

Preparation and Optimization of Natural Glues Based on Laricio Pine Resin

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Abstract. The main purpose of this work was to prepare and optimize glues consisting primarily of natural components. The fundamental component was the laricio pine resin to which different additives were added, varying their nature and quantity. The additives used were: charcoal, activated carbon and carbon nanotubes (MWCNTs). The optimization of the systems continued to identify and select suitable solvents, in order to improve dispersion and solubilization of the phases and to obtain glues in the fluid phase at room temperature. The best results were obtained with ethyl alcohol which, moreover, represents a solvent with a limited environmental impact. The evaluation of the adhesive capacity of the glues was carried out by cutting, tensile and flexural tests on prepared wooden specimens. Furthermore, the specimens and the same glue were subjected to thermal cycles and observed by Scanning Electron Microscope (SEM). The carbon nanotubes, used in very low percentages (1%, in a system consisting mainly of natural origin products) in the presence of an adequate solvent, such as ethyl alcohol, make it possible to obtain a glue that is easy to apply, with an excellent adhesive capacity.

1. Introduction

There are many polluting substances harmful to health in domestic or productive environments. The symptoms are known as SBS Sick Building Syndrome [1-3]. The sick building syndrome has been recognized as a real disease by the WHO (World Health Organization) since 1983. In order to create a home that is as compatible as possible with the environment and human health, future technology will have to take into consideration many aspects such as using innovative materials [4, 5] and adopting effective policies for their easy recovery and disposal [6-9]. The materials suitable for green building can be multi-functional ones [10-13], i.e. those which have new ones thanks to the combination with other materials capable of degrading or adsorbing pollutants from the environment in addition to their traditional functions [14-21]. It is believed that the pollutants due to the SBS originate essentially from acute and prolonged exposure to chemical and biological substances such as those contained in glues, paints, adhesives. [22, 23]. Dangers deriving from solvents and volatile compounds (VOC) in the latter are, in fact, hidden [24, 25].

The most ill-famed is formaldehyde (contained in the glues), which can cause serious health problems including severe respiratory changes and sensory discomforts. Other Volatile Organic Compounds are: hydrocarbons, aldehydes, chlorinated which may become even more dangerous in the presence of atmospheric particulate impregnated by these pollutants, thus increasing their residence



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time in environments [26-29]. The use of natural, biocompatible and renewable substances are always an alternative in the preparation of glues [30, 31]. Generally, however, natural glues have a lower binding power than glues that use synthetic substances [32]. It is for this reason, that our research has been directed towards the study and preparation of a glue that was mainly composed of natural substance and reserving only a very low percentage of synthetic substances that guarantee an increase in adhesion strength. In particular, the basic natural raw material used was the Laricio pine resin. The latter, however, if used alone during cooling crystallizes losing its adhesive power. Therefore, it was necessary to add additives (fillers) to the resin such as: charcoal, activated carbon and carbon nanotubes. Carbon nanotubes are very versatile materials thanks to their particular structure and can be applied in different fields as fibro reinforcing [33, 34] but also as adsorbent materials [35, 36]. The carbon nanotubes, though synthetic, were used in very low percentages, and this allows glue preparation with a mainly natural composition and a substantial improvement of the adhesive strength as regards to the traditional natural glues. Furthermore, we must emphasize that carbon nanotubes are not materials capable of delivering volatile substances into the environment, although they are still nano-materials. They must always be used with caution avoiding any dispersion [37- 39]. Another important objective was to find a sustainable solvent that would allow the preparation of a glue based on a resin that can be applied when cold, unlike procedure for resin based glues that must be first heated and then put into action function quickly before cooling and solidification.

2. Materials and methods

The work was carried out in several consecutive phases: a) Identification of the most suitable solvent; b) Identification of the most suitable filler; c) Characterization of the best mixtures.

For the preparation of the glues, different mixtures were prepared, varying in the nature and quantity of the components. The main basic raw material used was the Laricio pine resin and were used as additives charcoal, activated carbon and carbon nanotubes. These materials have already been characterized in a previous work and, therefore, for any information refer to this [31]. Furthermore, the use of solvents such as ethyl alcohol (VWR, 96%), petroleum ether (Merck) and chloroform (Merck, 98%), were evaluated in order to find the optimal conditions for preparing a glue that can be used cold. The resin, in its solid state was initially ground finely for the preparation of the mixtures. Subsequently 2 g of powdered resin were added to 10 ml of the selected solvent. To speed up the solvent evaporation process, the mixture was heated to temperatures ranging from 45 °C to 110 °C (depending on the solvent used), stirring continually, until almost complete evaporation of the solvent was reached and until a semi-liquid viscose mixture was formed. A selected filler of carbon nanotubes, charcoal or activated carbon was added to this mixture. For all three fillers, however, it was necessary to find the optimal weight percentage to be used, through some preliminary tests. All the mixtures prepared were subjected to characterization by tests through cutting carried out with a Vanderkamp VK 200 tester which measures in a range of 0 -3432.2 KPa, in order to identify the most suitable filler and solvent. The specimens were prepared with two pieces of larch pine, $1.5 \times 1 \times 0.4$ cm in size, glued together in a staggered position so that the glued surface was 1 cm^2 . (Figure 1 a, b).

Subsequently the best mixtures identified underwent:

Flexural resistance tests carried out with an "INSTRON 1195" with a 50 KN load cell and 1 cm diameter knives. The machine was calibrated at a speed of 20 mm / min in displacement control, the data was collected every 5 Hz. The specimens were prepared with two pieces of pine wood, measuring $8 \times 1 \times 0.2$ cm glued between them with the adhesive to be tested (Figures 1c, d).

After bonding, the specimens were placed under press for 48 h. In order to compare, the test of specimen of larico pine wood with size of $8 \times 1 \times 0.4$ cm was also tested. The tests were conducted in triplicate for each type.

Tensile resistance tests carried out with "INSTRON 5582", at a speed of 0.5 mm / min in displacement control, with a load cell of 100KN. The specimens were prepared with two pieces of larch pine, $12 \times 2 \times 0.2$ cm in size, glued together with the adhesive to be tested (Figures 1e, f).

The specimens were placed under press for 48 h after bonding. For the sake of comparison, the wood specimen of the laricio pine measuring $12 \times 2 \times 0.4$ cm was also tested. The tests were conducted in triplicate for each type.

Cutting tests at different temperatures carried out with a Vanderkamp VK 200 tester and using wood samples as described above.

SEM observation was carried out through Scanning Electron Microscope (SEM) FEI "Quanta" 200 EGF (E = 10kV, SE Image).

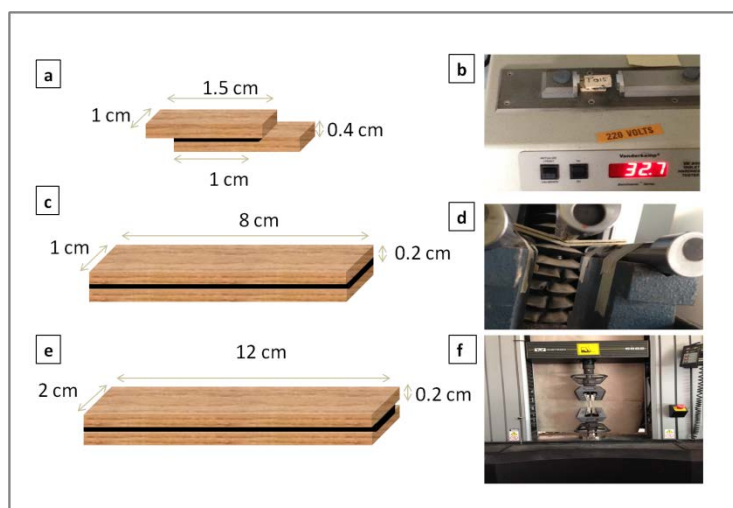


Figure 1. Specimens and instrumentation respectively for (a), (b) cutting tests; (c, d) flexural tests; (e, f) tensile tests.

3. Results and discussion

The results obtained from preliminary tests and the observation of the mixtures, regarding the use of the optimal solvent, made it able to discard the petroleum ether a priori, since the mixture returned solid and of inconsistent appearance, once it evaporated. In the following phase, the action of the other two selected solvents, chloroform and ethyl alcohol, was evaluated and compared. Consequently, mixtures of resin were added with the addition of 0.5, 1, 2, 3 and 6% in weight of nanotubes in the absence of solvent and in the presence of ethyl alcohol or chloroform. In this preliminary phase, we opted for the choice of operating mixtures of carbon nanotubes as well as representative of the other fillers.

In Figure 2, the data of a cutting test carried out on specimens as previously described in paragraph 2 are reported, depending on the solvent used, this shows how the nature of the solvent influences the test. In fact, ethanol had higher results for all percentages by weight, minus 6%. Solvent use as compared to pure resin (no solvent) produced improvements on all percentages, exclusion of 6% as always. As regards the quantity of CNTs, the best percentage is that obtained from 1% to 2% in weight for the ethanol mixture, reaching the end of the machine scale without breakage of the specimen (3432.3 KPa). Inferior results, on the other hand, for chloroform which reaches a maximum of 1% with 1539.6 KPa. Maximum value is found at 6% of nanotubes for the resin-CNTs mixture without solvent. From the evidence of the results obtained, our choice was to proceed experimentation by the sole usage of ethanol as a solvent in as much as chloroform proved to have not only a weaker effect but also a less sustainable one. The choice fell on ethanol which, once evaporated, left a semi-liquid mixture and therefore of easy use. Furthermore, ethanol was able to promote the dispersion of nanotubes and charcoal, whereas in the presence of activated carbons during the solvent evaporation process, a gradual precipitation of the filler at the base is recorded. Ethanol was therefore considered the best solvent. We proceeded with the identification of the optimal quantity of fillers to be used, consequently, once we had chosen and identified ethanol as being the best solvent.

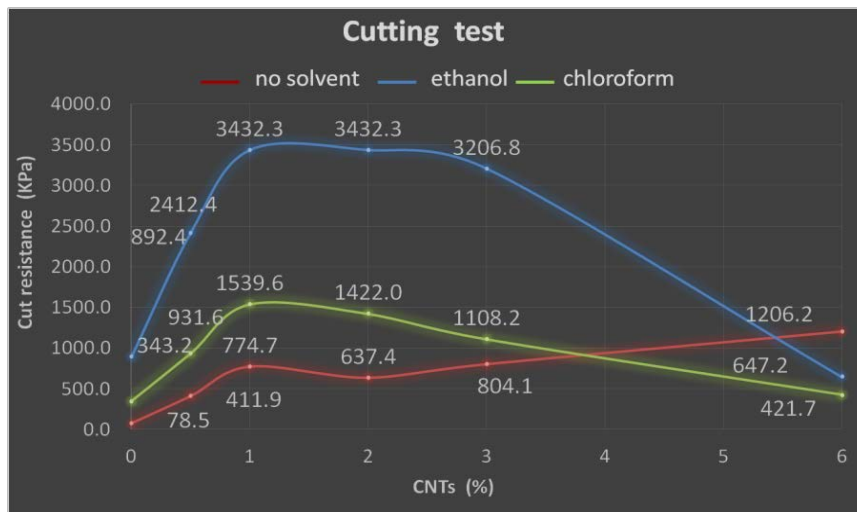


Figure 2. Cutting resistance (KPa) for wood samples glued with mixtures prepared in resin, in the absence and in the presence of solvent and with different quantities of nanotubes (CNTs).

The following Figure 3 shows the results of the cutting test on resin / ethanol systems with different types and quantities of filler. The results obtained confirm the validity of the glue produced with carbon nanotubes. In fact, these samples do not break, even if they reach the end of the scale of the instrument (3432.3 KPa). The results for the charcoal samples are lower than those of the nanotubes, with a maximum of 1.5% wt. of 3432.3 KPa. The active carbons, on the other hand, gave disappointing results up to 1.5% wt., then improving over this percentage until reaching 3366.9 KPa and then fracturing. Further investigation to identify the best filler, through tensile tests were carried out (according to the methods described in paragraph 2).

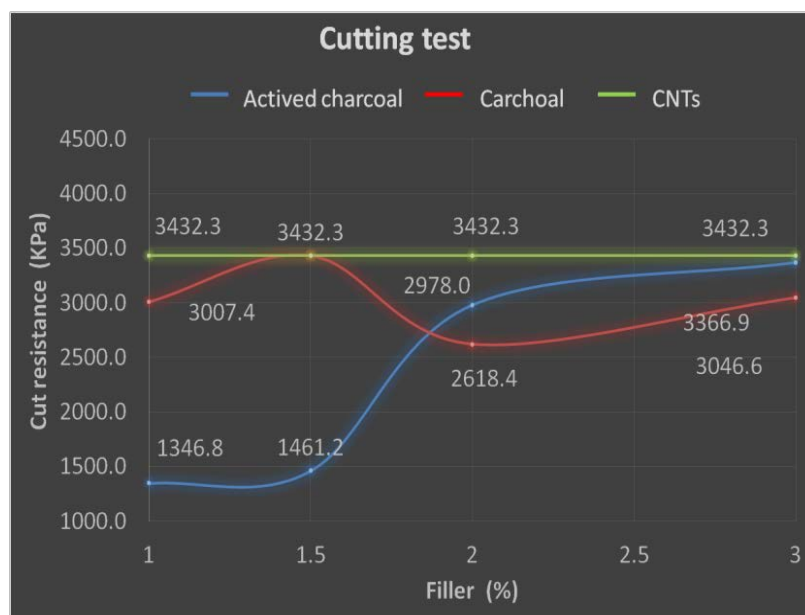


Figure 3. Cutting resistance (KPa) for wood specimens glued with mixtures containing resin / ethanol and different amount and nature of fillers.

Table 1 shows the data obtained from tensile tests carried out on specimens of solid wood only (massive wood) of larch pine of size $12 \times 2 \times 0.4$ cm and on specimens obtained by gluing two pieces of the same wood of measuring $12 \times 2 \times 0.2$ cm with mixtures prepared in ethanol and 1% filler.

Table 1. Tensile resistance, maximum (σ_{\max}) and breaking (σ_b), and strain (ϵ_b) of wood samples and samples with resin / ethanol mixtures and with 1% filler.

Sample	σ_{\max} (MPa)	σ_b (MPa)	ϵ_{\max} (%)	ϵ_b (%)
<i>Massive wood</i>	32.83	32.83	10.07	10.07
Resin + activated charcoal (1%)- Ethanol	28.71	21.61	8.80	8.78
Resin + Charcoal (1%)- Ethanol	40.29	40.29	8.81	8.86
Resin + CNTs(1%) -Ethanol	49.89	49.89	11.55	10.45

The data reported in Table 1 shows that the best results are obtained using mixtures prepared with carbon nanotubes that are higher even than the tests made of wood only.

Table 2 shows the flexural resistance of wood-only specimens and specimens prepared using resin / ethanol mixtures and with 1% filler.

Table 2. Flexural resistance, maximum (σ_{\max}) and breaking (σ_b) and breaking time (T_b), of wood-only specimens and specimens prepared using resin/ethanol mixtures and with 1% filler.

Sample	σ_{\max} (MPa)	σ_b (MPa)	T_b (s)
Massive wood	59.06	59.06	75
Resin+activated charcoal (1%)- Ethanol	59.06	51.19	130
Resin + Charcoal (1%)- Ethanol	61.03	59.06	130
Resin + CNTs(1%) -Ethanol	64.97	64.97	135

Carbon nanotubes are confirmed to be the best filler. The data show that, like all composite materials, they almost doubled the catastrophic breaking time, passing from 75 seconds (T_b) of the massive wood to 130-135 seconds of the specimens obtained using the prepared mixtures. Likewise, applied tensions are also higher, or, at least equal to those of the wood itself. Since a good glue must also be able to withstand temperatures above 50 °C without losing its adhesive power, the behavior of mixtures at different temperatures has been studied. Two mixtures to be compared were chosen: the glue obtained with dissolved resin in ethanol heated to 75 °C and the same matrix with the addition of 1.5% by weight of CNTs. The specimens are subjected to cutting tests as previously described in paragraph 2. The selected temperatures were: -16 °C, 20 °C, 50 °C, 90 °C, 110 °C and 130 °C. Three samples of the two types were created for all temperatures. After a two hour heat treatment, the specimens were left to rest at room temperature for 24h before the cutting test. Figure 4 compares the data obtained. The blue line relative to the resin / CNTs mixture remains constant up to 130 °C that is, (it reaches the end scale without breakage), with the exception of temperatures at -16 °C which resist up to a force of 3187.2 KPa. The resin-only mixture gave good results up to 50 °C, which then decreased almost constantly up to 130 °C to 2177.1 KPa of shear strength, leaving a symptom of loss in the adhesive strength as the temperature increased. Results improved slightly for $T = -16$ °C with 3285.2 KPa. It is very important to evaluate the trends of the two curves. In fact, resistance up to 50 °C is similar. Nanotubes are able to enhance their properties of the thermal resistance beyond this point, even if we consider the amount of evaporated ethanol thus transmitting adhesive capacity towards the matrix at a high temperature. Resin without nanotubes does not present this factor.

Once having identified the best mixtures obtained by the use of carbon nanotubes as fillers, observation by scanning electron microscopy was carried out on samples both in the absence and in the presence of carbon nanotubes. Figure 5a shows the surface of pure resin.

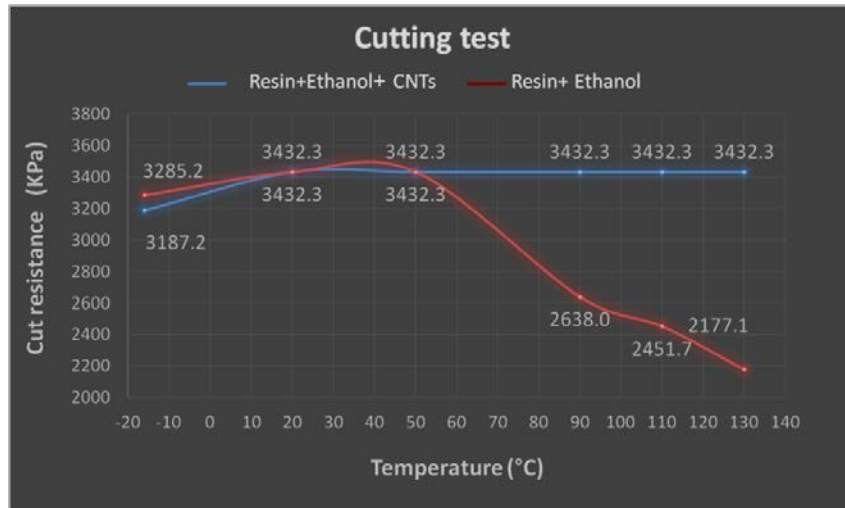


Figure 4. Cutting resistance (KPa) for wood specimens glued together with mixtures containing resin / ethanol with or without nanotubes (1.5%) after thermal cycles at different temperatures.

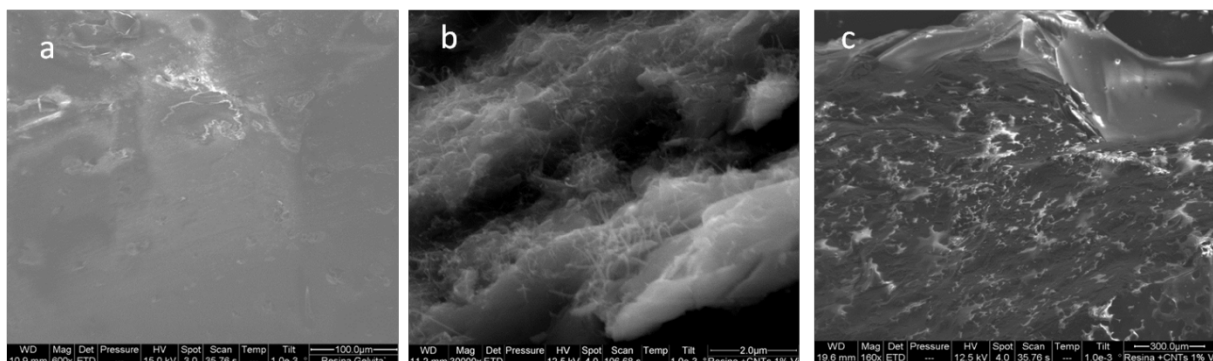


Figure 5. SEM images: (a) resin; (b) resin with carbon nanotubes; (c) breaking surface after cutting test of samples prepared with resin and carbon nanotubes (1%) in ethanol.

The sample is very homogeneous and compact and does not present any discontinuity or presence of pores or macro cavities on this. From the morphological point of view, the addition of the nanotubes does not have any kind of influence (Figure 5b). In fact, there is no known lack of homogeneity and / or diversity compared to the image of pure resin. Furthermore, in this case there are no pores or macrocavities, confirming the full "cohabitation" of these nano fibres in the resin matrix. A morphological study of the resin samples with nanotubes was also carried out after the cutting tests previously carried out on wood samples. Figure 5c shows the breaking surface of a resin-CNTs sample in ethanol. As you may observe, the "pull-out" phenomenon is completely absent. This is a very important problem in the field of composite materials, which consists in the extraction of the fibres from the matrix after a breaking point.

4. Conclusions

The primary objective of this work was to produce new glues of mainly natural composition.

Our choice was a natural and easily sourced material in nature that is the resin of the laricio pine. Research for a suitable solvent had double values, that is, to get free from high temperature preparation treatments and then to maximize dispersion of the fillers in the resin matrix. The characterization of the systems has led to the identification of ethyl alcohol as the most suitable solvent to be used. The latter allowed us to obtain a very fluid composite mixture able to be easily applied on the surfaces to be glued even at room temperature. Furthermore, the choice of ethyl alcohol enabled us to add another further element to the sustainability principle. Since evaporation of this solvent is tolerable towards health, unlike chloroform and petroleum ether, which are also a subject of study. Best results found during the cutting, tensile and flexural tests done on suitably prepared wood specimens were obtained with mixtures containing pine resin in ethanol and using carbon nanotubes as fillers in percentages of 1-2%. The cutting tests carried out, after thermal cycles at different temperatures, have brought to light that the presence of carbon nanotubes makes the glue thermally more stable than glue prepared without carbon nanotubes, thus suggesting a certain chemical interaction, not only to a mechanical matrix-fibre adhesion. The nanotubes, in fact, offer that increase in adhesive capacity and chemical-physical stability that the resin as it does not present and can be considered a good product with an acceptable sustainability, due to its prevailing natural extraction. The glue preparation and production procedures are simple and highly reproducible for eventual industrial production.

5. References

- [1] Norhidayah A, Lee C K, Azhar M K and Nurulwahida S 2013 *Procedia Eng.* **53** 93-98
- [2] Stolwijk J A J 1991 *Environ Health Perspect* **95** 99-100
- [3] Redlich C A, Spare J and Cullen M R 1997 *The Lancet* **349** 1013-16
- [4] De Luca P, Carbone I and Nagy B J 2017 *Journal of Green Building* **12** 141-161
- [5] Gong J, Kostro A, Motamed A and Schueler A 2016 *Solar Energy* **139** 412-425
- [6] Franzoni E 2001 *Procedia Eng.* **21** 883 – 890
- [7] Scofield J H 2000 *Environ. Sci Technol.* **34** 448A-448A
- [8] Warren L P and Peter A T 2008 *Building and Environment* **43** 1858–1870
- [9] Magnone G, De Luca P, Salituro A and Cosenza M G 2014 *Procedia Environmental Science, Engineering and Management* **1** 93-97
- [10] Han B, Zhang L and Ou J 2017 *Light-Emitting Concrete. Smart and Multifunctional Concrete Toward Sustainable Infrastructures.* Springer, Singapore
- [11] De Luca P, Chiodo A and B.Nagy J 2014 *Sustainable Chemistry*, Reniers G and Brebbia C Southampton: WIT Press **154** 155-165
- [12] Husken G, Hunger M and Brouwers H J H 2009 *Building and Environment* **44** 2463-74
- [13] Ballari M M, Hunger M, Husken G and Brouwers H J H 2010. *Applied Catalysis B: Environmental* **95** 245-254
- [14] Fujishima A, Rao T N and Tryk D A 2000 *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* **1** 1-21
- [15] Canpolat F, Yilmaz K, Kose M M, Sumer M and Yurdusev M A 2004 *Cem Concr Res* **34** 731–735
- [16] Krisnandi K, Southon P D, Adesina A A and Howe R F 2003 *International Journal of photoenergy* **5** 131-140
- [17] De Raffe G, Aloise A, De Luca P, Vuono D, Tagarelli A and B.Nagy J 2016 *J. Porous Mater.* **23** 389-400
- [18] Di Paola A, Garcia-Lopez E, Marci G and Palmisano L 2012 *J. Hazard. Mater.* 211-212, 3-29
- [19] De Luca P, Poulsen T G, Salituri A, Tedeschi A, Vuono D, Kònya Z, Madaràsz and B.Nagy J 2015 *J. Therm. Anal. Calorim.* **122** 1257-1267

- [20] Ramirez A M, Demeestere K, De Belie N, Mantyla T and Levanen E 2010 *Building and Environment* **45** 832-838
- [21] Marwa M H, Heather D, Louay N. M and Tyson R 2010 *Construction and Building Materials* **24** 1456-1461
- [22] Cooley J D, Woong W C, Jumper C A and Straus D C 1998 *Occup Environ Med* **55** 579-584
- [23] Apter A, Bracker A, Hodgson M, Sidman J and Wing-Yan Leung B S 1998 *Journal of Allergy and Clinical Immunology* **94** 277-288.
- [24] Hodgson M, Levin H and Wolkoff P 1994 *Journal of Allergy and Clinical Immunology* **94** 296-303
- [25] Chuck W F Y and Jeong T K 2010 *Indoor and Built Environment* **12** 30-39
- [26] Englert N 2004 *Toxicology Letters* **149** 235-242
- [27] Marcazzan G M, Valli G and Vecchi R 2002 *Science of the Total Environment* **298** 65-79
- [28] Filice M, De Luca P, Guido G P 2009 *Environ. Eng. Manag. J.* **8** 1407-1412
- [29] Pekkanen J, Timonen K L, Ruuskanen J, Reponen A and Mirme A. 1997 *Environ. Res.* **74** 24-33
- [30] Mathias J D, Grédiac M and Michaud P 2016 Bio-based adhesives. In *Biopolymers and Biotech Admixtures for Eco-efficient Construction Materials*, 369-385 (Eds) Pacheco-Torgal F, Ivanov V, Jonkers H and Karak N Elsevier Science and Technology, Abington Hall , Cambridge, UK
- [31] De Luca P, Pane L, Vuono D, Siciliano C, Candamano S, B.Nagy J, 2017 *Environ. Eng. Manag. J.* **16** 1659-72
- [32] Packham D E 2009 *Int. J. Adhes Adhes.* **29** 248-252
- [33] De Luca P, Nappo G, Siciliano C and B.Nagy J 2018 *J. Porous Mater.* **25** 283-296
- [34] Thostenson E T, Ren Z and Chou T W 2001 *Composites Science and Technology* **16** 1899-1912
- [35] Policicchio A, Vuono D, Rugiero T, De Luca P and B.Nagy J 2015 *Journal of CO₂ Utilization* **10** 30-39
- [36] Li Y H, Wang S, Luan Z, Ding J, Xu C and Wu D 2003 *Carbon* **41** 1057 1062
- [37] Pacheco-Blandino I, Vanner R and Buzea C 2012 *Toxicity of nanoparticles*. In: Pacheco-Torgal F, Jalali S, Fucic A, Editors. *Toxicity of building materials*. Cambridge, UK: Woodhead Publishing Limited- Elsevier Science and Technology, Abington Hall 427-475
- [38] Lopez de Ipina J et al., 2015 Strategies, methods and tools for managing nanorisks in construction. In: 4th International Conference on Safe Production and Use of Nanomaterials <http://iopscience.iop.org/article/10.1088/1742-6596/617/1/012035/meta>
- [39] Maynard A D, Aitken R J, Butz T, Colvin V, Donaldson K, Oberdörster G and Tinkle S S 2006 *Nature* **444** 267-269