

Abstract

First goal of this work was to produce thick fire-resistant coatings, which are able to withdraw the direct contact to flames. Preliminary tests had shown that thicknesses more than 10 μm are needed to measure effects on flammability. Here, 40 μm thick layers are prepared. The adhesion of such thick layers mainly depends on the use of surface treatment of polyolefin substrates. Plasma exposure and deposition of plasma polymer layers are easiest and most efficient methods to promote the adhesion of thick layers used for the fire protection of materials. Indeed, plasma processing doesn't modify the intrinsic properties of materials such as the mechanical properties, easily processed, and can be applied over a wide range of materials even though for metals.

To achieve very high adhesion of such thick coatings to the polymer substrates it has to be considered that the chemical nature of coating and polymers is different, strong different thermal expansion coefficients exist and therefore adhesion was most often absent.

Different techniques were used to prepare such thick layers and to promote strong adhesion. Coatings have to withdraw high temperatures at exposure to flame without self-peeling; otherwise flames and oxygen have access to the subjacent easy flammable polymer substrates. Combinations of two deposition techniques allow fulfilling these preconditions. Generally, plasma pre-treatment was used to improve the adhesion property of polyolefin substrates and deposition of plasma polymers onto the plasma-pretreated polyolefin served as adhesion-promoting basecoat responsible for maximal adhesion between polyolefin and thick coating. This basecoat was 0.1 to 1.0 μm thick. To deposit layers with thickness of 20 or 40 μm this plasma technique was too much time-consuming. Therefore, the thick

layers were deposited onto such basecoat by simple dipping into coating solution or by spraying.

Such combination of adhesion-promoting basecoats and thick coatings were tested using peel strength measurements and flammability tests. The most important problem was to find a suitable basecoat, which adheres very well onto the nonpolar polymer substrates (or plasma-pretreated substrates) but show also good adhesion to the dip or spray coating material as well as balancing of thermally induced stress at the interface of substrate and coating.

As flame retarding coating materials inorganic structures were chosen, which are inflammable, char former and, therefore, act as a barrier to oxygen. Here, precursors or materials forming siloxane-like structures were preferred. Intumescent layers releasing ammonia and nitrogen were also used. For this purpose urea and melamine products were preferred. Moreover, several melamine precursors were also in the focus. A third variant consists of the deposition of polyphosphates well-known as fire-retarding substances. It was expected that combination of these inorganic and organic layers are best suited for flame retarding under the condition of permanent high adhesion of coatings.

The layers were characterized by analytical methods such as X-ray Photoelectron Spectroscopy (XPS), Fourier Transform Infrared Spectroscopy (FTIR) in the Attenuated Total Reflectance mode (ATR), Thermal Gravimetric Analysis (TGA) as well as by 90° peel strength measurement, fire tests (according to DIN 4102-1) etc. Apolar polyolefin surfaces were made hydrophilic on a few seconds exposure to oxygen low-pressure plasma. Thus, several types of oxygen-containing groups were formed at the polymer surface capable to interact with the plasma polymer layer deposited for adhesion-promoting purpose.

To further promote the adhesion of thick silicate layers additional thin siloxane-like layers were deposited by low-pressure plasma polymerization of hexamethyldisiloxane (HMDSO) in presence of oxygen. The prepared 0.5 to 1.0 μm thick layers have SiO_2 stoichiometry. Alternatively, SiO_2 layers could be deposited under atmospheric pressure conditions very rapidly by a pyrolytic method (Silicoater process). Another possibility was the tested Electro Spray Ionization deposition (ESI) of Na-silicates. These atmospheric pressure processes for preparation of basecoats were also developed with regard to technical realization. Thick layers were deposited by dipping into Na-silicate solution (water glass) or by spraying it. Thus, 40 μm thick SiO_2 -like fire-retardant coatings were prepared.

To prepare well adherent thick coatings of melamine pre-polymers at the surface of polymer substrates allylamine as well as allyl alcohol plasma polymer layers were deposited. Moreover, the combination of plasma processing and layer-by-layer technique was also used for the deposition of fire-retardant layers made from poly(allylamine hydrochloride) and sodium polyphosphate.

Affirming the expectations it was possible to prepare very highly adherent thick coated laminate systems. In case of flammability tests the thick coatings had fulfilled the precondition of high adhesive bond strength to the polymer substrates and have withdrawn strongly any self-peeling at high temperatures. The successive change of material properties (gradient) from polymer substrate to inorganic or N-rich organic coatings by preparation of multi-layer system was the key for best adhesion.

The flammability tests have confirmed the efficiency of such coatings generally. Addition of polyphosphates has optimized the fire-retardant action of coatings. It should be mentioned that all fire-retardant coatings cannot produce complete non-

combustibility because of limited thickness of coatings but they can at least retard the flammability significantly.

Advantage of such coatings is the safe and cheap use of technical polymers as construction material and the safe protection of surface at pronounced points. The fire-retardant material is localized at the place of flame attack. A homogeneous addition of considerable amounts of fire retardant material is not necessary. The substrate materials retain its original properties.

It could be also demonstrated that these coatings can be also prepared easily, rapidly and with good properties by more simple methods working at atmospheric pressure.

In future, these techniques should be further developed and tested.