70 V (OPUS 7.0 software) FTIR spectrometer in the range of 4000 to 400 cm⁻¹ with an average of 100 scans and 1 cm^{-1} resolution.

2.2.4. X-ray Powder Diffraction Spectroscopy (XRD) Analysis

In layered clays such as montmorillonite, the variation of the interlayer spacing is taken into account to determine the type of composite prepared [63]. In order to examine the deformations in the crystal structures of the components, XRD diffractograms of hybrid composites prepared using mineral fillers with varying ratios with a fixed organo-clay ratio were taken using a PANalytical Empyrean X-ray Difractometer with Cu K α (1.540 Å) radiation operating at 5 kV and 40 mA in the range of 2 θ 9–90° and at the scanning speed of 4/min.

2.2.5. Scanning Electron Microscopy (SEM) Analysis

In order to observe and evaluate the morphological changes that may occur in the composites due to adhesion interactions between the organo-clay, polymer matrix and mineral fillers and the polymer matrix and encapsulated particles, SEM images of raw clay, mineral fillers and composites were taken using a Scanning Electron Microscope (SEM) (FEI-INSPECT S50 model) at 30 kV.

2.2.6. High-Resolution Transmittance Electron Microscopy (HRTEM) Analysis

An HRTEM analysis is of great importance in examining the textural structures of materials at the nanoscale, and especially the distribution of nanoparticles in nanocomposites [64]. In this study, HRTEM images of raw clay, organo-clay, mineral fillers and hybrid composites were taken to characterize their textural structures using a HITACHI HT7700 high-resolution transmission electron microscope (LaB6 filament) operating at 120.0 kV.

2.2.7. Mechanical Tests and Thermal Conductivity Measurements

Screw-holding tests and bending (bending and modulus of elasticity) tests of the MF-organo-clay nanocomposite and hybrid composites were performed using a universal testing machine (Zwick/Roell) according to ASTM 1037-16 [65] and ASTM D790 [66] standards, respectively. The thermal conductivity coefficients of the pure MF foam, MF-organo-clay nanocomposite and hybrid composites were also measured using a thermal conductivity meter with a probe consisting of a single heater wire and thermocouple (Quick Thermal Conductivity Meter QTM-500, Kyoto, Japan).

3. Results

3.1. Textural Characterization of Raw Montmorillonite (MMT), Organo-Montmorillonite (OMMT), Melamine Formaldehyde Resin (MF), Melamine Formaldehyde Organo-Clay Nanocomposite (MFCNC) and Hybrid Composites

In order to compare the differences in the textural structures of raw montmorillonite (MMT), organo-montmorillonite (OMMT) and raw pumice and to see the effectiveness of the modification made for lyophilization, HRTEM images of both were taken and are given in Figure 1a,b, respectively. Dark long fibrous lines appearing in HRTEM images indicate clay platelets with their 2:1 layered structure.



Figure 1. HRTEM images of raw montmorillonite (MMT) (**a**) and organo-montmorillonite (OMMT) (**b**).

From Figure 2a, it can be seen that pure melamine formaldehyde resin forms as aggregated microspheres and aggregates develop in three dimensions [67]. This textural arrangement is due to the use of the microwave-irradiation-assisted foaming method before curing. Figure 2b shows that the MF molecule clusters become regularly sparse or disaggregated, preserving their spherical structure, due to the exfoliation of the organo-clay platelets into the polymer matrix [68]. The HRTEM image of the MF-organo-clay–pumice composite (MFCPHC) in Figure 2c shows that the pumice has a vesicular coarse-textured and glassy structure, but the particles are effectively surrounded by spherical polymer clay nanocomposites [69]. From the HRTM image of the MF-organo-clay-pumice-gypsum hybrid composite (MFCPGHC) in Figure 2d, it can be seen that relatively regular gypsum plates are heterogeneously dispersed next to the pumice plates with a glassy structure, and the particles are surrounded by distinctly deformed polymer clay nanocomposite spheres [70]. On the other hand, in the image of the MF-organo-clay–kaolinite hybrid composite (MFCPKHC) in Figure 2e, it can be seen that coarse-textured glassy pumice plates, spherical polymer clay nanocomposites and kaolinite plates can exhibit an effective blending [71]. The HRTM image of the MF-organo-clay-hollow-glass-sphere hybrid composite (MFCPHHC) in Figure 2f shows that the pumice plates exhibit a more regular and relatively uniform arrangement with the inclusion of hollow glass spheres encapsulated by spherical polymer clay nanocomposites [72].

3.2. Surface Morphological Characterization of Melamine Formaldehyde Resin (MF), Melamine Formaldehyde Organo-Clay Nanocomposite (MFCNC) and Hybrid Composites

SEM patterns taken for the pure melamine formaldehyde resin (MF), MF-organoclay nanocomposite (MFCNC) and MF-organo-clay–pumice (MFCPHC), MF-organo-clay– pumice–gypsum (MFCPGHC), MF-organo-clay–pumice–kaolinite (MFCPKHC) and MForgano-clay–pumice–hollow-glass-sphere (MFCPPHHC) hybrid composites are given in Figure 3.

It can be seen from Figure 3a that the pattern of pure melamine formaldehyde resin clearly reflects the surface morphology showing that clusters of microspheres develop as branched structures in three dimensions [73,74]. Figure 3b reveals a surface morphology showing the ordered stacking of MF molecule clusters in which the branched structure almost disappears, preserving their spherical structure due to the exfoliation of the organoclay platelets into the polymer matrix. In the SEM pattern of the MF-organo-clay–pumice composite (MFCPHC) in Figure 3c, it is seen that the pumice with a vesicular coarse texture and glassy structure exhibits a surface morphology covered with spherical polymer clay nanocomposites, including its micro-cavities [75,76]. The SEM pattern of the MF-organo-clay-pumice-gypsum hybrid composite (MFCPGHC) in Figure 3d shows the morphological structure implying a regular coating formed with polymer clay nanocomposite spheres in the cavities in the porous pumice plates and superficial fold or fractures. It can be seen again from this figure that a rough surface appearance appears, indicating the presence of heterogeneous agglomerates in size. It can be argued that this appearance is related to the presence of glassy pumice plates, gypsum plate fractures and stacked forms of them, surrounded by polymer clay nanocomposite spheres [77]. The image of the MF-organo-clay-kaolinite hybrid composite (MFCPKHC) in Figure 3e shows that the coarse-textured glassy pumice plates exhibit a surface morphology that indicates a fairly uniform association of spherical polymer clay nanocomposites with kaolinite layers arranged in different directions but regularly. On the other hand, Figure 3f shows a surface morphology in which an ordered and relatively localized arrangement of hollow glass spheres clustered together and spherical polymer clay nanocomposites neatly surrounded by pumice plates and kaolinite layers appears [78,79].



(c)



Figure 2. HRTEM images of pure melamine formaldehyde resin (MF) (a), MF-organo-clay nanocomposite (MFCNC) (b) and MF-organo-clay-pumice (MFCPHC) (c), MF-organo-clay-pumice-gypsum (MFCPGHC) (d), MF-organo-clay-pumice-kaolinite (MFCPKHC) (e) and MF-organo-clay-pumicehallow-glass-sphere (MFCPHHC) (f) hybrid composites.



Figure 3. SEM patterns of pure melamine formaldehyde resin (MF) (**a**), MF-organo-clay nanocomposite (MFCNC) (**b**) and MF-organo-clay–pumice (MFCPHC) (**c**), MF-organo-clay–pumice–gypsum (MFCPGHC) (**d**), MF-organo-clay–pumice–kaolinite (MFCPKHC) (**e**) and MF-organo-clay–pumice–hallow-glass-sphere (MFCPHHC) (**f**) hybrid composites.

3.3. Analysis of FT-IR Spectra of Raw Montmorillonite (MMT), Organo-Montmorillonite (OMMT), Melamine Formaldehyde Resin (MF), Melamine Formaldehyde Organo-Clay Nanocomposite (MFCNC) and Hybrid Composites

FT-IR spectra of the pure melamine formaldehyde resin (MF), MF-organo-clay nanocomposite (MFCNC) and MF-organo-clay–pumice (MFCPHC), MF-organo-clay–pumice–gypsum (MFCPGHC), MF-organo-clay–pumice–kaolinite (MFCPKHC) and MF-organo-clay–pumice– hollow-glass-sphere (MFCPHHC) hybrid composites are given in Figure 4.



Figure 4. FT-IR spectra of pure melamine formaldehyde resin, MF-organo-clay nanocomposite and various hybrid composites.

The peaks at 3327 cm⁻¹, 1016 cm⁻¹, 1541 cm⁻¹ and 1450 cm⁻¹ in the FTIR spectrum of MF in Figure 4 correspond to the stretch vibration of N-H and O-H bonds, the stretch vibration of C-O-C bonds and the stretch vibration of C=N, respectively. Accordingly, it can be said that melamine formaldehyde resin was successfully synthesized [80].

In Figure 4, in the FT-IR spectrum of the MF-organo-clay nanocomposite (MFCNC), apart from the strong peak at 3354 cm⁻¹ from CTAB, three more peaks appeared at 2926, 2914 and 2881 cm⁻¹, corresponding to secondary amine group stretching, C–H anti-stretching and C–H stretching. All these specific peaks appeared both at lower density and shifted to lower values due to interactions between clay layers and CTA⁺ ions bound by long-chain hydrocarbon molecules. Also, two peaks were observed at 1454 cm⁻¹ and

1129 cm⁻¹, respectively, corresponding to C–N stretching and N–H bending of CTAB. On the other hand, it can be claimed that the peaks appearing in the 1302–1657 cm⁻¹ region are due to the CH₂ shear vibration mode and the O-H bending mode of the water molecule around the bound head group. Si-O and Al-OH are the main functional groups observed in the range of 1000 cm⁻¹ to 500 cm⁻¹. While the peak at 866 cm⁻¹ corresponds to Al-OH bending vibrations, the double Si-O-Si bonds in SiO₂ at 802 cm⁻¹ and Si-O stretching vibrations observed around 714–617 cm⁻¹ indicate the presence of quartz. Strong bands around 3356–3730 cm⁻¹ indicate the presence of hydroxyl bonds. The appearance of these peaks as low intensity and shifted from their specific values may also indicate intense interactions between clay plates and long-chain-hydrocarbon-bound CTA⁺ ions [81,82].

In the FT-IR spectrum of the MF-organo-clay–pumice composite (MFCPHC) in Figure 4, besides the characteristic peaks of organo-clay and MF origin, slightly shifted and low-intensity peaks corresponding to Al-OH bending vibrations and Si-O stretching vibrations appeared at 905 and 757–635 cm⁻¹. Similar to the other spectra, the peak around 3761 cm⁻¹ indicates the presence of hydroxyl groups originating from water [76,83]. The lower peak intensities and shifts can be attributed to the effective interactions between pumice plates and organo-clay layers, as implied with the HRTEM images of this hybrid composite.

The FT-IR spectrum of the MF-organo-clay–pumice–gypsum hybrid composite (MFCPGHC) in Figure 4 shows a very close similarity to the spectrum of the composite containing only pumice. This is in line with the HRTEM image, which shows that relatively regular gypsum plates are heterogeneously dispersed next to the pumice plates and the particles are surrounded by deformed polymer clay nanocomposite spheres. However, it can be seen that the spectrum also includes the peaks at 663 and 598 cm⁻¹, which correspond to the stretching and bending modes of the sulfate group and other low-intensity characteristic peaks at 1022 and 2337 cm⁻¹.

On the other hand, the FT-IR spectra of the MF-organo-clay–pumice–kaolinite (MFCP-KHC) and MF-organo-clay–pumice–hollow-glass-sphere (MFCPHHC) hybrid composites in Figure 4 seem to be quite similar. In terms of the nature of interactions, this is consistent with the fact that the pumice plates, spherical polymer clay nanocomposites and kaolinite plates exhibit an efficient blending, and the pumice plates show a more regular and relatively uniform arrangement with the inclusion of hollow glass spheres encapsulated by the spherical polymer clay nanocomposites (see Figure 3e,f). However, it can be argued that low-intensity but characteristic peaks at 3759, 3639, 3580 and 3578 cm⁻¹ indicate the regular structure of kaolinite. The peaks at 1112 cm⁻¹, 1074 cm⁻¹ and 1016 cm⁻¹ in the spectrum of the kaolinite-containing composite are Si-O stretching modes, and the peaks at 1112 and 1016 cm⁻¹ correspond to the symmetric and anti-symmetric stretching of Si-O bonds. The peak around 418 cm⁻¹ and the peak around 3435 cm⁻¹ and the low intensity peak around 1632 cm⁻¹ appearing in the spectra of both composites can be attributed to an O-Al-O bending and an OH bending, respectively [72,73,84–86].

3.4. Characterization of Mineralogical Structures of Raw Montmorillonite (MMT), Organo-Montmorillonite (OMMT), Melamine Formaldehyde Resin (MF), Melamine Formaldehyde Organo-Clay Nanocomposite (MFCNC) and Hybrid Composites

Figure 5 shows XRD diffractograms of the pure melamine formaldehyde resin (MF), MF-organo-clay nanocomposite (MFCNC) and the hybrid composites such as MF-organoclay–pumice (MFCPHC), MF-organo-clay–pumice–gypsum (MFCPGHC), MF-organoclay–pumice–kaolinite (MFCPKHC) and MF-organo-clay–pumice–hollow-glass-sphere (MFCPHHC).

Figure 5 shows that in the XRD pattern of the MF resin, two typical broad peaks appear at 9.4° and 23.8°, indicating an amorphous structure. This means that formaldehyde resin of melamine is formed from the methylol monomers and propagation of the polymeric backbone takes place. It can be seen from Figure 5 that the smaller of the two peaks of MF resin is partially overlapped with the characteristic smectite peak at 8.1°. [81,87]. This left-shifted and enlarged smectite peak clearly shows that polymer molecules are intercalated



in the interlayer space of the clay and the nanocomposite is formed. The HRTEM image in Figure 2b also supports this claim.

Figure 5. XRD diffractograms of pure melamine formaldehyde resin, MF-organo-clay nanocomposite and various hybrid composites.

The XRD pattern of the MF-organo-clay–pumice composite (MFCPHC) in Figure 5 shows a peak with a wider and shorter peak height at 23.2°, reflecting the amorphous structure of pumice and possibly overlapping the peak of MF. In addition, the smectite peak, which appears to be shifted more to the left at 7.2° in the same pattern, indicates further intercalation of polymer chains in the interlayer space [76,83].

From the XRD pattern of the MF-organo-clay–pumice–gypsum hybrid composite (MFCPGHC) in Figure 5, dihydrate calcium sulfate (at 14.6° and 25.8°) and Bassanite (at 47.9°, 49.5° and 50.5°) and calcite (36.3°) as the main mineral phase with certain proportions of anhydrite crystals can be seen [88,89]. Also, the same pattern includes overlapping pumice and MF peaks and a smectite peak at 6.5°, showing almost exfoliation of the organoclay layers. These findings are in line with the HRTEM image showing that relatively regular gypsum plates are heterogeneously dispersed next to pumice plates with a vitreous structure in which different phases are present as well as that the clay platelets are exfoliated in the MF matrix [90,91].

The XRD pattern of the MF-organo-clay–kaolinite hybrid composite (MFCPKHC) in Figure 5e shows well-defined and characteristic peaks of kaolinite at 12.2° and 26.9°. On the other hand, it can be seen from this pattern that the MF and pumice peaks are overlapped and the smectite peak is shifted more to the left, which indicates that the organo-clay platelets are well exfoliated in the polymer matrix. Also, peaks corresponding to 30°–36° and 39.1° reflect other mineral components of kaolinite. Thus, it can be said that pumice plates, spherical polymer clay nanocomposites and kaolinite plates can exhibit effective mixing due to interfacial compatibility (see Figures 2e and 3e) [86,92].

The XRD pattern of the MF-organo-clay–pumice–hollow-glass-sphere hybrid composite (MFCPHHC) in Figure 5 shows the overlapping MF, pumice and amorphous silica peaks and the smectite peak almost disappeared. Thus, as expected, the pumice plates and hollow glass spheres encapsulated by spherical polymer clay nanocomposites exhibited an ordered and relatively discrete arrangement (see Figures 2f and 3f) [79,87,93].

3.5. Thermal Conductivities of Raw Montmorillonite (MMT), Organo-Montmorillonite (OMMT), Melamine Formaldehyde Resin (MF), Melamine Formaldehyde Organo-Clay Nanocomposite (MFCNC) and Various Hybrid Composites

Thermal conductivity is an important indicator for evaluating the thermal performance of a material under stationary conditions. The thermal conductivity coefficients measured for different samples were taken into account to evaluate the thermal insulation performances of the materials [94]. In this study, melamine formaldehyde resin and its nanocomposite prepared using organo-clay were used as the main matrix and binder. While pumice was used as the main filling material, various hybrid composites were prepared by adding secondary fillers such as gypsum, kaolinite and a hollow glass sphere in certain proportions in order to improve the mechanical properties of the particularly brittle and friable material. The thermal conductivity coefficients of the pure melamine formaldehyde resin (MF), MF-organo-clay nanocomposite (MFCNC) and MForgano-clay-pumice (MFCPHC) and hybrid composites such as MF-organo-clay-pumicegypsum (MFCPGHC), MF-organo-clay-pumice-kaolinite (MFCPKHC) and MF-organoclay-pumice-hollow-glass-sphere (MFCPHHC) are shown in Table 4. It can be seen from this figure that the lowest thermal conductivity coefficients were obtained in the MF-organoclay nanocomposite (MFCNC) and MF-organo-clay-pumice-hollow-glass-sphere hybrid composite (MFCPHHC), respectively. In contrast, higher thermal conductivity coefficients were observed in the MF-organo-clay-pumice (MFCPHC) and MF-organo-clay-pumicekaolinite (MFCPKHC) hybrid composite and pure melamine formaldehyde resin (MF) composite, respectively.

Table 4. Analysis results of thermal conductivities of pure melamine formaldehyde resin, MF-organoclay nanocomposite and various hybrid composites.

Codes of Specimen	Thermal Conductivity Coefficient (λ) (W/m K)	Standard Deviation		
MF (Melamine formaldehyde foam)	0.0826	0.001216		
MFCNC (MF-organo-clay nanocomposite)	0.0640	0.004660		
MFCPHC (MF-organo-clay-pumice hybrid composite)	0.1003	0.004105		
MFCPGHC (MF-organo-clay–pumice–gypsum hybrid composite)	0.0763	0.001899		
MFCPKHC (MF-organo-clay–kaolinite hybrid composite)	0.0915	0.001228		
MFCPHHC (MF-organo-clay–hallow-glass-sphere hybrid composite)	0.0642	0.002535		

The thermal conductivity of composites is anisotropic in nature and their correct design requires knowledge of the thermal conductivity of composites. Data on the thermal conductivity of resins facilitate the reduction in stresses caused by the shrinkage of the composites during curing and the mismatch in the coefficients of thermal expansion. Matrix materials can be of different types such as metal, mineral, ceramic and polymer. Polymer matrices, which can be thermoplastic or thermoset, are the most widely used due to their cost efficiency and ease of manufacturing, and they also have excellent room temperature properties compared to other matrices [95]. Thermoset matrices are synthesized with the irreversible chemical reaction of a resin to an amorphous crosslinked polymer matrix. Due to their large molecular structure, thermoset resins provide good electrical and thermal insulation. Thermosets have a low viscosity, which allows for proper wetting of other additives, excellent thermal stability and better creep resistance. Thermoset resins can be formulated to give a wide variety of properties. Melamine formaldehyde resin hardens through the condensation reaction that produces water during the reaction and exhibits low shrinkage after curing, and has good chemical resistance and excellent mechanical properties. It also has excellent properties such as high temperature and creep resistance, good thermal insulation and sound damping properties, as well as superior flame retardancy properties [74,96].

The decrease in thermal conduction or the dominance of thermal insulation depends on the reduction in heat flow by limiting heat conduction, convection, radiation or all three. Thermal insulation materials can be categorized into three general types, which can be categorized as fibrous, cellular and granular. Fibrous insulations consist of small-diameter fibers that finely divide the air space. The fibers may be perpendicular or parallel to the insulated surface and may or may not be bonded together. Silica, glass, rock wool, slag wool and alumina silica fibers are used. The most commonly used insulations of this type are fiberglass and mineral wool. Cellular insulations contain small individual cells separated from each other and glass or polystyrene (closed cell) and other polymeric foams are typical examples. Granular insulators have small nodules that contain voids or cavities, and they are not considered true cellular materials as there may be material transfer between the voids. Granular insulations such as calcium silicate, expanded vermiculite, perlite, pumice, gypsum, cellulose, diatomaceous earth and expanded polystyrene can be produced as a loose or crumbly material but combined with a binder and fiber to form a rigid insulation material [97].

Thermal conductivity is strongly correlated with filler/polymer interface properties. The use of different fillers or chemical modification of fillers can be widely used to improve polymer/filler interface interactions [98]. Improved filler/matrix affinity can increase the effectiveness of interfacial attraction interactions and significantly reduce interfacial energy, as for nanocomposites with polymer and nano-fillers [99].

In the thermoset melamine formaldehyde matrix, regular spherical clusters were formed during foaming due to the exfoliation of organo-clay platelets and the reduction in the solvent and polymer chain interface energy, resulting in a very high thermal insulation performance and a lower thermal conductivity coefficient (see Figures 2b and 3b).

In the composite, where the pumice plates exhibit a more regular and relatively uniform arrangement with the inclusion of hollow glass spheres encapsulated by spherical polymer clay nanocomposites, the negative effect of the presence of pumice in terms of thermal insulation was compensated for with the hollow glass spheres and thus the second lowest thermal conductivity coefficient with the granular insulation types was obtained [100].

The gypsum-containing composite, in which the relatively regular gypsum boards are surrounded by heterogeneously dispersed and significantly deformed polymer clay nanocomposite spheres (see Figures 2d and 3d), next to the pumice boards with a vitreous structure, exhibited a relatively high thermal insulation performance. This can be explained with the fact that the deformed nanocomposite spheres inhibit the flow of heat through the fibril structures of the exfoliated organo-clay platelets [101].

The kaolin-containing composite, in which the coarse-textured glassy pumice sheets, spherical polymer clay nanocomposite and kaolin sheets exhibited an effective blending, showed a lower void ratio and higher thermal conductivity coefficient, and therefore a lower thermal insulation performance, in parallel with its compact structure (see Figures 2e and 3e) [102].

3.6. Dependence of Densities, Flexural Strengths, Modulus of Elasticity and Screw Holding Strengths of Hybrid Composites on Their Composition

Table 5 shows the comparison of density, bending strength, modulus of elasticity and screw holding strength of hybrid composites such as the MF-organo-clay–pumice (MFCPHC), MF-organo-clay–pumice–gypsum (MFCPGHC), MF-organo-clay–pumice–kaolin (MFCP-KHC) and MF-organo-clay–pumice–hallow-glass-sphere (MFCPHHC).

It can be seen from Table 5 that the hybrid composites' bulk densities follow the order of (MFCPHHC) < (MFCPKHC) < (MFCPHC) < (MFCPGHC). As expected, the lowest density was found in the composite containing a hallow glass sphere, and the highest density was found in the composite containing gypsum. In the gypsum-containing composite, the deformation of the globular clusters of the organo-clay nanocomposite resulted in a more rigid and compact structure, and thus a higher density. The composite containing

the partially swelling kaolin with resin intercalation exhibited a slightly smaller density in parallel with the expanding volume. Density of the composite bulk, besides being dependent on resin/composite content, is also a determinant in mechanical properties such as flexural strength, modulus of elasticity and screw holding strength [103].

Specimen Codes	Bulk Density (g/cm ³)	Bending Strength (MPa)	Standard Deviation	Screw Holding Resistance (N/mm ²)	Standard Deviation	Elasticity Modulus (MPa)	Standard Deviation
MFCPHC	0.41	270.69	3.1	3.59	0.031	2.00	0.10
MFCPGHC	0.51	116.72	3.0	0.16	0.020	0.75	0.05
MFCPKHC	0.39	250.36	4.0	2.52	0.060	1.80	0.20
MFCPHHC	0.36	228.41	7.0	3.59	0.090	2.22	0.30

Table 5. Variation of densities, flexural strengths, modulus of elasticity and screw holding strengths of hybrid composites with their composition.

As can be seen from Table 5, the highest bending strength of the four hybrid composites was observed in the sample containing only pumice, and the lowest strength was observed in the sample containing gypsum. With a relatively low density and a surface morphology indicating a highly effective inter-granular interaction between coarse-textured glassy pumice plates, spherical polymer clay nanocomposites and kaolin layers arranged in different directions but regularly, the kaolin-containing composite exhibited a very high bending strength (see Figure 3) [104]. In contrast, the low-density composite containing relatively-low-impact-strength hollow glass spheres with a surface morphology created by clustered hollow glass spheres effectively surrounded by arranged layers of kaolin, pumice plates and spherical polymer clay nanocomposites has a demonstrated extremely high bending strength, which may imply very efficient interface compatibility (see Figure 3) [105]. Low flexural strength of the gypsum-containing composite is an expected mechanical behavior due to its morphological structure, which indicates a structuring of polymer clay nanocomposite spheres in the voids and superficial folds or fractures of the porous pumice plates, and the presence of heterogeneous agglomerates (see Figure 2 and 3) [106].

From the same table, it can be seen that the modulus of elasticity of the composites follows the sequence MFCPHHC > MFCPHC > MFCPKHC > MFCPGHC. This table shows that the screw holding strengths also follow a similar sequence. From this close similarity, it can be concluded that composites containing only pumice and a hollow glass sphere are ductile materials with high performance and high toughness [107].

On the other hand, when the thermal conductivity values of composites containing only pumice and a hollow glass sphere are compared, it can be seen from Table 4 that the composite containing pumice has a value approximately twice as high as the composite containing a hollow glass sphere. Thus, although the pumice-containing composite does not contain a highly porous structure, its high elasticity and screw holding resistance can be explained with the construction of a very stable network structure. Both the low modulus of elasticity and the very low screw holding resistance indicate that the gypsum-containing composite is a brittle material with an unstable textural structure [108].

Consequently, it can be argued that the composite containing a hollow glass sphere is the most suitable hybrid composite in terms of both thermal insulation and mechanical strength.

4. Conclusions

In this study, melamine formaldehyde foam was successfully prepared by using a new agent for foaming and a combination of microwave radiation and heat treatments for curing. Foam-based hybrid composites, which have improved properties in terms of thermal insulation, mechanical strength, dimensional stability and molding cycle time, have been produced using various materials such as organo-montmorillonite as nano-filler, pumice as primary filler and gypsum, kaolinite and a hollow glass sphere as secondary filler. Spectroscopic and microscopic analyses have shown that there are effective adhesion interactions between polymer clay nanocomposite particles and filler grains, and therefore materials with different textural arrangements and superior properties can be obtained. From the thermal conductivity test results, it was determined that melamine-formaldehyde-organo-clay nanocomposite foam (MFCNC) exhibited a very good thermal insulation performance despite its weak mechanical strength (λ : 0.0640 W/m K). Thermal conductivity test results determined that melamine-formaldehyde-organo-clay nanocomposite foam (MFCNC) exhibited a very good thermal insulation performance despite its weak mechanical strength (λ : 0.0640 W/m K). Thermal conductivity test results determined that melamine-formaldehyde-organo-clay nanocomposite foam (MFCNC) exhibits a very good thermal insulation performance despite its weak mechanical strength (λ : 0.0640 W/m K).

The bending strength order of the prepared hybrid composites is the MF-organoclay–pumice hybrid composite (MFCPHC) > MF-organo-clay–kaolinite hybrid composite (MFCPKHC) > MF-organo-clay–hallow-glass-sphere hybrid composite (MFCPHHC) > MForgano-clay-pumice-gypsum hybrid composite (MFCPGHC). The elasticity modulus order is the MF-organo-clay-hallow-glass-sphere hybrid composite (MFCPHHC) > MF-organoclay–pumice hybrid composite (MFCPHC) > MF-organo-clay–kaolinite hybrid composite (MFCPKHC) > MF-organo-clay-pumice-gypsum hybrid composite (MFCPGHC). On the other hand, the screw holding resistance order is also the MF-organo-clay-pumice hybrid composite (MFCPHC) = MF-organo-clay-hallow-glass-sphere hybrid composite (MFCPHHC) > MF-organo-clay-kaolinite hybrid composite (MFCPKHC) > MF-organoclay-pumice-gypsum hybrid composite (MFCPGHC). Also, the thermal insulation performance order is the MF-organo-clay nanocomposite (MFCNC) > MF-organo-clay–hallowglass-sphere hybrid composite (MFCPHHC) > MF-organo-clay-pumice-gypsum hybrid composite (MFCPGHC) > melamine formaldehyde foam (MF) > MF-organo-clay-kaolinite hybrid composite (MFCPKHC) > MF-organo-clay–pumice hybrid composite (MFCPHC). The hybrid composite containing hollow cam spheres (MFCPHHC) was found to be the highest performing material in terms of thermal insulation and mechanical strength (λ : 0.642 W/m K, mass density: 0.36 g/cm³, durability: 228.41 MPa, elasticity modulus: 2.22 MPa and screw holding resistance: 3.59 N/mm^2).

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