Progress in Organic Coatings 127 (2019) 330–337

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

UV-curable acrylic coatings containing biomacromolecules: A new fire retardant strategy for ethylene-vinyl acetate copolymers

Giulio Malucelli*, Marco Barbalini

Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Viale Teresa Michel 5, 15121 Alessandria, Italy

ARTICLE INFO

Keywords:
UV-curing
Ethylene vinyl acetate copolymers
Acrylic coatings
Caseins
Deoxyribonucleic acid (DNA)
Flame retardancy

ABSTRACT

This work aims at demonstrating the suitability of selected biomacromolecules, namely caseins and deoxyribonucleic acids, as low environmental impact flame retardant additives for UV-curable coatings. To this aim, Bisphenol A hydroxyl ethyl diacrylate was utilized as UV-curable system, in the presence of a suitable photoinitiator (i.e. 2-hydroxy-2-methyl-1-phenylpropan-1-one), for coating ethylene-vinyl acetate copolymer thick plates. The flame retardant features of the coatings were evaluated in the presence of caseins or deoxyribonucleic acids – DNA – (at 10 and 15 wt.% loading) or a mixture of the two biomacromolecules (15 wt.% total loading) embedded in the UV-curable coating system, by means of forced combustion (i.e. cone calorimetry) tests. The coatings containing the biomacromolecules (namely 10 wt.% of DNA or 15 wt.% of casein) showed a decrease of peak of heat release rate and an increase of the time to peak as compared to the unfilled UV-cured counterparts. The proposed strategy may represent a possible starting point for the development of green and durable alternatives to the use of standard and more environmental impacting flame retarded coatings.

1. Introduction

The use of plastics in everyone's life is more and more growing, thanks to all the advantages (such as lightness, non-toxicity, corrosion resistance, reliability, among a few worthy to mention), this class of materials exhibits. Conversely, almost all polymeric materials are easy to ignite, when exposed to a heat flux or to a flame: this detrimental issue is influencing (and in some cases drastically limiting) the applications of polymers, especially in those fields where the risk of fire is very high and can cause dramatic effects. In fact, though it has been an important tool throughout human history, fire can generate very problematic consequences if not properly managed. According to the quite recent data from 2016 National Fire Protection Association (NFPA) [1], the public fire departments in the U.S. responded to 1,342,000 fires that caused 3390 civilian deaths, 14,650 civilian injuries, and an estimated $10.6 billion loss in direct property.

In this context, the use of flame retardants (FRs) can reduce these hazards and significantly contribute to save lives and resources. Thus, it is about 65–70 years that both the academic and industrial world are designing, synthesising and proposing for a market exploitation very effective flame retardant products for different plastics (also including textiles). According to a quite recent review [2], the history of flame retardants has undergone a continuous evolution according to the main following periods:

1) the 'golden period' of flame retardant research (1950–1980)
2) the 1980–late 1990s period
3) the 2000 onward period

During the first (and longest) period, the first patents for organophosphorus-based FRs were invented. The second period was characterized by very limited research, while the 2000 onward period saw a significant development of char-promoting flame retardants; these latter were often combined with phosphorus-containing species, in order to possibly exploit synergisms. This was also the period, during which the toxicity of bromine-based FRs was demonstrated, hence leading to the seeking for possible effective alternatives. Besides, the third period is also very well known for the exploitation of nanotechnology and nanomaterials (in particular in form of nanoparticles or nanolamellae, such as in the case of nanoclays) as a potential efficient strategy for creating self-assembled nanolayer ceramic structures, able to act as a thermal shield, hence limiting the heat and mass transfer from and to the plastic material.

Nowadays, despite the high efficiency of some commercially-available FRs, the academic research is exploring possible alternatives that, on one side, could also result in less fire protection (as compared with

---

* Corresponding author.
E-mail address: giulio.malucelli@polito.it (G. Malucelli).

https://doi.org/10.1016/j.porgcoat.2018.11.039
Received 9 July 2018; Received in revised form 16 November 2018; Accepted 29 November 2018

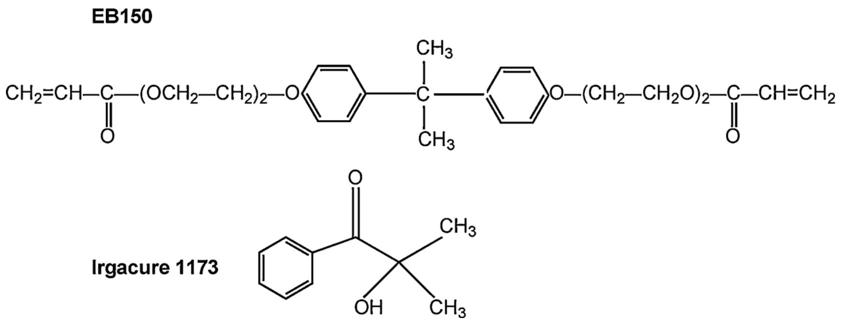

Fig. 1. chemical structures of EB150 and Irgacure 1173.

the very efficient systems containing halogens or halogen-derivatives), but, at the same time, showing a lower environmental impact. In fact, some of the halogenated FRs (such as polychlorinated biphenyls, pentabromodiphenyl ether and decabromodiphenyl ether) have proven to be persistent, bioaccumulative, and/or environmentally toxic for animals and humans [3,4]. At present, the most promising substituents of halogens are phosphorus-based FRs, which can be applied either in bulk or in the recipes of intumescent formulations [5,6]; however, these compounds have not reached the same performances of halogens yet, and some doubts on their toxicity have encouraged alternative ways to explore. Within this breaking point, the design of green flame retardants, even possibly recovered from wastes and crops, seems to be more acceptable for the environment and may deserve further investigation, despite a possible reduced flame retardant efficiency [7].

Quite recently, our research group started investigating the potential use of selected biomacromolecules (namely, whey proteins, hydrophobins, caseins and nucleic acids) as low environmental impact flame retardant for textiles [8–12].

Some of the investigated biomacromolecules (in particular nucleic acids and caseins) also exhibited intumescent features, as, upon exposure to a flame or a heat flux, they give rise to the formation of a swollen protective char on the underlying textile substrate, able to act as a physical barrier limiting the heat, fuel and oxygen transfer between the flame and the polymer [13,14].

These findings could be useful for the design and development of new FRs even for non-char-forming polymers like polyesters, polyolefins and in particular ethylene vinyl acetate (EVA) copolymers. These latter represent important thermoplastic materials used in many fields such as hot melt adhesives [15], electrical wires and cables [16], and biomedical devices. Unfortunately, EVA copolymers are highly flammable and this peculiarity significantly limits their application fields. Usually, this drawback can be overcome by melt blending the copolymers with such flame retardants as inorganic hydroxides (namely, aluminum trihydrate and magnesium hydroxide). These latter are able to enhance the resistance of EVA to ignition, thus reducing its combustion kinetics. Conversely, the main disadvantage associated with the use of inorganic hydroxides refers to the high loading required for achieving acceptable fire performances: as a consequence, the processability of the flame retardant blend, as well as its flexibility, toughness and transparency are worsened [17,18].

We have already demonstrated that DNA can be exploited as an effective flame retardant additive in bulk for EVA copolymers [19]. Furthermore, because of the high cost of the biomacromolecule, α-cellulose or β-cyclodextrins have been considered as alternative carbon sources, aiming at reducing the DNA loading in the copolymers, but still keeping high fire performances and designing an economically sustainable formulation [20].

Pursuing this research, in this work we demonstrate that it is possible to design and prepare flame retardant coatings based on a UV-curable acrylic formulation containing DNA, caseins or both the biomacromolecules, for the fire protection of EVA copolymers. Therefore, a surface engineered approach is proposed, which shows several advantages as compared to the melt blending strategy: first of all, the flame retardant is incorporated into the UV-cured coating deposited on EVA, i.e. where the fire protection is really needed, as the surface of the material is the first to come in contact with the applied flame or the heat flux. Besides, the biomacromolecule loading needed for achieving acceptable flame retardant features is lower as compared to the bulk flame retarded counterparts; last but not least, the biomacromolecules can withstand washing treatments, as they are embedded in the UV-cured polymer matrix and cannot be washed out, hence ensuring durability of the flame retardant coating treatment.

2. Materials and methods

2.1. Materials

An EVA copolymer containing 18 wt.-% vinyl acetate (Elvax®470 front DuPont™; melt flow index: 0.7 g/l0min) was used. Casein powder from bovine milk (phosphorus content: 3.5%) was purchased from Sigma-Aldrich (USA) and stored at 4 °C before its application to the fabrics. The DNA used in this work is a slight yellow powder (consisting of a mixture of oligonucleotides; phosphorus content: 8.5%), extracted from herring sperm; the biomacromolecule, purchased from Sigma-Aldrich, was stored at 4 °C prior its use. A commercially available acrylic resin, Ebecryl 150 (EB150, Bisphenol-A-ethoxylate-diacrylate) was kindly supplied by Allnex (Brussels, Belgium); 2-hydroxy-2-methyl-1-phenylpropan-1-one (Irgacure 1173, Sigma Aldrich, USA) was used as radical photoinitiator at 4 wt.% concentration. The chemical structures of EB150 and Irgacure 1173 are shown in Fig. 1.

2.2. Preparation of EVA plates

EVA pellets were placed in a steel mold ($100 \times 100 \times 3mm^3$), hot-pressed using a Collin -Teach Line equipment at 180 °C, 100 bar for 2 min and finally cooled down at room temperature (r.t.) while keeping the pressure.

2.3. Preparation of the UV-curable mixtures

The UV-curable mixtures were obtained by adding 4 wt.% of photoinitiator to EB150. Then, the biomacromolecules were incorporated to the UV-curable mixtures, by means of a simple mechanical stirring, at the selected loadings collected in Table 1.

2.4. Preparation of free standing UV-cured films and of coated EVA plates

The selected UV-curable mixtures were exploited either for obtaining free-standing UV-cured films, or for coating EVA plates. More specifically, the UV-curable mixtures were deposited on glass slides or EVA plates, respectively, using a wire wound applicator (film thickness: 200 μm); then, they were exposed to UV radiation using a Fusion F300 S apparatus operating in static mode. The total exposure time was 10 s; the radiation intensity on the sample surface, as determined by using a

Table 1
Composition (wt.%) of the UV-curable systems investigated.

Sample code	EB150	DNA	Casein
EB150	100	0	0
EB150DNA10	90	10	0
EB150CAS10	90	0	10
EB150DNA15	85	15	0
EB150CAS15	85	0	15
EB150DNA7.5CAS7.5	85	7.5	7.5

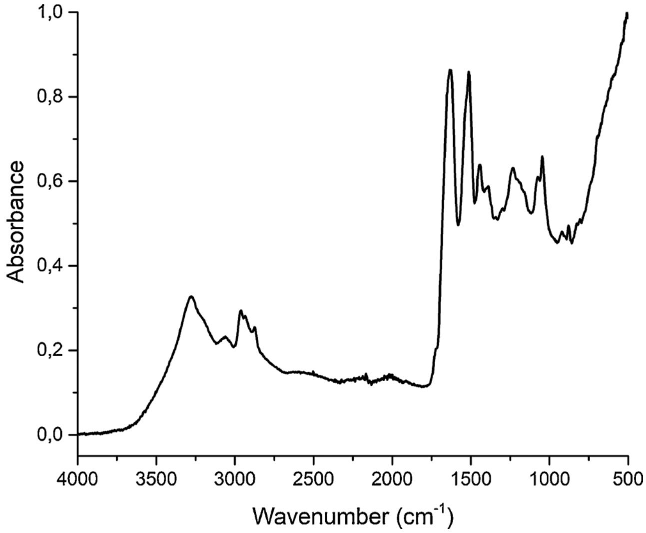

Fig. 2. FT-IR ATR spectrum of casein.

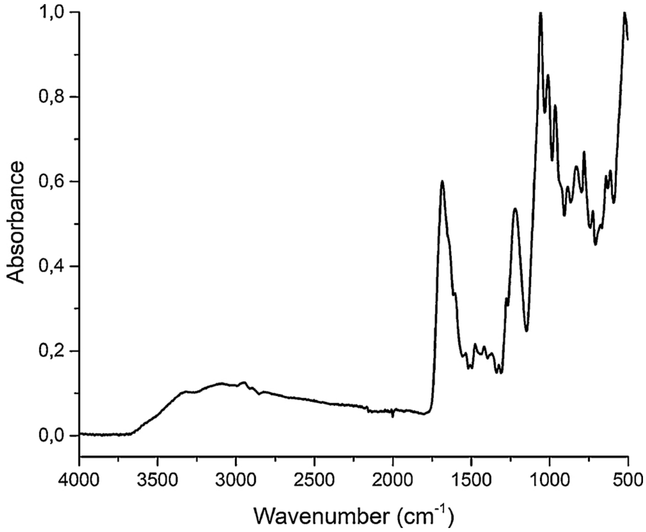

Fig. 3. FT-IR ATR spectrum of DNA.

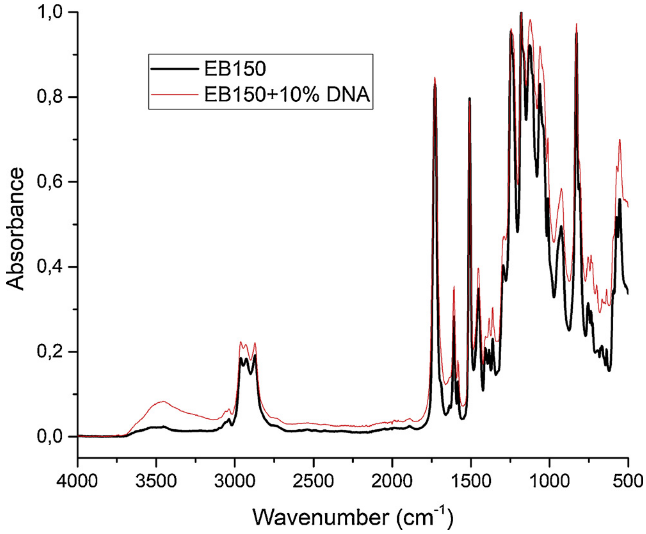

Fig. 4. FT-IR ATR spectra of EB150 and EB150 + DNA 10%.

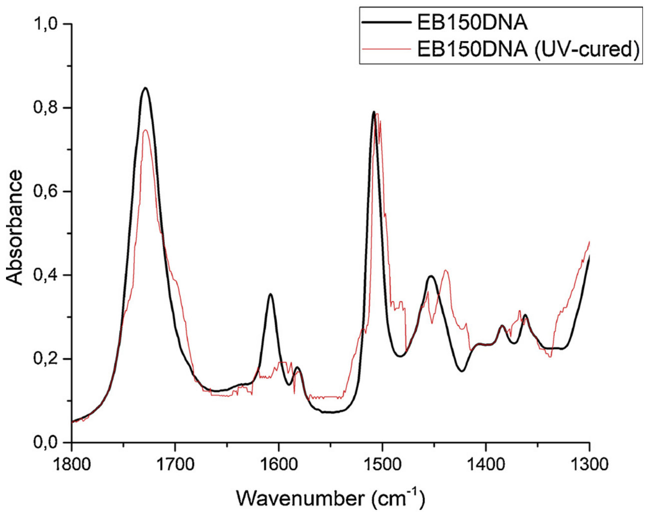

Fig. 5. FT-IR ATR spectra of EB150DNA10 before and after the UV-curing process.

PowerPuck radiometer, was about 1200 mW/cm^2. Free-standing UV-cured films were peeled-off from the glass slides and subjected to the different characterization techniques.

2.5. Characterization techniques

FTIR spectroscopy measurements in ATR (Attenuated Total Reflectance) were performed by using a Frontier FT-IR/FIR spectrophotometer, equipped with a diamond crystal. ATR spectra were collected at room temperature in the range between 4000 and 600 cm^{-1} (32 scans and 4 cm^{-1} resolution).

Differential scanning calorimetry (DSC) analyses were performed using a QA1000 apparatus (TA Instrument Inc., Waters LLC, USA), according to the following cycle:

- First scan: heating up (0/150 °C at 10 °C min^{-1}) and isothermal step at 150 °C for 3 min.
- Second scan: cooling down (150/0 °C at 10 °C min^{-1}) and isothermal step at 0 °C for 3 min.
- Third scan: heating up (using the same conditions as in the first scan).

The thermal and thermo-oxidative stability of the samples was evaluated by thermogravimetric (TG) analyses carried out in nitrogen and in air, respectively, from 50 to 700 °C with a heating rate of 10 °C/min. A TAQ500 analyzer (TA Instrument Inc., Waters LLC, USA) was used, placing the samples (approximately 10 mg) in open alumina pans, in inert or oxidative atmosphere (gas flow: 35 ml/min). In the followings, $T_{onset5\%}$ and T_{peak} will be defined as the temperature corresponding to a 5 wt.% weight loss and to the maximum weight loss rate, as determined from the derivative (dTG) curve, respectively. TG measurements were duplicated in order to assess their reproducibility. The experimental error was ± 0.5 wt.% and ± 1 °C on weight and temperature, respectively.

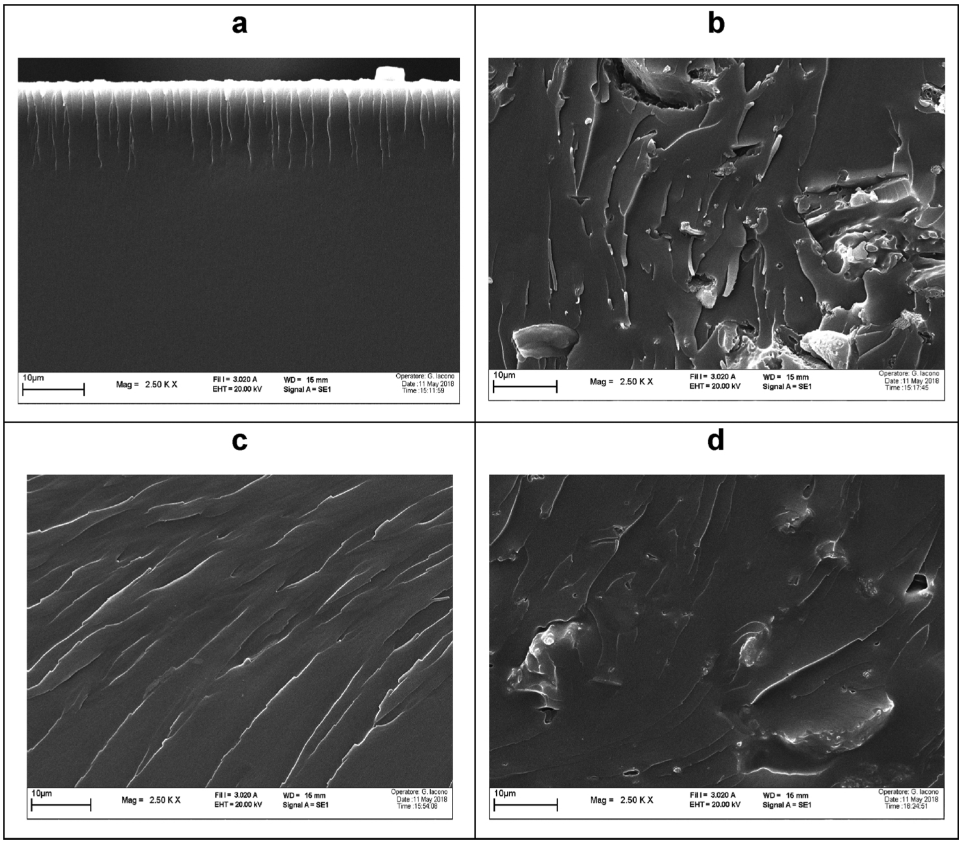

Fig. 6. SEM images of EB150 (a), EB150DNA10 (b), EB150CAS10 (c) and EB150DNA7.5CAS7.5 (d).

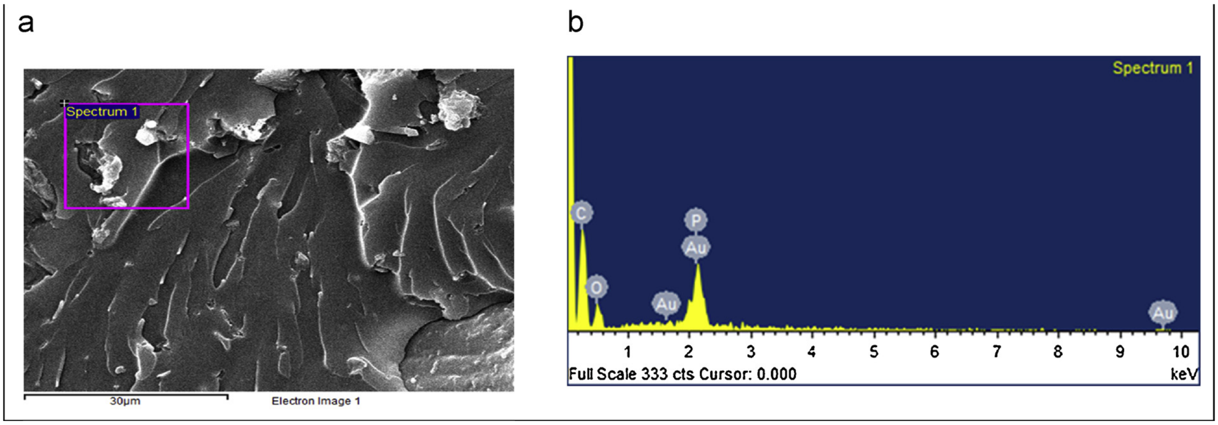

Fig. 7. SEM-EDS analysis of EB150DNA7.5CAS7.5 UV-cured film.

Table 2

Thermal properties of the obtained UV cured coatings.

Sample code	Tg DSC [°C] (1st heating up)	Tg DSC [°C] (2nd heating up)
EB150	41.0	41.3
EB150DNA10	54.1	54.2
EB150CAS10	43.0	43.1
EB150DNA15	52.2	51.4
EB150CAS15	44.9	45.4
EB150DNA7.5CAS7.5	45.6	45.5

The morphology of the obtained samples was studied using a LEO-1450VP Scanning Electron Microscope (beam voltage: 5 kV), coupled to an energy dispersive X-ray micro-analyzer (EDS, mod. INCA Energy 300, Oxford instruments, UK).; fragments of the UV-cured films obtained by a fragile fracture in liquid nitrogen (about 5 × 5mm^2) were fixed to conductive adhesive tapes and gold-metallized.

Cone calorimetry tests (Fire Testing Technology, FTT) were performed according to the ISO 5660 standard. The samples were irradiated at a heat flux of 35 kW/m^2 in horizontal configuration and were placed on an Aluminum shape. For each formulation, the tests were repeated three times and the results averaged; a standard deviation of 2% has been calculated for all the following measured parameters: Time To Ignition (TTI, s), average Heat Release Rate (HRR, kW/m^2), Total Heat Release (THR, kW/m^2), peak of Heat Release Rate (pkHRR, kW/m^2) and time to pkHRR (s). The residues at the end of the tests were evaluated as well.

Table 3
Thermal and thermo-oxidative stability of the obtained UV cured coatings.

Atmosphere: nitrogen

Sample code	$T_{onset5\%}$ (°C)	T_{peak} (°C)*	Residue @ T_{peak} (%)	Residue @ 700 °C (%)
EB150	392	475	40.0	6.4
EB150DNA10	260	460	47.1	16.9
EB150CAS10	309	468	46.2	9.4
EB150DNA15	248	443	52.2	22.2
EB150CAS15	267	470	42.3	10.1
EB150DNA7.5CAS7.5	273	466	50.5	15.5

Atmosphere: air

Sample code	$T_{onset5\%}$ (°C)	T_{peak1} (°C)*	Residue @ T_{peak1} (%)	T_{peak2} (°C) *	Residue @ T_{peak2} (%)	Residue @700 °C (%)
EB150	342	428	63.5	621	12.0	2.6
EB150DNA10	236	443	49.4	608	16.7	6.9
EB150CAS10	320	464	52.1	615	13.3	4.3
EB150DNA15	227	431	55.5	613	18.8	8.5
EB150CAS15	244	451	57.2	606	15.0	5.2
EB150DNA7.5CAS7.5	300	454	48.1	607	13.2	7.4

* from dTG curves.

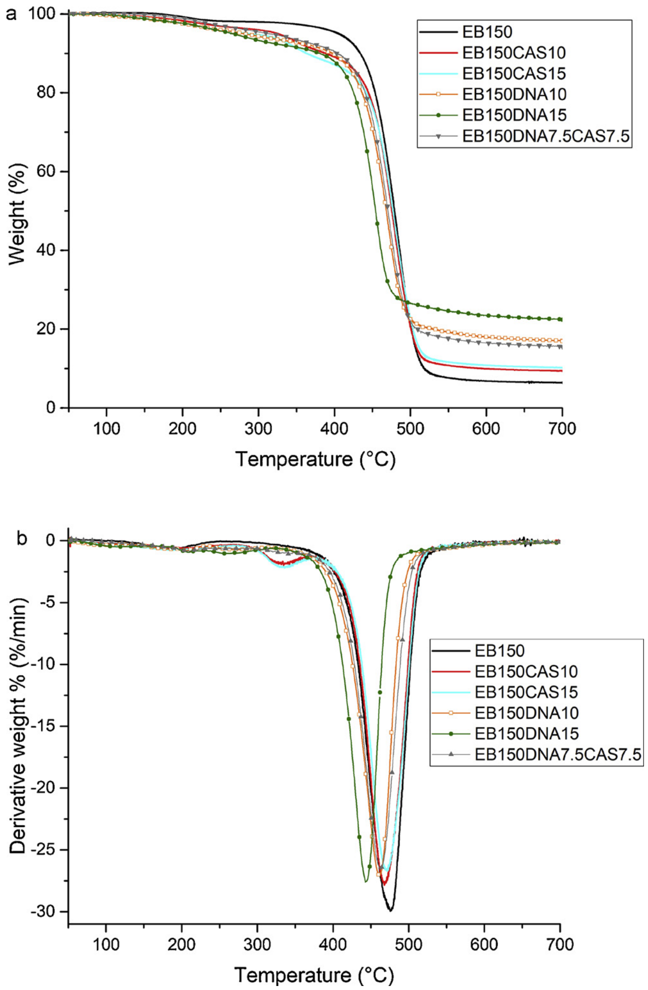

Fig. 8. Tg (a) and dTG (b) curves for the UV-cured coatings in nitrogen.

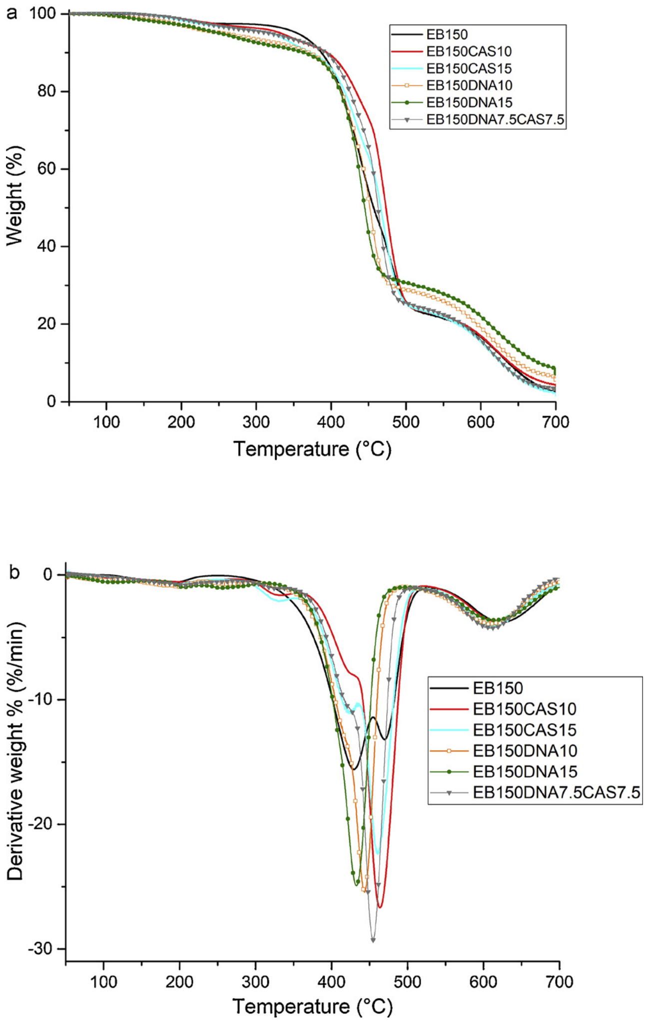

Fig. 9. Tg (a) and dTG (b) curves for the UV-cured coatings in air.

3. Results

3.1. FT-IR ATR spectroscopy

The FT-IR ATR spectra of DNA and casein powders are reported in Figs. 2 and 3, respectively. Casein (Fig. 2) shows some typical bands located at 3200 cm^{-1} (attributable to aromatic aminoacids and OH groups), and at 1635 cm^{-1} and 1514 cm^{-1} (attributable to amide groups) [21].

Table 4
Combustion data (heat flux: 35 kW/m^2) of EVA plates coated with the neat UV-cured system and with the coatings containing the biomacromolecules.

Sample	Time To Ignition (s)	HRR (kW/m^2)	pkHRR (kW/m^2)	Time to pkHRR (s)	THR (MJ/m^2)	Residue (%)
EVA + EB150	70	466.1	1366	222	112	0.2
EVA + EB150DNA10	78	386.9	940	258	110	0.8
EVA + EB150CAS10	67	493.4	1262	236	129	0.3
EVA + EB150DNA15	70	367.1	1012	252	108	1.1
EVA + EB150CAS15	69	490.5	984	235	113	0.4
EVA + EB150DNA7.5CAS7.5	58	412.5	902	261	110	0.7

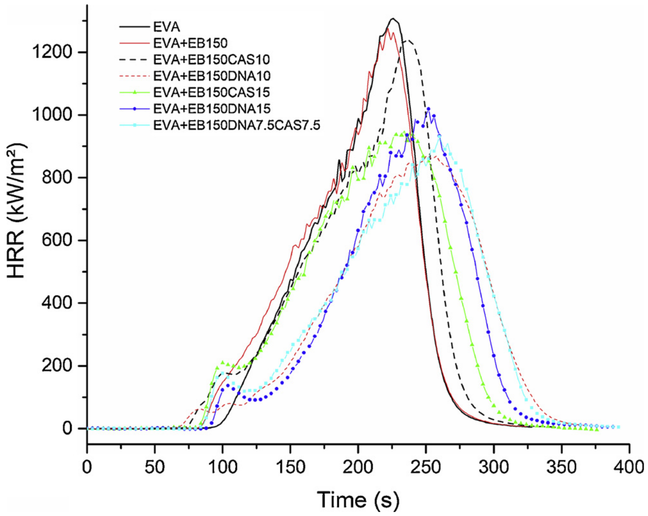

Fig. 10. HRR vs. time for EVA plates coated with the different UV-cured systems.

In the FTIR ATR spectrum of DNA (Fig. 3), three characteristic peaks located at 1680, 1220 and 1060 cm^{-1} and attributable to P=O and asymmetric and symmetric PO_2 vibration modes are observable [21].

The aforementioned peaks are still detectable in the FTIR-ATR spectra of the UV-curable systems containing the two biomacromolecules, as shown in Fig. 4 for EB150 and its mixture containing 10 wt.% of DNA, despite a certain attenuation.

Furthermore, the signal attributable to the acrylic double bonds of the resin, located at about 1635 cm^{-1} [21] completely disappears after the quick exposure to the UV radiation, even in the presence of the biomacromolecules (Fig. 5): this finding indicates that 10 s exposure is enough for achieving the complete curing of the system and that the presence of the biomacromolecules, irrespective of the type and content, does not affect the photo-induced polymerization process.

3.2. *Morphological characterization*

Fig. 6 shows some typical SEM images of the UV-cured films with and without the biomacromolecules: these latter show a good dispersion within the polymer matrix, despite the presence of some agglomerates, the average size of which does not exceed 10 μm.

Furthermore, EDS analysis of all the UV-cured films containing the biomacromolecules confirm the presence of DNA and Casein (as reported in Fig. 7 for EB150DNA7.5CAS7.5). In fact, the analyzed area (Fig. 7a) shows the presence of phosphorus (Fig. 7b), a typical element of DNA and casein.

3.3. *Thermal behavior of the UV-cured films*

The thermal behavior the UV-cured systems has been investigated first through DSC analyses; the obtained results are collected in Table 2.

It is worthy to note that the Tg values do not change in between the two heating scans; in addition, the DSC thermograms do not show any exothermal effect, which may be attributed to a post-curing occurring during the first heating up of the samples. This is another indication that further supports the completeness of the UV-curing reaction. Besides, unlike the caseins, which do not exert any effect on the Tg of the polymer matrix, probably because of their globular structure and higher tendency to agglomerate, the presence of the DNA biomacromolecule, which is in form of strands and less agglomerated, significantly increases the Tg values of the network: this finding indicates that DNA can behave as a reinforcing agent, limiting the mobility of the polymer segments, hence increasing the glass transition temperature of the UV-cured network [22].

Table 3 collects the results from thermogravimetric analyses carried out either in nitrogen and in air; the corresponding TG and dTG curves are shown in Figs. 8 and 9.

In inert atmosphere, the decomposition of the unfilled UV-cured resin takes place according to a single main degradation step; the degradation onset occurs at about 390 °C and the maximum degradation rate is observed at 475 °C. Besides, at the end of the test, the final residue is somehow limited (around 6.4%). The presence of the biomacromolecules, irrespective of the type and loading, significantly affects the thermal stability of the UV-cured network: in particular, both casein and DNA anticipate the degradation of the UV-cured system, as shown by the decrease of $T_{5\%}$ values; it is noteworthy that these latter decrease with increasing the biomacromolecule content. This finding can be ascribed to the lower thermal stability of the biomacromolecules [9–12], which start decomposing at a lower temperature as compared to the polymer network. This finding is also very important as far as the flame retardant behavior is concerned: in fact, upon exposure to a flame or a heat flux, the biomacromolecules have to activate (i.e. degrade) prior to the degradation of the polymer system. In doing so, as already reported in the literature [11], they can favor the formation of a stable carbonaceous residue (*char*), able to act as a thermal shield when the polymer is exposed to a flame or a heat flux. As a consequence, the final

Table 5
Combustion data (heat flux: 35 kW/m^2) of EVA plates coated with the neat UV-cured system and with the coatings containing the biomacromolecules, after washing.

Sample	Time To Ignition (s)	HRR (kW/m^2)	pkHRR (kW/m^2)	Time to pkHRR (s)	THR (MJ/m^2)	Residue (%)
EVA + EB150	70	458.8	1375	223	115	0.2
EVA + EB150DNA10	79	382.3	947	255	110	0.8
EVA + EB150CAS10	67	490.0	1243	236	126	0.3
EVA + EB150DNA15	71	370.1	1006	252	106	1.0
EVA + EB150CAS15	68	494.2	980	234	115	0.4
EVA + EB150DNA7.5CAS7.5	60	407.6	898	260	110	0.6

residues at high temperature increase with increasing the biomacromolecule loading in the UV-cured films. Besides, the EB150DNA7.5CAS7.5 film, containing the same amounts of the two biomacromolecules, shows an intermediate behavior with respect to the systems incorporating lower or higher amounts of each single biomacromolecule. This finding clearly shows that the two biomacromolecules are not able to act in synergism.

In air, the decomposition of the UV-cured coatings occurs according to two main steps: the first, located at lower temperature, is attributable to the breaking of the polymer network, which gives rise to the formation of small fragments; these latter are further oxidized during the second degradation step, occurring at higher temperature (at about 615 °C).

Once again, the presence of the biomacromolecules significantly anticipates the degradation onset of the UV-cured films, as revealed by the decreased $T_{onset5\%}$ values; furthermore, the biomacromolecules, irrespective of the type, do not seem to remarkably affect the second degradation step, but favor the formation of the char, as indicated by the increased final residues at 700 °C. Therefore, both casein and DNA, notwithstanding an anticipation of the degradation of the UV-cured network, are capable of exerting a protection effect that can be further exploited in forced combustion tests, as described in the next paragraph.

3.4. Cone calorimetry tests

Cone calorimetry has been widely used to simulate the fire behavior of a material in a real fire scenario. Heat release rate (HRR) and total heat release (THR) are key parameters to evaluate the combustion behavior of a material exposed to certain heat flux. The data for all the investigated UV-cured coatings deposited on EVA plates are collected in Table 4. More specifically, the combustion of EVA coated with the neat UV-cured coating rapidly proceeds through a single step mechanism with a maximum pkHRR of 1366 kW/m^2 (Table 4). The typical HRR curves vs. time are plotted in Fig. 10.

The presence of the biomacromolecules in the UV-cured coating significantly affects EVA combustion in terms of an anticipation of the ignition (specifically referring to casein- and DNA/casein- containing coatings), a decrease of pkHRR and an increase of the time to pkHRR as well; furthermore, only the DNA-containing UV-cured coatings are able to decrease HRR with respect to the unfilled counterpart, while the Total Heat Release does not change significantly in the presence of the biomacromolecules. Once again, the biomacromolecules show a certain protection effect on EVA, notwithstanding that they are embedded in only 200 μm thick coatings and therefore, their final concentration in the overall polymer (i.e. considering EVA + the UV-cured coating) is much lower as compared to that already employed in EVA melt-blended with DNA [19,20]. Besides, the protective effect shown by the decrease of HRR and pkHRR could to be strictly related to the homogeneity of distribution of the biomacromolecules within the UV-cured network, though it was not possible to prove this hypothesis through SEM analyses.

Finally, as already stated for thermogravimetric analyses, DNA and casein do not show any synergistic effect: however, because of the high cost of the former, it was worthy to try to reduce its loading in the UV-curable formulation, while assessing the fire retardant performances provided by the concurrent presence of the two biomacromolecules.

Therefore, this surface engineered approach could be a possible strategy to further develop in order to optimize the overall fire performances of the designed coatings. Last but not least, it is worthy to mention that the UV-curable coatings containing the biomacromolecules show a good washing fastness: in fact, when the coated EVA plates were subjected to washing cycles (i.e. operating in water at 60 °C in the presence of a detergent for 1 h), their fire performances under the cone calorimeter did not change at all, as shown in Table 5.

4. Conclusions

In the present work, UV-curable acrylic systems containing two different biomacromolecules (namely, caseins and/or DNA) were designed and coated onto EVA plates, aiming at investigating the effect of these coatings on the fire behavior of the underlying copolymer. First of all, free standing UV-cured films showing a homogeneous distribution of the selected biomacromolecules were obtained: their thermal behavior was assessed through DSC and thermogravimetric analyses. In particular, it was found that only DNA is able to noticeably increase the glass transition temperature of the network, hence revealing good interactions taking place between the polymer matrix and the flame retardant additive. This finding could be ascribed to the higher aspect ratio of DNA with respect to casein, which increases the polymer/biomacromolecule interface, notwithstanding some agglomeration phenomena of both the biomacromolecules occurring in the UV-cured coatings.

Besides, from an overall point of view, the biomacromolecules turned out to anticipate the thermal and thermo-oxidative degradation of the UV-cured coatings, favoring, at the same time, the formation of a stable char, as revealed by the high residues at the end of thermogravimetric tests found in both the atmospheres.

Then, the designed coatings were deposited on EVA plates, which were subjected to forced combustion tests under the cone calorimeter: once again, the biomacromolecules turned out to anticipate the ignition of the samples, but, at the same time, were able to reduce the pkHRR and HRR values, while increasing the time to pkHRR. Besides, the fire performances, which did not reveal any synergism between the two biomacromolecules, did not change after having performed washing cycles on the coated EVA plates.

Therefore, the proposed strategy seems to indicate a new potential use of the selected biomacromolecules, specifically referred to a surface engineered approach: further studies are ongoing, aiming at optimizing the fire performances of these coatings as a function of the biomacromolecule loading.

Acknowledgements

H2020 DAFIA Project (Biomacromolecules from municipal solid bio-waste fractions and fish waste for high added value applications - Grant no. 720770) is gratefully acknowledged for financial support.

References

[1] J.G. Haynes, Fire loss in the United States during 2016, Natl. Fire Protect. Assoc. J. (September) (2017).

[2] A.R. Horrocks, Flame retardant challenges for textiles and fibers: new chemistry versus innovatory solutions, Polym. Degrad. Stab. 96 (3) (2011) 377–392.

[3] I. Van der Veen, J. De Boer, Phosphorus flame retardants: properties, production, environmental occurrence, toxicity and analysis, Chemosphere 88 (10) (2012) 1119–1153.

[4] S. Pakalin, T. Cole, J. Steinkellner, R. Nicolas, C. Tissier, S. Munn, S. Eisenreich, Review on Production Processes of Decabromodiphenyl Ether (decaBDE) Used in Polymeric Applications in Electrical and Electronic Equipment, and Assessment of the Availability of Potential Alternatives to decaBDE. European Report EUR 22693 EN, Brussels (2007).

[5] K.A. Salmeia, S. Gaan, G. Malucelli, Recent advances for flame retardancy of textiles based on phosphorus chemistry, Polymers 8 (319) (2016) 1–36.

[6] L.N. Shuyu, N. Matthias, G. Sabyasachi, Recent developments in flame retardant polymeric coatings, Prog. Org. Coat. 76 (11) (2013) 1642–1665.

[7] F. Bosco, A. Casale, G. Gribaudo, C. Mollea, G. Malucelli, Nucleic acids from agro-industrial wastes: a green recovery method for fire retardant applications, Ind. Crops Prod. 108 (2017) 208–218.

[8] F. Bosco, R.A. Carletto, J. Alongi, L. Marmo, A. Di Blasio, G. Malucelli, Thermal stability and flame resistance of cotton fabrics treated with whey proteins, Carbohydr. Polym. 94 (2013) 372–377.

[9] F. Carosio, A. Di Blasio, F. Cuttica, J. Alongi, G. Malucelli, Flame retardancy of polyester and polyester-cotton blends treated with caseins, Ind. Eng. Chem. Res. 53 (10) (2014) 3917–3923.

[10] J. Alongi, R.A. Carletto, F. Bosco, F. Carosio, A. Di Blasio, F. Cuttica, V. Antonucci, M. Giordano, G. Malucelli, Caseins and hydrophobins as novel green flame retardants for cotton fabrics, Polym. Degrad. Stab. 99 (2014) 111–117.

[11] G. Malucelli, F. Bosco, J. Alongi, F. Carosio, A. Di Blasio, C. Mollea, F. Cuttica, A. Casale, Biomacromolecules as novel green flame retardant systems for textiles: an overview, RSC Adv. 86 (2014) 46024–46039.
[12] J. Alongi, R.A. Carletto, A. Di Blasio, F. Carosio, F. Bosco, G. Malucelli, DNA: a novel, green, natural flame retardant and suppressant for cotton, J. Mater. Chem. A Mater. Energy Sustain. 1 (15) (2013) 4779–4785.
[13] F. Carosio, A. Di Blasio, F. Cuttica, J. Alongi, G. Malucelli, Flame retardancy of polyester and polyester-cotton blends treated with caseins, Ind. Eng. Chem. Res. 53 (10) (2014) 3917–3923.
[14] J. Alongi, A. Di Blasio, J. Milnes, G. Malucelli, S. Bourbigot, G. Camino, Thermal degradation of DNA, an all-in-one natural intumescent flame retardant, Polym. Degrad. Stab. 113 (2015) 110–118.
[15] S.K. Dutta, A.K. Bhowmick, P.G. Mukunda, T.K. Chaki, Thermal degradation studies of electron beam cured ethylene-vinyl acetate copolymer, Polym. Degrad. Stabil. 50 (1) (1995) 75–82.
[16] M. Holmes, Wire and cable: some new developments, Plast. Additiv. Compound. 6 (2004) 32–36.
[17] C. Nyambo, E. Kandare, C.A. Wilkie, Thermal stability und flammability characteristics of ethylene vinyl acetate (EVA) composites blended with a phenyl phosphonate-intercalated layered double hydroxide (LDH) melamine polyphosphate and/or boric acid, Polym. Degrad. Stab. 94 (4) (2009) 513–520.
[18] A.I. Fernandez, L. Haurie, J. Formosa, J.M. Chimenos, M. Antunes, J.I. Velasco, Characterization of poly(ethylene-co-vinyl acetate) (EVA) filled with low grade magnesium hydroxide, Polym. Degrad. Stab. 84 (1) (2009) 57–60.
[19] J. Alongi, A. Di Blasio, F. Cuttica, F. Carosio, G. Malucelli, Bulk or surface treatments of ethylene vinyl acetate copolymers with DNA: investigation on the flame retardant properties, Eur. Polym. J. 51 (2014) 112–119.
[20] J. Alongi, A. Di Blasio, F. Cuttica, F. Carosio, G. Malucelli, Flame retardant properties of ethylene vinyl acetate copolymers melt-compounded with deoxyribonucleic acid in the presence of α-cellulose or β-cyclodextrins, Curr. Org. Chem. 18 (2014) 1651–1660.
[21] G. Socrates, Infrared and Raman Characteristic Group Frequencies: Tables and Charts, 3rd edition, Wiley, New York, 2004.
[22] R.F. Landel, L.E. Nielsen, Mechanical Properties of Polymers and Composites, 2nd edition, Marcel Dekker, New York, 1994.