Production and characterization of polyurethane/expanded graphite composites for industrial food preservation

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Abstract: Thermal insulation materials extend the shelf life of food and reduce energy consumption. Polyurethane (PU) insulation materials are often used to keep food hot and cold. Improving the thermal insulation properties of PU can significantly contribute to energy savings and lower food-related costs in the food and pharmaceutical industries. Polyurethane/expanded graphite (PU/EG) composites were obtained by hot-pressing by adding expanded graphite (EG) to PU foams. Composites with 0.05%, 5%, and 10% EG were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), and thermogravimetric analysis (TGA).

Keywords: polyurethane, expanded graphite, composites, insulation.

Otrzymywanie i charakterystyka kompozytów poliuretan/grafit ekspandowany do konserwacji żywności metodą przemysłową

Streszczenie: Materiały termoizolacyjne wydłużają okres przydatności do spożycia żywności oraz zmniejszają zużycie energii. Poliuretanowe (PU) materiały izolacyjne są często stosowane do przechowywania żywności na gorąco i na zimno. Poprawa właściwości termoizolacyjnych PU może znacząco przyczynić się do oszczędności energii i obniżenia kosztów związanych z żywnością w przemyśle spożywczym i farmaceutycznym. Kompozyty poliuretan/ekspandowany grafit (PU/EG) wytworzono metodą prasowania na gorąco poprzez dodanie ekspandowanego grafitu (EG) do pianek PU. Kompozyty z udziałem 0,05% mas., 5% mas. i 10% mas. EG scharakteryzowano za pomocą spektroskopii w podczerwieni z transformacją Fouriera (FTIR), skaningowego mikroskopu elektronowego (SEM) i analizy termograwimetrycznej (TGA).

Słowa kluczowe: poliuretan, grafit ekspandowany, kompozyty, izolacja.

In recent years, the growing demand for food along with the growth of the world's population has led to significant energy consumption for the production and storage of high-quality food. Improving insulation systems and extending the cooling time is the key to saving electricity. Therefore, composite insulation materials are often used to store food (fresh fruit, vegetables, meat, milk, etc.) in cold rooms. Insulation material plays a key role in the presence of dramatic temperature differences inside and outside warehouses in food storage. Promoting the thermal resistance of insulation materials saves energy, but the efficiency of this process varies depending on the component's properties. Insulation materials used in cold stores can offer energy savings ranging from 8% to 72% [1]. In addition, another important criterion for choosing the right insulation material is its ability to pay back its costs within 0–6 years [2].

Recently, polyurethanes (PU) have been considered versatile polymers that are biocompatible and biodegradable [3–5] and have attracted more attention from industry and researchers. Thermoplastic PUs exhibits high tensile strength, high tear resistance [6], and excellent chemical resistance to oils, greases, and solvents [7]. Previously, different zero-size (0-D) (*e.g.*, silica nanoparticles [8, 9], one-dimensional (1-D) (*e.g.*, carbon nanotubes) [10], two-dimensional (2-D) crystals (*e.g.*, graphene) [11], layered silicates [12, 13], hexagonal boron nitride flakes [14], defective 2-D crystals (graphene oxides (GO), reduced graphene oxides (RGO) [15–19] and three-dimensional (3-D) fillers, such as separated graphene nanoplatelets (stacked graphene layers or simply graphite) [20, 21], have been successfully incorporated into polymer films.

Polyurethane (PU), a thermoplastic, is a suitable polymer for fresh product storage in food preservation [22, 23]. It is the most important polymer produced by the polyaddition process of PU diisocyanatos [24]. PU polyols are tough due to their short chain length and aromatic rings. PU polyols are strong due to their short chain length and aromatic rings. In addition, PU foams, which can provide

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lightness, strength, and good thermal shock resistance, which are preferred for sandwich panels in grocery stores, are considered unsuitable for contact with food [25]. In case of contact with food, it must not contain peroxides and isocyanates. Polyurethane-based materials cannot be in long-term contact with food, and the time of direct contact varies depending on the polyurethane content and is 24 hours, 8 hours, and 10 minutes. Therefore, the sandwich panel model is ideal for food preservation. Polyurethane materials with good insulation properties offer high energy savings when used in cold storage. In addition to being lightweight, rigid polyurethane material is also fire-resistant [26].

EG has a higher volume index than pure graphite. Even modified graphite has a porous structure with acid and hydroxyl functional groups that facilitate adsorption in polymer graphite [27]. The pores of expanded graphite range from 2 to 10 nm, and the average pore size is about 2 mm. This form of graphite can be incorporated into molecules including monomers and polymers and between layers of expanded graphene to form a modified composite structure due to its easy bonding properties. EG was developed as a polymer supplement in the early 20th century [28]. While traditional melt extrusion and injection molding techniques were initially applied to polymer/EG composites, later research focused on optimal processing techniques for high-performance composites exploiting the most cost-effective properties of EG [29].

The addition of EG reduces PU heat dissipation. Therefore, the greater the EG content, the lower the rate of heat transfer from the hot to the cold side. This means that the specific heat and density of EG-containing composite materials increase, *e.g.*, after adding 5% EG, the density is 57.8 kg/m^3 and the thermal expansion is 0.428 mm^2/s. In the presence of 20% EG, the density is 73.9 kg/m^3 and the heat spread is 0.214 mm^2/s [30]. Considering the heat dissipation rate as the heat transfer rate from the hot zone to the cold zone, the heat transfer rate decreases when EG is added. Slow heat transfer is a desirable property for food storage materials. In other words, although EG is a material that increases thermal conductivity, it reduces the rate of heat dissipation due to the increased density and thus increases the material thermal insulation. In addition, the fire-retardant properties of EG reduce the amount of smoke per unit area in a fire, providing a rate of smoke at which a person can escape from the fire [31].

Hot-pressing is a widely used method of producing PU, polystyrene (PS) and thermoplastic polyurethane/natural rubber (TPU/NR) composites [32-35]. The addition of carbon nanotubes caused the formation of a conductive network in the molten polymer [33]. In addition, TPU composites reinforced with roselle fibers and sugar palm fibers were prepared by hot pressing at 170°C for 10 minutes and at 190°C under a pressure of 10 MPa, respectively [36, 37]. Graphene/aqueous polyurethane composites and TPU/graphite nanoplate nanocomposites were also obtained by hot-pressing [38, 39]. The polymerization process is commonly used in the production of PU/EG composite materials and KOH, dimethyl phosphonate, dichloromethane, polyols, 4,4′-methylenediphenyl diisocyanate, etc. The composites are produced under specific conditions of pressure and temperature [40]. Biological resources are also used in PU research, and rigid, flexible polyurethane foams have been obtained by synthesizing two biopolyols from rapeseed oil [41], as well as chopped carbon fiber as a filler, and polyurethane composites are prepared using glass frit [42].

For commonly used packaging materials for food insulation, rigid polyurethane foams in shipping packaging, density and temperature are the most common and intuitive coefficients of thermal conductivity [43]. The presence of additives is particularly important, and it has been observed that the thermal stability of PU foams modified with montmorillonite or hybrid fillers is better than that of unmodified ones [44]. If the EG load exceeds a certain percentage, the burn rate is reduced [45].

Therefore, EG was used to obtain fire-resistant PU-based composite foams with increased thermal insulation in cold stores applications. The influence of EG content (0.05; 5 and 10 wt%) on the structure and thermal properties of PU foams was investigated. FTIR, SEM and TGA methods were used to determine the chemical structure, morphology and thermal resistance. PU/EG composite foams were obtained in a two-stage process, i.e. mixing and hot-pressing in a solvent environment. Thanks to the hot-pressing method, which is a well-established industrial forming technique, the product has acquired the potential for profitable mass production in the industry.

EXPERIMENTAL PART

Materials

The polyurethane (PU) with the trade name Akfix 805 was obtained from Akkim Construction Chemicals Inc., which is produced by reacting a polyether polyol with methylene diphenyl diisocyanate. 99% pure EG, trade name Salgraf SGS 0, purchased from Salmarcon A.Ş. 99.5% pure ethyl acetate (EA) and 99% pure methyl ethyl ketone (MEK) were purchased from Merck Company.

Preparation of PU/EG composite foams

The PU and EA were mixed at room temperature (25°C) at 110 rpm for 30 minutes using a mechanical stirrer (IKA Rw 16 Basic). EG (0.05; 5; 10 wt%) and MEK were added to the solution at 400 rpm and stirring was continued for 30 minutes. The prepared mixtures were dried in an oven at 30°C for 24 hours. In the second step, the 4 mm tiles were placed in a press (HOFER HP3000) and pressed at 170°C under a load of 120 kg/cm^2 for 4 minutes (Figure 1).

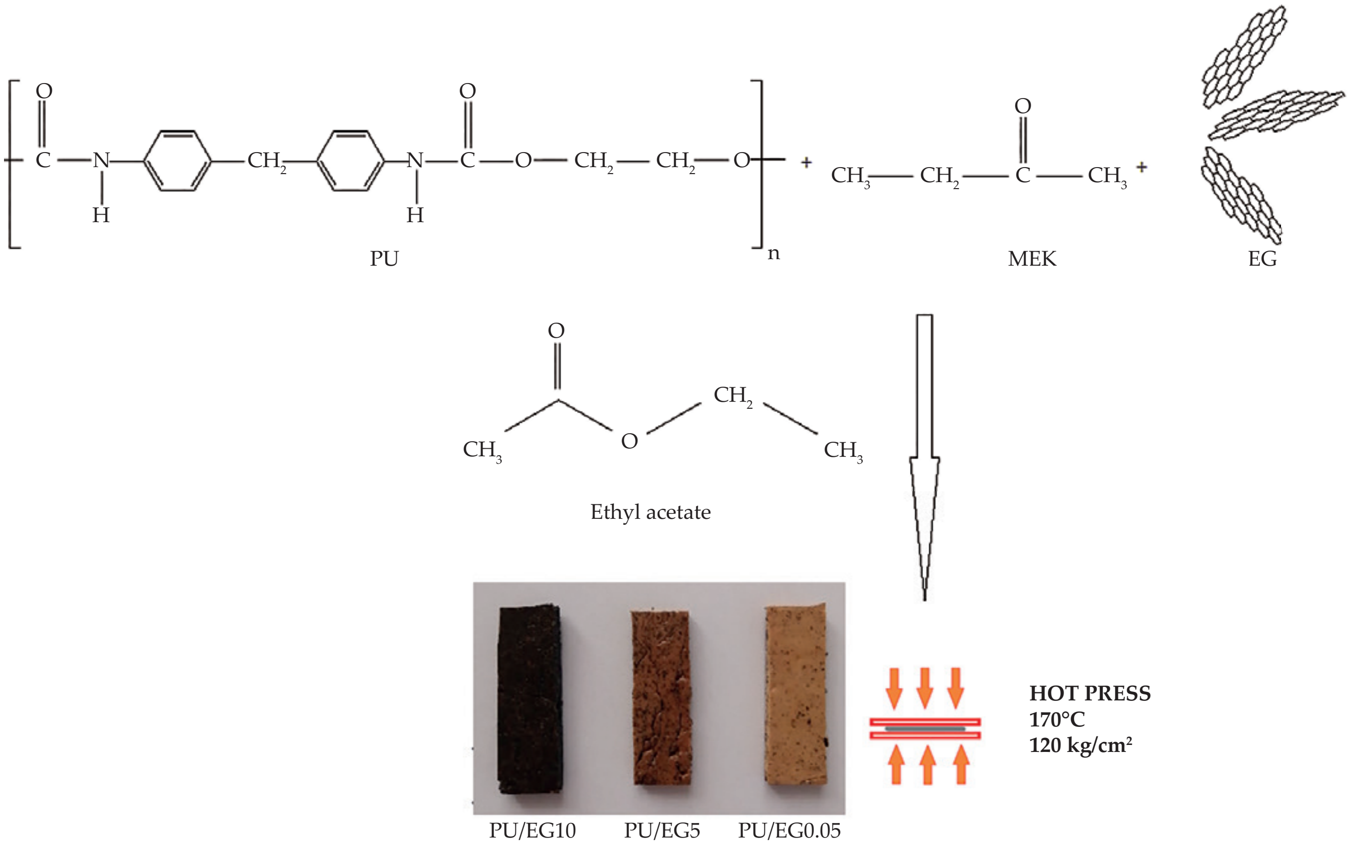

Fig. 1. PU/EG composite preparation scheme

Methods

The FTIR spectra (transmission) were measured on an FTIR spectrophotometer with a PerkinElmer Spectrum operating between 4000 and 650 cm^{-1} at a resolution of 4 cm^{-1}.

The scanning electron microscopy (SEM) analyses were visualized with the high-resolution Carl Zeiss 300VP, working with Gemini SEM Technology and able to detect a pressure of 150 Pa by using real lenses with Nano VP feature, which reduces beam expansion.

Thermogravimetric analysis (TGA) was performed on PerkinElmer Diamond TA/TGA at a heating rate of 10°C/min under nitrogen flow.

RESULTS AND DISCUSSION

FTIR analysis

FTIR was used to confirm the formation of urethane bonds between the isocyanate NCO groups and EG to monitor the extent of this reaction. Figure 2 shows the FTIR spectra of pure PU and PU/EG composites. The vibrations of hydrogen-bonded and NH-free groups at 3250 and 3450 cm^{-1} wavenumbers are typical for pure PU. The loss of absorption bands at 2972 cm^{-1} and the increase at 2966 cm^{-1} wavenumbers are related to the asymmetrical and symmetric CH_2 stress vibrations, respectively. A decrease in peak intensity (CN) was observed at a wavenumber of 1650 cm^{-1}. The peaks at the wavenumbers 1722 cm^{-1}, 1232 cm^{-1}, and 1072 cm^{-1} correspond, respectively, to the stretching vibrations of the carbonyl groups (C=O), the aromatic ring, and the asymmetrical stretching vibrations (C-O-C) [46]. The NH and CN deformation vibrations occur at the wavenumber of 1532 cm^{-1} and 1230 cm^{-1}, respectively [47]. The peak at wavenumber 2262 cm^{-1} almost disappeared due to the depletion of the isocyanate group (NCO) in the polymerization process, while the intensity of the peak at wavenumber 1450 cm^{-1} corresponding to imide (CN) band stretching vibrations increased. Comparing the FTIR spectra, it can be seen that the relative position of the characteristic peaks of PU/EG composite foams is similar to the position of pure PU foams [48]. The FTIR spectra confirmed that the addition of EG caused a significant change in the PU foam chemical structure.

Thermogravimetric analysis

Polymer-based materials have poor thermal resistance at high temperatures. The addition of EG can improve their thermal resistance [49].

Figures 3 and 4 show thermal decomposition curves corresponding to TGA thermograms of pure PU and PU/EG samples. Below 295°C, the thermal behavior of the sample was almost the same. The initial decomposition temperature (T_{on}) of pure PU, which was not hot-pressed as part of the thermal pre-treatment, was 220°C. The ini-

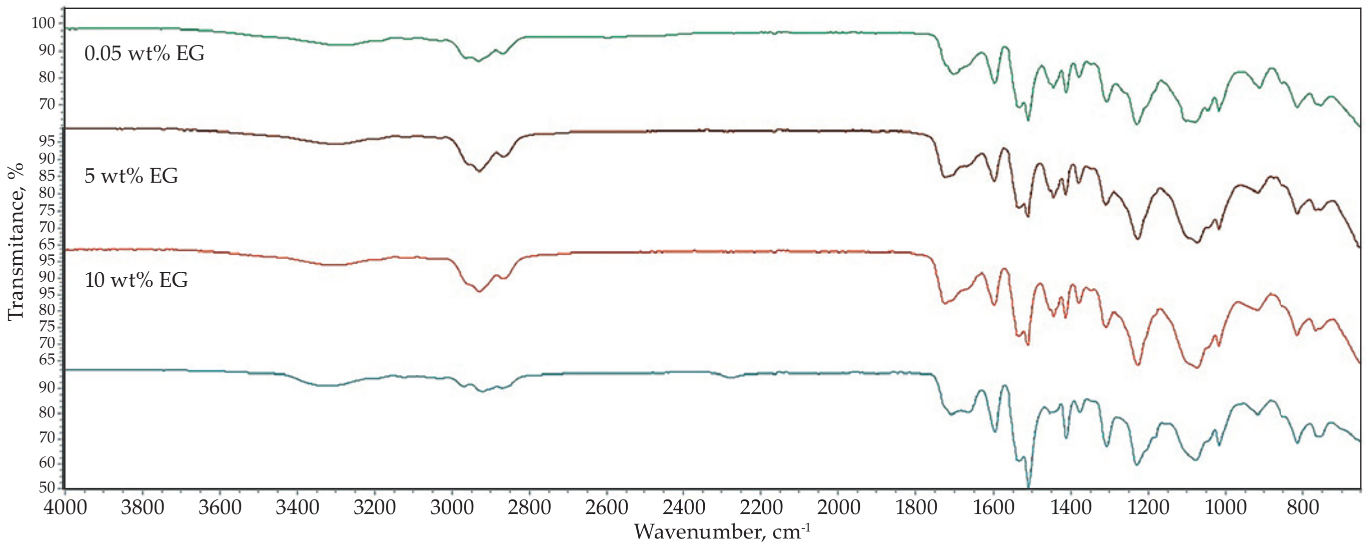

Fig. 2. FTIR spectra of pure PU and PU/EG composites

tial thermal decomposition temperature of the composites increased to 240°C, 245°C, and 260°C, respectively, as a result of hot pressing and EG addition (Table 1). This phenomenon can be explained by the limited movements of the PU chain surrounded by EG particles. Complete thermal decomposition of the samples occurred at 880°C. At the temperature of 470°C, the mass loss for pure PU is 52%, while for the PU/EG10 composite it is 44%. Moreover, two-stage decomposition was observed for PU/EG10 between 200°C and 600°C, while PU/EG 0.05, PU/EG5, and pure PU showed a similar three-stage thermal decomposition. This can be attributed to the EG's ability to reduce heat flow. The results clearly show that adding EG improves thermal stability. Pure PU did not undergo further decomposition in the temperature range of 450-560°C, and PU/EG0.05, PU/EG5, and PU/EG10 composites, respectively, at approx. 480°C, 440°C, and 445°C as the effect of the reaction of carbodiimide with alcohol or water, respectively, and the decomposition of the resulting precursors.

Table 1. TGA data of pure PU and PU/EG composites

Samples	T_{on}, °C	T_{max}, °C	Residue, wt%
Pure PU	220	260.340	4.5
PU/EG 0.05	240	280.330	9.0
PU/EG 5	245	290.350	11.0
PU/EG 10	260	290	6.0

Morphology of pure PU and PU/EG composites

SEM analysis is important when studying the structures of composite foams. During mixing, air bubbles are usually introduced into the reaction mixture and cause blowing agent nucleation, which occurs as a reaction between the isocyanate and the blowing agent. The growth of the bubbles creates a network of bubbles responsible for the cellular structure of the PU. The morphologies of various sections of PU/EG foams are presented in Figure 5, showing the formation of a porous microstructure. A porous structure was found in the pure PU foam, and many small air holes were observed in it, as PU coagulation and solvent extraction caused non-uniform holes in the pure PU foam. In addition to the smaller pores, quite large and deep pores were present in the PU. The pore walls were not of regular shape.

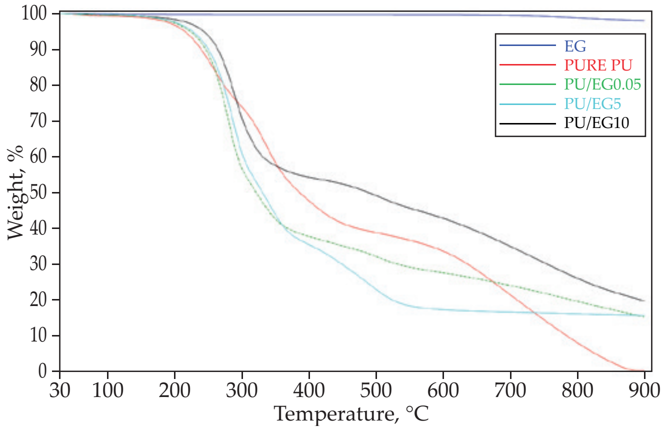

Fig. 3. TGA thermograms of pure PU and PU/EG composites

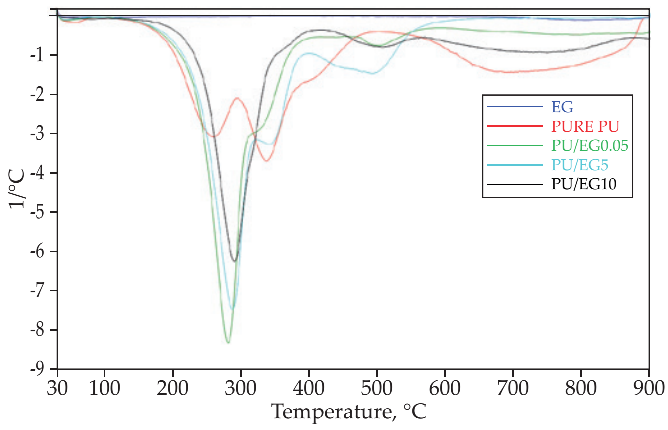

Fig. 4. DTG thermograms of pure PU and PU/EG composites

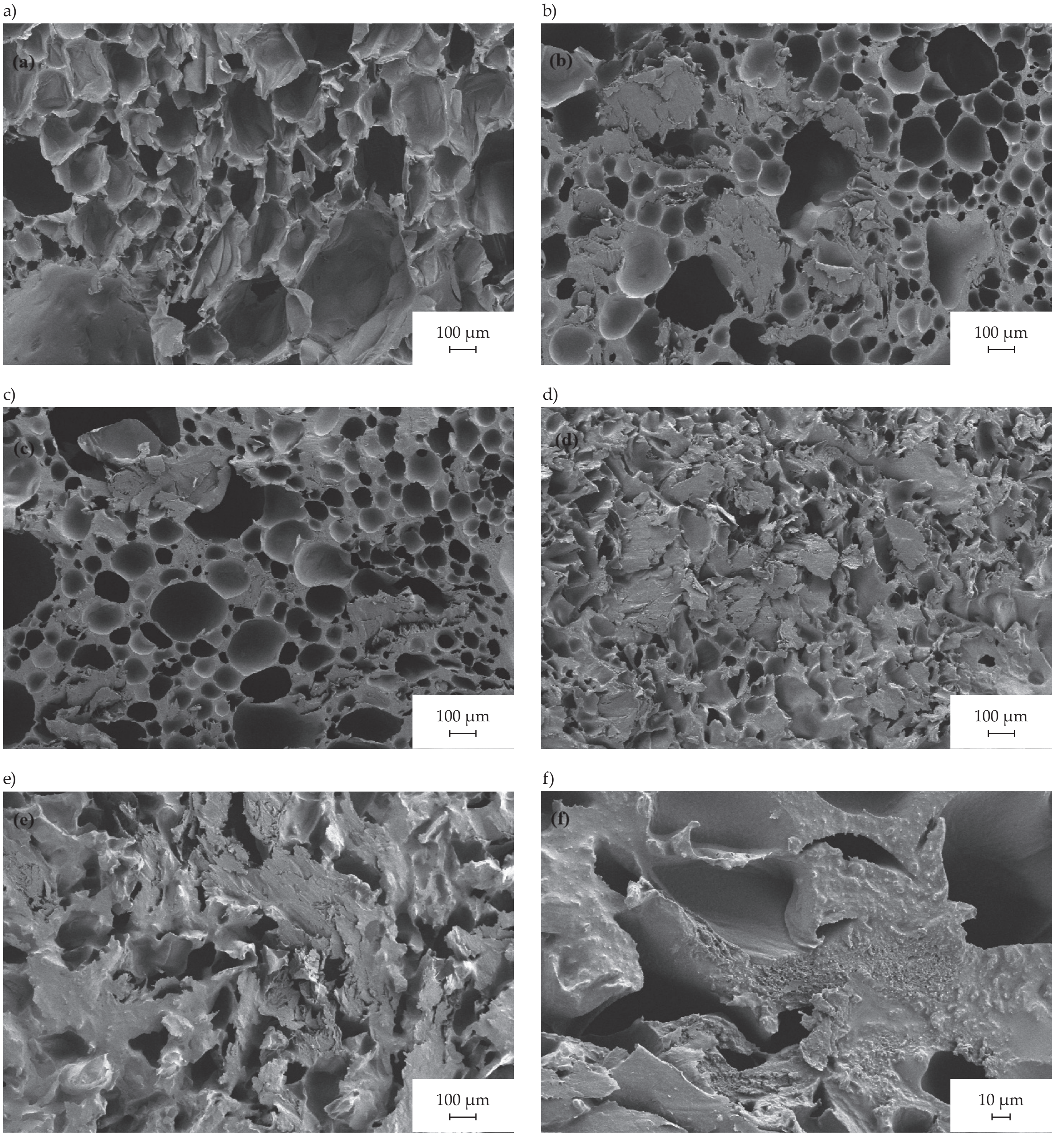

Fig. 5. SEM images of pure PU (a) and PU/EG composite foams before hot-pressing 0.05 wt% EG (b), after hot-pressing: 0.05 wt% EG (c), 10 wt% EG (d), and 5 wt% EG at different magnification (e, f)

These were thin, protruding pores with irregular walls (Fig. 5a). No thin expansions were observed in the pre-hot press structure of the prepared PU/EG composites. There were even more small pores, but they had a thicker wall (Fig. 5b). After hot pressing in the composite containing 0.05 wt% EG, the volume of large-diameter pores significantly decreased and became shallower. The small pores were still too large, the oval shape flattened, and the pore volume decreased (Fig. 5c).

The pores in the EG/PU10 composite were also flattened and closed. There were no large pores, but flatter ones (Fig. 5d). In the EG/PU5 composite, the walls of the small-diameter pores were closed after hot pressing, and all the large-diameter pores disappeared (Fig. 5e, f). Physical changes in the pores after hot pressing in all composites resulted in significant differences. The formation of this highly ordered structure was due to the shear forces of the hot-pressing process. Leafy protuberances and thicker cell walls were observed after the addition of EG (Fig. 5c-f). At higher loading, agglomeration and collapse of the pore structures occurred (Fig. 5d-f). It is clear from the SEM micrographs that the EG particles were added to the PU matrix without any defects or deformations.

CONCLUSIONS

PU/EG composites were prepared by mixing and hot-pressing in a solvent environment. It is a well-established industrial molding technique. PU/EG composites are promising materials for long-term food preservation at low and feverish temperatures. In addition, their fire-retardant properties make them suitable for occupational health and safety applications. SEM results showed that cell size decreases with increasing EG content. FTIR analysis showed characteristic peaks for the ad hoc prepared composite foam. The EG filling significantly changed the chemical structure of the PU foam. The TGA results showed that the thermal decomposition temperature of the PU/EG10 composite was 40°C higher than that of pure PU. The addition of EG caused a decrease in the heat transfer rate from the hot to the cold side, i.e., a decrease in thermal conductivity and the ability to retard combustion [30], which made these composites functional materials. Hot-pressed PU/EG composites can prevent thermal insulation and temperature fluctuations, which is significant for preserving food and saving energy by maintaining storage temperature with less energy for longer periods.

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