Fire Retarded Insulating Sheets from Recycled Materials

Szabolcs Matkó,[1] *Sándor Keszei,*[1] *István Csontos,*[1] *Péter Anna,*[1] *György Marosi,**[1]
Miklós Zsuga,[2] *Jenő Borda,*[2] *Gábor Nagy*[3]

Summary: In this work we aimed at forming partially recycled polymer composites of appropriate mechanical properties and flame retardancy. Multilayer composite structures proved to be suitable to fulfill all of these requirements. Core-shell structures presented here contain two-component thermosets, i.e. epoxy, recycled polyurethane and polyisocyanurate, as matrices reinforced with waste fillers such as short basalt fibers and wood chips. Flame retardancy and mechanical properties of the core-shell structures were investigated by the conventional methods of characterization. The developed cost-effective multilayer composites can be applied as heat and sound insulating panels e.g. multifunctional sheets for construction or automotive industry.

Keywords: basalt fiber; flame retardance; multilayer composites; recycling; wood chips

Introduction

The construction industry currently uses large scale of porous panels as heat, fire and sound insulators in buildings. However, as the complex requirements increase research has been started worldwide for development and application of new materials to replace the less suitable ones and eliminate their unfavourable properties. For example the heat insulating polystyrene foam is undesirable because of its high flammability.[1] The heat and sound insulating polyurethane foams tend to degrade strongly in the presence of humidity by losing their use-value.[2] The fire insulating asbestos sheet is banned because of its carcinogenic effect.[3] The fire-, heat- and sound-adsorbing glass-wool insulators are excellent in many respects, but their structure collapses in fire. Basalt rock-wool and wood chips seem to be economic components to substitute glass fibers and synthetic polymers in insulating composites.

Experimental results known about application of short basalt fibers in polyolefin matrix, using reactive surfactant to improve the fiber-matrix interaction, are promising for the purposes of this work.[4] Similar interface modification proved to be advantageous for wood chips containing composites.[5] Efficient combination of mechanical and fire retardant properties has been attributed recently to polyolefin-based recycled multilayer structures.[6] These composites have appropriate mechanical and flame retardant characteristics, but their high density, weak thermal and sound insulating capability restrict their applicability.

In this work, initiated by the cited results, we tried to achieve advantageous combination of properties with composite sheets of porous structure.

Experimental

Test Methods

UL-94 flammability test: Horizontally and vertically fixed $120 \times 10 \times 4$ mm test bars

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[1] Organic Chemical Technology Department, Budapest University of Technology and Economics, Műegyetem rkp. 3. 1111 Budapest, Hungary
E-mail: gmarosi@mail.bme.hu

[2] Department of Applied chemistry, University of Debrecen, Egyetem tér 1. 4010 Debrecen, Hungary

[3] Polinvent Kft., Ady Endre u. 59. 1221 Budapest, Hungary

were ignited in air atmosphere. The classification of the samples in the HB (lowest), V-2, V-1 and V-0 (highest, self-extinguish) classes is based on the duration of their burning and flame velocity.

Limited Oxygen Index (ASTM D 2863, LOI): Vertically fixed 120 × 10 × 4 mm test bars were ignited at their top in O_2-N_2 mixture. The concentration of the O_2 was increased up to that limit where the test bars burned continuously for 180 s or 5 cm long after the ignition.

Three-point bending test (ISO 178:2001): 80 × 10 × 4 mm test bars were bent in a Zwick Z020 universal equipment. The values of the bending strength and modulus were calculated from the initial slope of the time-bend curves registered by the Testexpert 7.0 software.

Thermal Gravimetry Analysis (TGA): 15 mg of the samples was heated in a Setaram Labsys instrument up to 500 °C in air atmosphere with the heating rate of 10 K/min. The TG curves were registered and evaluated by the SetSoft 2000 software.

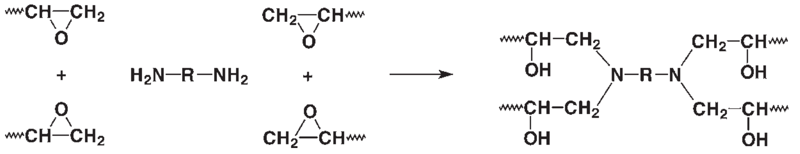
Scanning electron microscopy (SEM): The SEM images were taken in a Jeol 5500 LV equipment. Gold vapor, generated from an Au-Pd alloy in Ar atmosphere at 10^{-4} atm pressure, was deposited on the surface of the samples making them electrically conductive.

Micro-Raman spectroscopy: The stoichiometry of the chemical reaction between the recycled polyol and the isocyanate component was determined with a Raman microscope (Jobin Yvon Labram). The reagents were mixed in a 100 μl Al crucible at room temperature and monitored for 270 s. The isocyanate/polyol ratio was changed systematically from 1:0 to 1:3. The characteristic signs of the isocyanate and urethane groups obtain in the range of 1497–1510 cm^{-1} and 1248–1262 cm^{-1} wave numbers respectively. The spectra were registered and evaluated with the LabSpec software. The disappearance of isocyanate band was considered as the optimal stoichiometry of components, which took place at a 1:2 ratio of isocyanate/recycled polyol.

Materials

1. Polymer Matrices

Epoxy resin (P + M Polimerkémia Kft., Hungary; abbr: EP): The epoxy component (Eporezit AH-16) was crosslinked with an amine type crosslinker (Eporezit T-58):

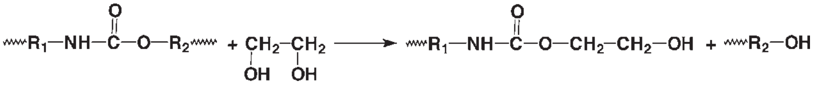


Eq. 1

The commercial two-component EP resin was applied as it was recommended by the producer.

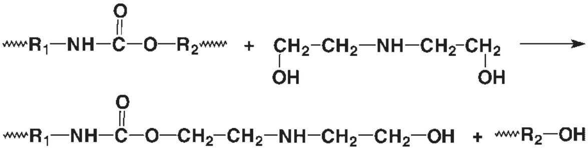
Characteristics: Density: 1.3 g/cm^3, LOI: 24 (V/V)%, UL-94: HB, Bending strength: 75.7 MPa, Bending modulus: 2110 MPa.

Polyurethane (abbr: PU): The polyol component (PEMÜ Rt., Hungary) was a recycled type produced by glycolysis of polyurethane elastomer waste. In the process grinded polyurethane is decomposed with a 3:1 mixture of ethanol amine and ethylene glycol in an autoclave in N_2 atmosphere at 155–170 °C.[7] Some of the chemical reactions taking place are as follows:



$$\sim R_1{-}NH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}R_2\sim + \underset{OH}{CH_2}{-}\underset{OH}{CH_2} \longrightarrow \sim R_1{-}NH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}CH_2{-}CH_2{-}OH + \sim R_2{-}OH$$

Eq. 2

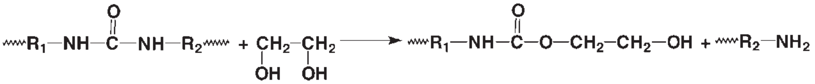


$$\sim\mathrm{R_1{-}NH{-}\overset{\overset{O}{\|}}{C}{-}O{-}R_2}\sim + \mathrm{\underset{OH}{CH_2}{-}CH_2{-}NH{-}CH_2{-}\underset{OH}{CH_2}} \longrightarrow$$
$$\sim\mathrm{R_1{-}NH{-}\overset{\overset{O}{\|}}{C}{-}O{-}CH_2{-}CH_2{-}NH{-}CH_2{-}CH_2{-}OH} + \sim\mathrm{R_2{-}OH}$$

Eq. 3

$$\sim\mathrm{R_1{-}NH{-}\overset{\overset{O}{\|}}{C}{-}O{-}CH_2{-}CH_2{-}OH} \longrightarrow \sim\mathrm{R_1{-}NH{-}CH_2{-}CH_2{-}OH + CO_2}$$

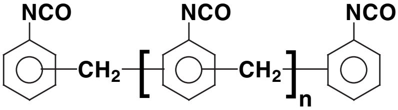
Eq. 4



$$\sim\mathrm{R_1{-}NH{-}\overset{\overset{O}{\|}}{C}{-}NH{-}R_2}\sim + \mathrm{\underset{OH}{CH_2}{-}\underset{OH}{CH_2}} \longrightarrow \sim\mathrm{R_1{-}NH{-}\overset{\overset{O}{\|}}{C}{-}O{-}CH_2{-}CH_2{-}OH} + \sim\mathrm{R_2{-}NH_2}$$

Eq. 5

Although the glycolysis product is a two-phase system henceforth we used only the upper polyol-rich (in our case polyether-type polyol) phase. This can react with original diisocyanate readily to produce urethane groups (Eq. 6). In our case the isocyanate component was the mixture of methylene diphenyl diisocyanates (mainly 4,4′-MDIs) and their oligomers (Polinvent Kft., Hungary).



Scheme 1.
Methylene diphenyl diisocyanates and their oligomers ($n = 0$–10).

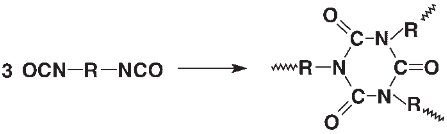
$$\sim\mathrm{R_1{-}N{=}C{=}O + HO{-}R_2}\sim \longrightarrow \sim\mathrm{R_1{-}NH{-}\overset{\overset{O}{\|}}{C}{-}O{-}R_2}\sim$$

Eq. 6

In the case of the PU the optimal isocyanate/recycled polyol ratio turned out to be 1:2. The optimal stoichiometry of components was determined in modell reactions, where the reaction was detected by Raman spectoroscopy as described below. The chemical reaction between the components took place very quickly.

Characteristics: Density: 1.3 g/cm^3, LOI: 22 (V/V)%, UL-94: HB, Bending strength: 32.3 MPa, Bending modulus: 710 MPa.

Polyisocyanurate resin (Polinvent Kft., Hungary; abbr: CYA): The resin was prepared from its components, from methylendiphenyilisocyanate and polysilicic acid in the presence of appropriate catalysts.[8–10] Isocyanates in this system form partially polyurethanes but mainly triisocyanurate structures by cyclotrimerization reaction of the isocyanate (Eq. 7). In parallel with the main trimerization reaction, other complex side-reactions (e.g. production of urethane, urea and carbodiimide groups) take place. The isocyanate component of the commercial isocyanurate resin used was a mixture of methylene diphenyl diisocyanates (mainly 4,4′-MDIs) and their oligomers as it is shown in Scheme 1.



Eq. 7

The commercial two-component CYA thermoset resin was applied as it was recommended by the producer.

Characteristics: Density: 1.3 g/cm^3, LOI: 34 (V/V)%, UL-94: V-1, Bending strength: 23.5 MPa, Bending modulus: 640 MPa.

2. Other used Materials

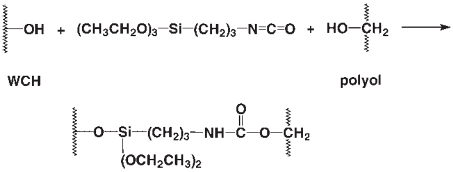
Short basalt fibers (Toplan Tapolcai Bazaltgyapot Kft., Hungary; abbr: SBF): Waste of the so-called Junkers technology suitable to produce long fibers in length of 5–10 cm was grinded. The short fibers in length of 1–20 mm and diameter of 2–50 μm were applied without any further purification.

Wood chips (abbr: WCH): Timber industrial waste pine wood chips in length of 1–20 mm were applied as filler.

Glass fiber fleece (Saint-Gobain Vertex, a.s., Czech Republic; abbr: GFF): Reinforcing fleece, manufactured of chopped, non-oriented, laid glass fibre strands.

Ammonium polyphosthate (Clariant Gmbh; abbr: APP): Exolit AP 422 type ($[NH_4PO_3]_n$, $n > 1000$; P: 31.0–32.0 (w/w)%; N: 14.0–15.0 (w/w)%; decomp. temp.: >275 °C) was applied as a flame retardant additive.

Silane coupling agent (Sigma Aldrich; abbr: SilNCO): 3-(Triethoxysilyl) propyl isocyanate: $(CH_3CH_2O)_3$–Si–$(CH_2)_3$–NCO. This agent is able to adhere to both the PU matrix and the WCH filler chemically:



Eq. 8

Preparation

Surface treatment of the wood chips: Wood chips were put in the toluene solution of the SilNCO coupling agent. Then the solvent was evaporated at about 40–50 °C. The amount of the SilNCO coupling agent was 2 (w/w)% on the total amount of the dry wood chips.

Preparation of resin samples: After the mixing of their components the resins were thrown in a 160 × 160 × 4 mm rectangular steel frame and were left to crosslink at room temperature for 24 hours.

Monolayer composites: The chips wetted with the resin were put in the above mentioned frame and pressed in a Collin P200E machine with pressure of 10 atm to form composite panels. The panels were left to crosslink at room temperature for 24 hours.

Multilayer composites: Reinforcing fillers (wood chips, fibers) mixed with the resins were put between two GFF layers, impregnated with EP or CYA resin, and compressed to composite panels as given above. EP matrix and CYA layer combination is indicated as EP/CYA.

Results and Discussion

The mechanical, thermal and flame retardant characteristics of the pure EP, PU and CYA matrices were determined as reference (given in the Experimental part).

As expected the pure EP resin has the best mechanical properties (the highest bending strength and modulus) but low flame retardancy. As it is shown in Fig. 1, at the beginnings the CYA resin produces higher mass loss rate than the other two matrices. Up to 250 °C a 20% relative mass loss occurs. Probably because of its more stable structure than those of pure EP and PU matrices the decomposition rate slows down considerably above 300 °C. At 450 °C an approximately 20% less relative mass

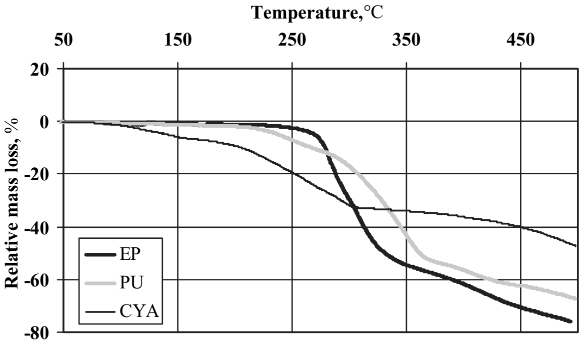


Figure 1.
TG curves of the pure EP, PU and CYA matrices.

loss occurs. This resin has far better UL-94 and LOI values than the other matrix polymers, because of the presence of structure elments of isocyanurate, which have an inherently higher thermal stability than the urethane linkage.[11] The flammability of urethane foams was proposed to be decreased recently by increasing the proportion of isocyanurate in the composition.[12–15] Hauk et al.[16] proposed a possible reactions mechanism for the combustion process of a poly(aminoarylisocyanurate) containing thermoset resin. In contrast to its good flame-retardancy CYA has quite poor mechanical properties because of its heterogeneous structure, shown in Fig. 2.

The SEM image shows that spheres of $Na_2CO_3 \times 10\ H_2O$ (formed at preparation as by-product) in size of 2–60 μm are incorporated in the continuous crosslinked matrix. (Therefore both its bending strength and modulus are less than one third of those of EP resin).

Thermal insulating multilayer panels were made of SBF, GFF, EP and CYA materials. These cost-effective, partially recycled systems contain more than 50 (w/w)% of waste basalt fibers. Their properties are given in Table 1.

Due to their loose core layer (SBF:resin = 9:1 w/w) the multilayer composites have far less density than the compactly structured references (given in the Experimental part). A decrease of nearly 40% is realized. The lower compactness of the multilayer structures causes considerable decrease in bending strength comparing to the pure EP and CYA matrices. Modulus changes differently, some decrease (EP) or increase (CYA), comparing to the references, occur.

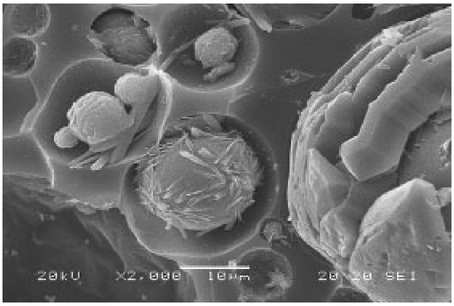


Figure 2.
SEM image (magnification of 2000 ×) of the pure isocyanurate resin (CYA).

Table 1.
Properties of the multilayer EP, CYA and EP/CYA composites.

Multilayer composites	EP	CYA	EP/CYA
Composition, (w/w)%			
		Core layer	
EP	6.3	—	—
CYA	—	6.3	6.3
SBF	56.7	56.7	56.7
		Shell layers	
EP	23.7	—	15.8
CYA	—	23.7	7.9
GFF	13.3	13.3	13.3
Total	100.0	100.0	100.0
Properties			
Density, g/cm^3	0.8	0.8	0.8
Bend. str., MPa	10.6	6.8	9.2
Bend. mod., MPa	1818	1115	1602
UL-94	HB	V-0	V-0
LOI, (V/V)%	25	35	35

The multilayer EP has 55% higher bending strength and approximately 60% higher modulus than the multilayer CYA composites, but it burns completely even at the horizontal UL-94 test (similarly to the pure EP). On the other hand, owing to the high resistance of the triisocyanurate rings to heat, the CYA-based systems have far better flame retardancy than the EP-based ones. (The pure CYA resin and the multilayer CYA composite are qualified as V-1 and V-0 (self-extinguish) respectively.) Increase of 10 unit LOI value is realized comparing to the EP-based systems.

To combine the advantageous properties of the multilayer EP and multilayer CYA structures, we prepared also a multilayer EP/CYA composite in which the EP structure was coated with a CYA/GFF layer. This type of multilayer structure provides optimal combination of density, mechanical properties and flame retardancy as shown in Table 1.

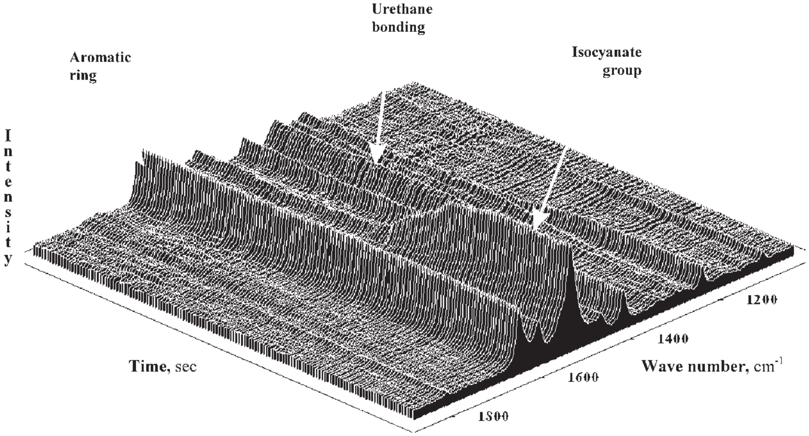


Figure 3.
Continuous monitoring of the crosslinking reaction of PU resin using micro-Raman spectroscopy.

Further mono- and multilayer composites were made of PU and CYA matrices reinforced with WCH, GFF fibres. Whereas the chemical reaction between the polyol and the isocyanate components of the PU matrix took place too quickly, we chose an unusual way to introduce the wood chips in it. First, the WCH were mixed together with the polyol component. Then the isocyanate component was added. The progress of the crosslinking process was determined by micro-Raman spectroscopy. As it is shown in Fig. 3 the applied method resulted in reduced reactivity and provided enough time to put the wetted chips in the frame of compression moulding machine.

The results of these composites, containing considerable amount of waste WCH, are given in Table 2. The properties can be compared also to those of the pure polymers given in the Experimental part.

Comparing of Table 1 and Table 2 a surprising conclusion occurs. Although the amount of the impregnated shell layers is nearly the same in the multilayer composites (37.0 (w/w)% in the EP, CYA and EP/CYA, and 40.0 (w/w)% in the ML 1 and ML 2 composites) their mechanical properties differs considerably. The ML 1 and ML 2 composites have far better mechanical properties (bending strength and modulus) than the EP, CYA and EP/CYA composites. This can be explained, according to observations during the preparation and mechanical testing of composites, by higher shear strength of the core layer and the lower delamination of the skin and core layers of ML 1 and ML 2 composites, which are substantial elements in mechanical properties of the multilayer structures.[17] The monolayer PU composites (Ref 1 and Ref 2) containing wood chips have quite pure mechanical properties even if coupling

Table 2.
Properties of WCH filled mono- and multilayer PU composites.

Composites	Monolayers		Multilayers	
	Ref 1	Ref 2	ML 1	ML 2
Composition, (w/w)%				
			Core layer	
PU	50.0	50.0	30.0	24.0
WCH	50.0	49.0	29.4	29.4
SilNCO	—	1.0	0.6	0.6
APP	—	—	—	6.0
			Shell layers	
CYA	—	—	29.0	29.0
GFF	—	—	11.0	11.0
Total	100.0	100.0	100.0	100.0
Properties				
Density, g/cm^3	0.5	0.5	0.8	0.8
Bend. str., MPa	2.0	2.3	30.5	30.0
Bend. mod., MPa	135	155	2080	2082
UL-94	HB	HB	HB	V0
LOI, (V/V)%	23	23	31	33

agent is applied. The SilNCO coupling agent clearly has a positive effect on the mechanical properties: bending strength and modulus increases by approximately 12% and 15% respectively. However, both monolayer composites are very sensitive to fire. In accordance with their very low LOI values, their UL-94 performance does not reach the lowest rating of the test method.

Multilayer structure consisting of a PU/WCH(SilNCO) core and CYA-impregnated-GFF shell layers reaches 15 × higher bending strength and modulus, furthermore, the CYA resin of outstanding heat resistance provides considerably improved flame retardancy (LOI increased from 23 to 31). Contrary to the monolayer composites this system extinguishes at the horizontal UL-94 test but the V-0 level is still not achieved. For this purpose addition of a small amount of APP flame retardant is required (ML 2 in Table 2). This type of multilayer structure provides further improvement in density, mechanical properties and flame retardancy as shown in Table 2. The lowest UL-94 value of the references turns to the best (V-0). The explanation of the improved flame-retardancy is that the APP additive and the core components constitute an intumescent flame-retardant system, where APP is acid source and spumific agent and core materials are the charring components.[5] These components form a very stable charred foam during ignition, which protects the core as an efficient thermal and gas transport barrier and slows down the decomposition process of the polymer bulk. Otherwise, the mechanical properties improve further comparing to the EP/CYA multilayer composite (Table 1).

Conclusion

Cost-effective EP-, PU-, and CYA-based mono- and multilayer composites, containing considerable amount (29.4–56.7%) of waste (WCH and SBF) and partially recycled (PU) materials, have been elaborated and investigated.

Advantageous properties of the epoxi and the polyisocyanurate matrices can be combined in the form of EP/CYA multilayer composite structure. This system of low density provides improved mechanical properties and high level of flame retardancy.

The SilNCO treatment of the wood chips is efficient improving the mechanical properties of the PU/WCH foam but the fire sensitivity restricts its applicability. Additional layer of reinforced CYA resin and 6.0% of APP additive provide the PU/WCH(SilNCO) with high improvement of mechanical flame retardancy performance. This multilayer composite of low density and high waste content is not only economic and environmental but also engineering system as it combines the high strength and stiffness with self-extinguishing character.

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