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Plasma deposition of adhesion-promoting polymer layers onto polypropylene for subsequent covering with thick fire retardant coatings

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Melamine resins were used as 50- μm -thick fire retardant coatings for polypropylene (PP). Preceding deposition, low-pressure plasma polymer films of allyl alcohol were coated onto PP to improve the adhesion between PP and melamine resin coatings. The efficiency of such fire retardant coatings was confirmed by flame tests. The plasma-deposited polymer and the dip-coated melamine resin films were characterized by Fourier transform infrared-attenuated total reflectance spectroscopy and X-ray photoelectron spectroscopy (XPS). The adhesion of coatings was measured using a 90° peel test with a doubled-faced adhesive tape. To detect the locus of failure, the peeled layer surfaces were inspected using optical microscopy and XPS. Thermal properties of PP thick melamine resin-coated films were analyzed by thermogravimetric analysis.

Keywords: melamine precursors; plasma polymerization; allyl alcohol; polypropylene; flame retardants; curing

1. Introduction

Polypropylene (PP) is a thermoplastic polymer used in a wide variety of applications such as packaging, textiles, fibers, and floors. In this work, cured melamine pre-polymers were used as flame retardant coatings for PP because the melamine nucleus is rich in nitrogen. Upon exposure of such melamine resin coatings to flame water, ammonia, nitrogen, etc. were released which are able to quench flame propagation as shown recently for melamine resin-coated polystyrene, etc.[1] Moreover, these emitted flame-quenching gases also dilute the flame.[2] Another action of melamine resins is the formation of char or intumescent layer which acts as a shielding barrier between oxygen from air and flammable decomposition gases of polymer substrates. The char stability is increased if melamine combined with phosphorous synergists or pentaerythritol through formation of nitrogen–phosphorous compounds.[3,4]

In this work, the main goal is to coat PP foils with melamine resin layers of sufficient thickness ($\geq 50 \mu\text{m}$) by a simple, cheap, and fast procedure. Previously,

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dip-coating into or spraying with polymer solutions fulfills the conditions of simplicity and high rate deposition of thick layers.[5] Due to the needed high thickness of coatings, expansion of materials takes place because of differences in thermal expansion coefficients of polyolefin substrate and melamine resin coatings. Moreover, very high-temperature gradients from flamed surface to the bulk also introduce strong mechanical stress to the interface between polyolefin and coating. Blowing, blistering, self-peeling are likely, thus, the flame front can propagate directly and more rapidly to the bulk material. To hinder such excavation of unprotected PP, the melamine coatings must have an excellent adhesion to the polyolefin substrate also in case of flame exposure.[6] Introduction of functional groups into the polyolefin surface,[7] deposition of adhesion-promoting plasma polymer layers,[8,9] formation of chemical bonds, or bonding via spacer introduction [10,11] have promoted substantially the adhesion between coatings and substrate.

In this work, a special interlayer consisting of plasma polymerized allyl alcohol was introduced between PP and thick melamine coatings as adhesion promoter. Previously, plasma polymers were successfully used for adhesion promotion.[1] Such plasma polymer modification of PP surfaces could be achieved using processing under low- or atmospheric pressure conditions.[12–14]

To increase the mechanical stability of dip-coated melamine pre-condensates as thick layers on PP, the pre-condensates, which are rich with secondary amino groups ($-\text{NH}-\text{CH}_2-\text{OR}$), were cured in acid medium using ethylene glycol (EG) as bifunctional cross-linker.[15–18] Such processing requires immediate application by dipping the PP substrates into the acidic resin solution before the curing was completed and the solution has thickened. Then, the layers were cured within several hours. Now, the cross-linked layers were tested by flame exposure for improving their mechanical stability and hindered more efficiently the oxygen transport to PP substrates during flame exposure.

2. Experimental

2.1. Materials

PP sheets of 0.1-mm thickness (Goodfellow) were used as substrate. It was first ultrasonicated with diethyl ether for 15 min to remove residual slip agents, light stabilizers, antioxidants at the surface, etc. Allyl alcohol (99.9% grade) used for plasma polymerization was obtained from Merck-Schuchardt. Solution of methylated poly(melamine-co-formaldehyde) (mPMF, average molar mass $M_n \sim 432$, 84 wt.%) in 1-butanol was obtained from Sigma-Aldrich. EG was purchased from Sigma-Aldrich.

2.2. Plasma polymerization

The plasma polymerization was carried out in a cylindrical stainless steel reactor (Ilmvac, Germany, volume of 50 dm³). The grounded reactor was equipped with a powered electrode (5 cm × 35 cm) which was supplied by continuous-wave radio frequency (rf) generator (13.56 MHz, Dressler Caesar 13) and an automatic matching unit. The rf power was pulsed with a duty cycle of 0.1 and a repetition frequency of 10³ Hz.

A stainless steel plate with dimensions 25 cm × 10 cm served as a ground electrode. It was mounted in a distance of 2.5 cm to the powered ('hot') electrode. The effective area of the ground electrode was 1.5 times larger than that of the rf one. The sample (substrate polymer) was placed onto the ground electrode. The pressure of allyl alcohol vapor was

adjusted to 5 Pa. The vapor was introduced through heated tubes to perforated metallic tubes in the reactor used for homogeneous distribution of allyl alcohol in the recipient. The pressure was adjusted by varying the speed of the turbo molecular pump and by adjusting an automatic butterfly valve (V.A.T., Switzerland). A quartz microbalance was taken for *in situ* monitoring of the deposition rate (EDWARDS, FTM7, England). Since the needed densities of ultra-thin plasma polymer layers are difficult to measure, a density of 1 g cm^{-3} was assumed for calculation the film thickness approximately. Therefore, the absolute values of the thickness can have some error, but this potential error is the same for all measurements. Moreover, one can argue that the density of the deposited layers can depend on the plasma conditions like the pressure and wattage.

2.3. Curing of melamine resins

The methylated poly(melamine-co-formaldehyde) resin (mPMF, dissolved in 1-butanol) was crosslinked using 10wt.% EG with respect to the mPMF. p-Toluene sulfonic acid was used as catalyst.[15–19] The, thus, produced solution used immediately to coat PP films by dipping. Figure 1(a) represents the cross-linking reaction.

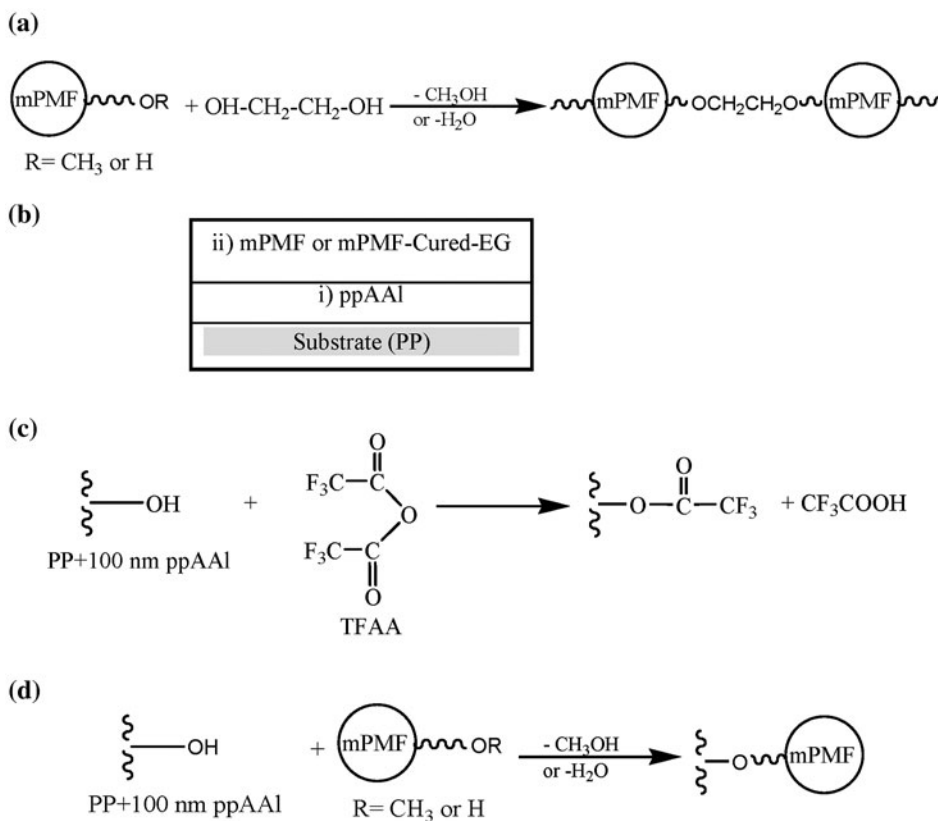


Figure 1. Reaction scheme and build-up of laminates. (a) The cross-linking reaction of melamine resin, (b) schematics of PP thick coated with mPMF resin, (c) hydroxyl group derivatization of ppAAI with TFAA, and (d) chemical bonding between plasma-pretreated PP and mPMF resin.

2.4. Preparation of thick layers

PP substrates were pre-coated first with each 100-nm plasma-polymerized allyl alcohol (ppAAI) layers as adhesion promoter.[20] Then the pre-coated polymers were dipped one time using mPMF/1-butanol solution (4:1 wt/v (g/ml)), then dried; the second dipping was performed into freshly prepared melamine-1-butanol solution with addition of EG, thus producing a total layer thickness of approximately $\approx 50 \mu\text{m}$. The dip-coated foils were subsequently dried in an oven under vacuum for 24 h at 80 °C. Figure 1(b) represents the schematic build-up of PP thick-coated layers.

The whole thickness of the layer pack was measured roughly, using a Mitutoyo 3305(2) DIGIMATIC Messuhr, ID-C, Germany, in different regions. Then, the average thickness was calculated.

2.5. Surface analysis by XPS

The surface composition of the deposited films was analyzed by X-ray photoelectron spectroscopy (XPS) monitoring the C1s, O1s, N1s, and F1s peaks. The spectrometer was a SAGE 150 (Specs, Berlin, Germany) spectrometer equipped with the hemispherical analyzer Phoibos 100 MCD-5. Non-monochromatic Mg K α radiation with 11 kV and a power 220 W was used at a pressure ca. 10^{-7} Pa in the analysis chamber. The angle between the axis of the X-ray source and the analyzer lens was 54.9°. The analyzer was mounted at 18° to the surface normal. XPS spectra were acquired in the constant analyzer energy mode. The analyzed surface area was about 3 mm \times 4 mm.

To calculate the real concentration of OH groups at the surface of ppAAI, the ppAAI layer was exposed to trifluoroacetic anhydride (TFAA) in the vapor phase for 15 min.[21–23] Figure 1(c) represents this gas-phase reaction of hydroxyl group derivatization. In this reaction, the OH groups are converted into trifluoroacetates and, therefore, the F1s peaks in XPS spectra were used for quantifying the OH groups assuming 100% consumption and absence of side reactions.

2.6. Fourier transform infrared-attenuated total reflectance mode

Fourier transform infrared (FTIR) spectra were recorded from 550 to 4000 cm^{-1} accumulating each 64 scans at a resolution of 4 cm^{-1} using a Nicolet Nexus 8700 FTIR spectrometer (Nicolet, USA) in the ATR mode (Diamond Golden Gate, Nicolet, USA). All spectra were subjected to the ATR correction for diamond, smoothed, and baseline corrected. In contrast to surface-sensitive XPS with a sampling depth of about 6 nm, about 2500 nm (2.5 μm) are analyzed by ATR.

2.7. Peel strength measurements

A 90° peel was carried out in accordance with DIN EN 60249 at a speed of 25 mm/min using the tensile testing machine TH2730 (Thümler, Germany). A double-sided tape (TESA Type 4965, Beiersdorf AG, Germany) was applied. The calculated standard deviation varied between 10 and 15%. The test tape was pressed onto the coating with 5 kg for 6 h before peeling. After peeling of the composite systems, the peeled surfaces were inspected using XPS to detect the locus of peel front propagation as well as the type of mechanical failure if it is either interface failure or cohesive failure in the coating or the substrate material. The schematic build-up of PP thick coated with mPMF resin is shown in Figure 1(b).

2.8. Thermal properties of layers

Thermogravimetric analysis was performed using the thermoscale NETZSCH STA 409, GmbH in oxidizing environment (synthetic air). The samples were measured in the range beginning from room temperature and ending at 1000 °C with a heating rate of 10 K/min. Gas-phase products could be identified by FTIR analysis.

2.9. Fire retardant effect measurements

The flame test was carried on the basis of Standard flame test DIN 4102-1.[24] The exposure time of samples to the flame of a Bunsen burner follows the standards. The ignition of vertically oriented samples was tested by direct contact with a small propane flame.

The ignition time is one characteristic of the prepared PP specimens. Therefore, the propane flame was targeted to the specimen as long as it ignites the specimen. After ignition, the burner was immediately removed. To get an impression, the first tests were carried out with the specimens synthesized without any fire preventatives. Afterward, the same test (under the same conditions) was carried out PP samples coated with fire retardant or preventives layers.

3. Results and discussion

3.1. Plasma polymerization of allyl alcohol

Each 100 nm of ppAAI films was deposited onto PP substrates. Figure 2 displays the thickness growth of the deposited layers vs. the deposition time. The thickness of the deposited plasma polymers has linearly grown with deposition time; thus, the needed thickness of 100 nm could be easily adjusted. The deposition rate was nearly constant for all the time but slightly lower at beginning, may be due to the establishing of a steady state between deposition and etching.

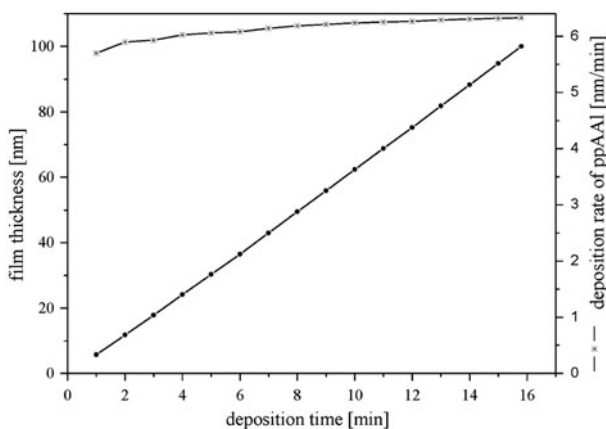


Figure 2. Thickness growing and deposition rate of plasma-polymerized allyl alcohol in dependence on deposition time.

3.2. Characterization of plasma-deposited poly(allyl alcohol) layers

The chemical structure and elemental composition of the deposited ppAAI layers was investigated using Fourier transform infrared -attenuated total reflectance mode (FTIR-ATR) and XPS.

Figure 3 represents the FTIR spectra of PP, PP coated with ppAAI, PP coated with ppAAI + mPMF, and PP coated with ppAAI + mPMF + EG.

The deposited ppAAI layers show a stretching absorption band at $\approx 3370\text{ cm}^{-1}$ corresponding to $-\text{OH}$ groups. After labeling of OH groups with TFAA, this band diminished and a new one at 1210 cm^{-1} appears due to the stretching absorption of C–F in CF_3 groups of the TFAA.[9,23]

For the melamine resin, a strong and broad absorption band was observed in the region of $3500\text{--}3100\text{ cm}^{-1}$ which could be assigned to the N–H stretching vibration of amino groups consisting of overlapped asymmetric (3368 cm^{-1}) and symmetric (3290 cm^{-1}) N–H stretching vibrations. In addition, an absorption band situated at about 1610 cm^{-1} , which corresponds to scissor ‘amide II’ band. Moreover, OH stretching vibration bands are expected to overlap with the neighboring amine peaks around 3500 cm^{-1} .

The C 1s peak was fitted into four components: C–C, C–H at 284.7 eV, C–O at 286.3 eV, C=O at 287.5 eV, and carboxyl (COOH) at 289 eV as seen in Figure 4(a).[8,9] The XPS survey spectra of ppAAI and of the derivatized reaction product with TFAA [8,9] are represented in Figure 4(b). More previously, the derivatization of OH groups was proved to be highly selective (ca. >90%) for measuring the OH group concentration in ppAAI films.[23] The OH concentration determined here varied from 25 to 30% OH/C, thus slightly lower than theoretically expected (33% OH/C).

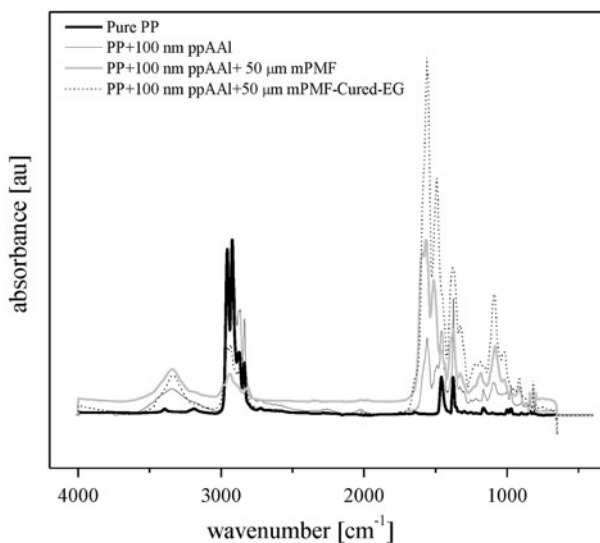


Figure 3. FTIR-ATR spectra of PP samples coated with plasma-polymerized allyl alcohol and melamine resins.

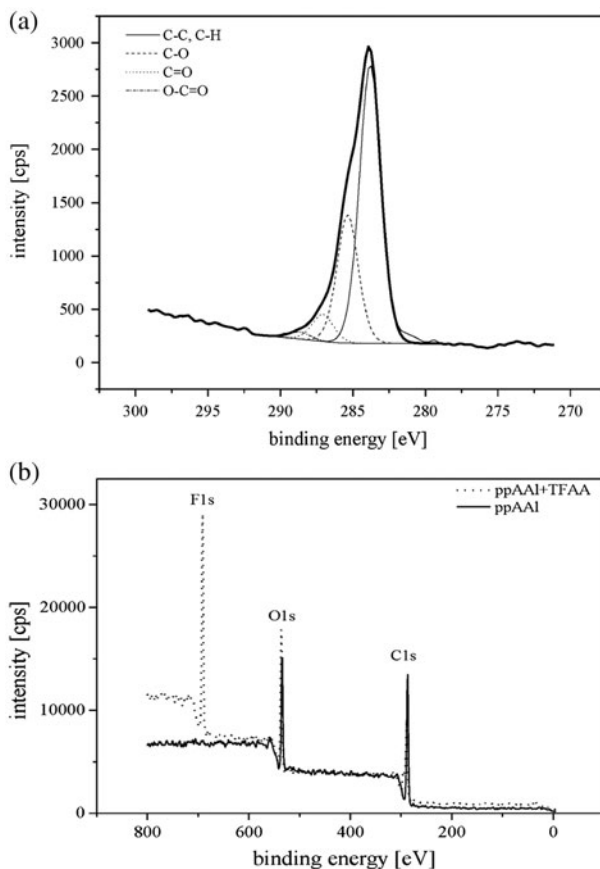


Figure 4. XPS spectra of coating. (a) Fitting of C1s peak of plasma-polymerized allyl alcohol and (b) XPS survey spectra of plasma-polymerized allyl alcohol before and after derivatization with TFAA.

3.3. Preparation of the thick melamine–formaldehyde layer

One of the key factors for good flame retardant properties is the control of oxygen transport through the surface coating. Precondition is the durable adhesion of the coating to the substrate also in case of high temperatures as occurring in flame attacks. Here, 100-nm ppAAI layers were used as adhesion-promoting primers of thick flame retardant layers consisting of mPMF. These thick melamine resin layers with thicknesses of $\geq 50 \mu\text{m}$ were deposited simply by dipping into mPMF solutions.

The adhesion between the substrate, the adhesion-promoting plasma polymer interlayer, and the mPMF coating is determined by formation of covalent bonds, physical interactions, and hydrogen bonds. Chemical bonding was expected between mPMF thick layers and ppAAI interlayer as shown in Figure 1(d), which would increase strongly the adhesion between mPMF resin and the plasma-pretreated substrate. This was confirmed indirectly by extensive washing of plasma-pretreated PP sample thick coated with mPMF (without curing with EG) followed by XPS analysis of the washed surface. Figure 5 indicates the permanent presence of uncured mPMF. This result suggests that the melamine resin should be chemically bonded predominantly to the

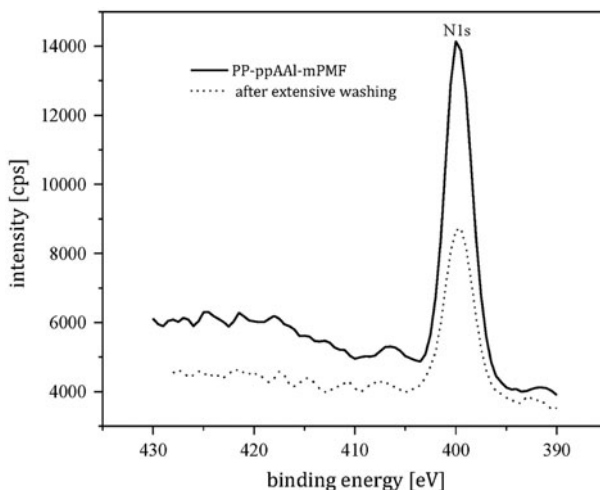


Figure 5. XPS N1s peak of PP coated with plasma-polymerized allyl alcohol and uncured melamine resin.

plasma-pretreated PP surface as schematically shown in Figure 1(d). The extraction of the poly(allyl alcohol) layer plasma deposited onto the PP substrate could also not remove the plasma polymer completely. Also at this interface, covalent bonds should be formed during the plasma deposition.

3.4. Peel strength of the deposited layers

Peel strengths of plasma polymer deposited, dip-coated mPMF, and EG cured PP laminates were measured. The test results are presented in Figure 6(a). The double-faced adhesive tape could not remove either the 100-nm poly(allyl alcohol) polymer layer or the 50- μm coating made of cured melamine resin (mPMF) during the peeling. The tape was stripped from the surface of EG-cured mPMF coating without any sticking residues of coating, thus excellent adhesion signaling without interface or cohesive failure. Only the samples coated with 100-nm poly(allyl alcohol) and with 50- μm mPMF without curing with EG could be peeled. Nevertheless, the measured peel strength was still very high. The XPS analysis of the peeled surfaces showed a cohesive failure within the uncured mPMF surface layer thus confirming the necessity of curing it with EG. To improve the adhesion further and to avoid the cohesive failing within the mPMF layer, the mPMF systems must be crosslinked with EG. It should also be noticed as derived from the peel strength results depicted in Figure 6(a) that the plasma-polymerized layer of allyl alcohol polymer is indispensable for adhesion promotion. In absence of the adhesion-promoting ppAAI layer, the XPS analysis of the peeled laminate surfaces indicated that the peel front propagates along the interface between the polymer and the thick layer of EG-cured melamine resin. Thus, a self-peeling during flame exposure is to be feared.

The microscopic images of the peeled mPMF systems were represented in Figure 6(b). They show that the surface of mPMF cured with EG after peeling is smooth, homogeneous, and intact, while that of the non-cured one has cracks and pits.

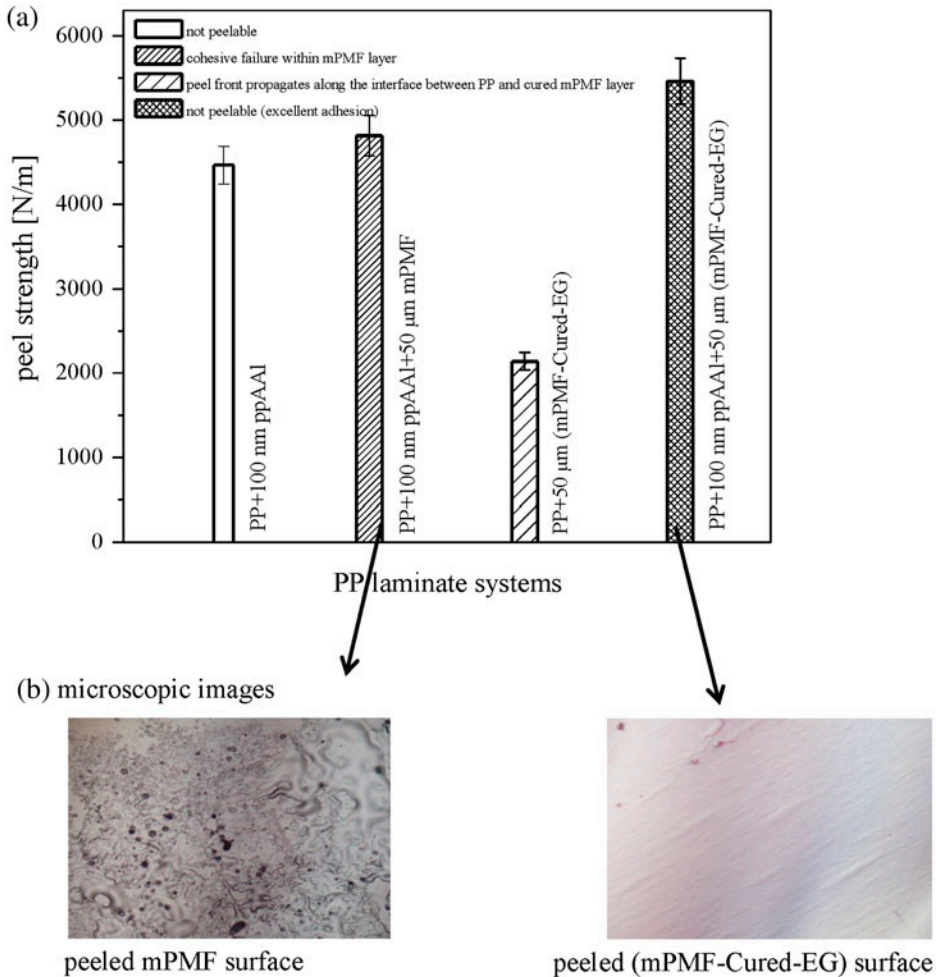


Figure 6. Peeling of coatings. (a) Peel test measurements of PP-mPMF laminates and (b) microscopic images of the peeled mPMF systems.

3.5. Thermal behavior of poly melamine layer-coated polymers

Thermogravimetric analysis (TGA) curves show that the maximum weight loss of the virgin PP was approximately at 330 °C, while the polymer composites begins to decompose already at lower temperature (Figure 7). Nevertheless, TGA curves reflect also an evident improvement in thermal resistivity at higher temperature accompanied with formation of non-combustible residues.

The TGA curve of 50- μ m-thick-coated films exhibits four temperature ranges indicating different degradation processes.[19] The weight loss in the range of 150–200 °C is due to the removal of water, the second one at 200–350 °C corresponds to the elimination of formaldehyde. In the temperature region beginning from 350 °C and ending near 400 °C, the scission of the methylene bridges occurs accompanied with the evolution of ammonia, and beyond 400 °C the degradation of the triazine ring occurs as detected by FTIR analysis of gas-phase products. The char formation at

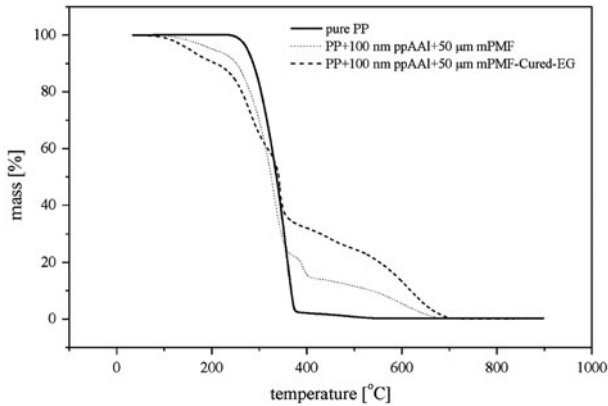


Figure 7. Thermogravimetric analyses of PP samples.

temperatures >400 °C should have a stabilizing effect by barrier formation and therefore shielding the laminate for extensive flaming. The emission of such diluent gases as nitrogen and ammonia, as measured by gas-phase FTIR analysis, enhances the fire retardant properties.

3.6. Flammability tests

The fire behavior of PP composites was measured similar to DIN 4102-1.[24] It could be observed visually and also measured that the 50- μm coating of cured melamine resin improves significantly the fire stability. The laboratory tests give a useful indication of flame retardancy. The results are summarized in Table 1.

The results show an improvement in the thermal properties of the modified PP samples. The visual observations of the flame-tested samples showed that non-treated PP melts, drips, and burns very rapidly, while PP laminates show no dripping, the flame rate and intensity also lowered as well as char formation occurs. However, it can be suggested that the complete prevention of inflammation of such PP laminates requires much thicker coatings, may be 100- μm thick or more and/or the combination with other coating materials, such as water glass [14] or polyphosphates.[25]

Table 1. Flame test results of the modified PP samples.

Sample	Time to ignition (s)	Burning behavior
Pure PP	Ignited too fast for exact measurement (<1 s)	Melt with dripping completely burned after 3 s
PP + 50 μm mPMF	4 s	No dripping charring
PP + 50 μm (mPMF-Cured-EG)	6 s	No dripping charring Time to flame out is larger than that of the mPMF sample

4. Summary

The main goal of this work is the coating of PP with 50- μm -thick well adherent flame retardant layers. This could be achieved by the deposition of a 100-nm-thick plasma polymer layer of allyl alcohol with adhesion-promoting property followed by dipping the pretreated specimen into a solution of melamine resins. Such surface treatment modifies the surface without affecting the intrinsic bulk properties of modified polymer as demonstrated by FTIR and TGA results.

The peel strength of the EG-cured melamine layer was strongly improved by the plasma-polymerized poly(allyl alcohol). The cured melamine resin coatings could not be peeled at any way. Only the peeling of the uncured melamine resin was possible showing a cohesive failure within the melamine resin.

The fire behavior of the PP composites was also improved upon introducing a 50- μm -thick coating of the cured melamine layers. Then, dripping was absent, ignition time was prolonged, and flame-shielding char formation was observed. However, it was assumed that high efficient fire protection needs layer thickness greater than 100 μm , preferably with addition of polyphosphates.

Disclosure statement

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