Promotion of Adhesive Polymer Bonding by Plasma Modification Using Defined Ambient Conditions and Process Gases

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Abstract: Adhesive bonding technology is often the preferred solution for the joining of polymers. In many cases a wet chemical pretreatment has to be used to achieve sufficient adhesion strength and durability of the adhesive joint. Since several years, plasma treatment has been a proven method to attain these goals. However, conventional treatments in oxidizing gases such as air are often not satisfying. In this work, the PP (polymers polypropylene), PVDF (polyvinylidene fluoride), PA6 (polyamide 6), POM (polyoxymethylene) and PC (polycarbonate) were pretreated by means of a plasma jet running at atmospheric pressure in a virtually oxygen-free atmosphere. The goal was the grafting of reactive nitrogen-containing functional groups on the plastic surfaces in order to increase the adhesive strength.

Key words: Plasma modification, functionalization, functional groups, atmospheric pressure plasma, oxygen-free atmosphere.

1. Introduction

In many application areas, for example in the automotive industry, biomedicine and aerospace industry, there is an increase in the use of plastics that are difficult to bond. This poses a huge challenge to the joining technology. Since classic methods for the joining of polymers are limited in their application, the adhesive bonding technology is the preferred solution. In this case, the surface pretreatment is essential for sufficient adhesion strength and the durability of the adhesive joint. Adhesives have been developed and implemented for a variety of plastics. But some interesting technical polymers such as PTFE (polytetrafluorethylene), PVDF (polyvinylidene fluoride) or POM (polyoxymethylene) can only be bonded with great effort.

That is why the surface pretreatment of these polymers plays a very important role. The industrially

interesting pretreatment method, activation by atmospheric pressure plasma in ambient atmosphere, is not widely implemented for this group of plastics, because better results can be achieved with wet chemical methods [1].

Research results have shown that the functionalization of polymer surfaces by means of atmospheric pressure plasma in an oxygen-free atmosphere (N₂-atmosphere) and the use of defined process gases can be a suitable method [2].

The goal of this study is to graft nucleophilic nitrogen-containing functional groups to the polymer surfaces by atmospheric pressure plasma, in order to achieve covalent bonding between the polymer surface and the adhesive.

2. Plasma Pretreatment

2.1 Surface Functionalization

Basically, there are four major effects of plasma on surfaces. Each effect is always present to some degree,

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but depending on the parameters one effect may be favoured over the others. The effects are surface cleaning (removal of organic contaminations), ablation or etching of material from the surface (remove a weak boundary layer), crosslinking of near-surface molecules and surface chemistry modification [3, 4].

The last effect is the most significant and widely reported one, because chemical groups are created on the surface, which are capable of interaction with an adhesive. For this reason surface functionalization is the core subject of this paper.

2.2 Surface Treatment

There are two different types of plasma systems available at the Fraunhofer IST (Fraunhofer Institute for Surface Engineering und Thin Films) which were used for the surface pretreatment.

The first is the so-called RotoTEC-System (Tantec GmbH) that generates a corona discharge. The plant consists of two discs, each with eight electrode tips. Both discs are set in rotation during operation, so that a relatively homogeneous plasma field is created (Fig. 1). This allows the pretreatment of flat and three-dimensional components.

The second system is a plasma jet (Plasmatrete GmbH). At the upper end of the jet is the inlet for the process gas flowing from top to bottom. At the same time, a pulsed arc is generated inside the jet, where the process gas passes by. This produces plasma, which is transported by the gas flow through the nozzle head to the outside.

To perform the surface functionalization in a defined ambient atmosphere, both the RotoTEC-System as well as the plasma jet are encapsulated (Fig. 2). In the case of the plasma jet, this is realized by means of an airtight glovebox [5]. For this purpose, the box is rinsed with pure nitrogen (N_2) until a virtually oxygen-free atmosphere (< 20 ppm O_2) is reached. Subsequently, the pretreatment takes place inside the glovebox.

Since the results after pretreatment with the plasma jet and the RotoTEC-System are very similar and

Fig. 1 RotoTEC-System for the pretreatment of flat and three-dimensional components.

Fig. 2 Glovebox for the generation of a virtually oxygen-free atmosphere.

comparable, all results shown below refer to the pretreatment with the plasma jet. The optimal pretreatment parameters were determined in preliminary tests for both plasma systems.

3. Methods and Materials

3.1 Methods

Adhesive bond strength was measured by lap shear measurements according to DIN EN 1465. In addition, the effect of the plasma pretreatment on the surface energy was determined by contact angle measurements.

For the detection of nitrogen-containing functional groups on the surface, chemical derivatization and fluorescent marker were used. Due to the strong autofluorescence contained in some plastics such as PVDF, the two latter methods could not be applied with these polymers. In this case, the analysis is done by means of XPS (X-ray photoelectron spectroscopy).

Fig. 3 Environmental cycle test according to PV 1200.

To check the temporal stability of the pretreatment effect, some samples are stored after pretreatment for one day, one week and one month under laboratory conditions before they are then bonded and tested.

In addition, an environmental cycle test (Fig. 3) according to Ref. [6] is performed to evaluate the aging resistance of the adhesive bonds.

3.2 Materials

Table 1 shows the investigated polymers as well as the adhesives used in each case. The samples size was $100 \times 25 \times 4$ mm. The thickness of the adhesive layer was 250 μ m with an overlap of 12.5 mm between the samples.

4. Results

4.1 Influence of Process Gas and Atmosphere

In order to investigate the influence of the process gas and the ambient atmosphere on the pretreatment effect, the samples are pretreated under variation of these two factors.

As expected the pretreatment in normal ambient atmosphere with air plasma has only a minor impact on the lap shear strength. Only the water contact angle of PC (polycarbonate), PP (polymers polypropylene) and PA6 (polyamide 6) shows a significant change, but all specimens still fail adhesively (Fig. 4).

In the next step forming gas is used instead of air, but the pretreatment still takes place in ambient atmosphere. This time, the effect of plasma is much stronger and can be observed for all materials. The results reveal an interesting aspect in the case of polypropylene. Although the contact angle is very high (94°), the N_2/H_2 -plasma treatment yields a better bond strength compared with the air plasma treatment. This effect is already known and illustrates that the contact angle is not appropriate to characterize the treatment quality [7, 8].

In the last step, the pretreatment is carried out inside the glovebox. This causes a further increase of the adhesive bond strength, especially in the case of PC and PVDF. In addition, all specimens fail cohesively, except of POM. In the case of PA6 it is even substrate failure.

4.2 Temporal Stability

To investigate how much time can elapse between the pretreatment and the adhesive bonding the samples were pretreated inside the glovebox and then stored for different periods of time before bonding.

The results show that the functionalization with N_2/H_2 -plasma in an oxygen-free atmosphere has a significant effect on the surface properties even one month after the pretreatment. The water contact angle remained almost constant, the lap shear strength was slightly lower and the fracture pattern remained unchanged and stayed cohesive. Fig. 5 illustrates this with the example of PVDF.

4.3 XPS Measurements

With the help of XPS measurements, it is checked whether there is a relationship between the bonding

Table 1 Tested polymers and adhesives used.

Polymers		Adhesives	
PP (polypropylene)	SIMONA® PP-DWST	1-K polyurethane	Sikaflex®-254
PC (polycarbonate)	Makrolon® 2605	1-K polyurethane	Sikaflex®-254
PVDF (polyvinylidene fluoride)	SIMONA® PVDF	1-K polyurethane	Sikaflex®-254
PA6 (polyamide 6)	SUSTAMID® 6	2-K polyurethane	DELO-PUR® 9895
POM (polyoxymethylene)	SUSTARIN® C	2-K epoxy resin	DELO-DUOPOX® AD840

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Fig. 4 Variation of process gas and ambient atmosphere for the examination of POM, PC, PVDF, PP and PA6.

Fig. 5 Temporal stability of PVDF (storage time: 0 days, 1 day, 1 week and 1 month).

Table 2 XPS Measurement of PVDF.

Pretreatment	C (at.-%)	O (at.-%)	F (at.-%)	N (at.-%)
Untreated	79.75	7.23	13.02	-
Air-plasma (ambient atmosphere)	75.75	7.35	15.13	-
N ₂ /H ₂ -plasma (ambient atmosphere)	70.49	7.62	20.06	0.68
N ₂ /H ₂ -plasma (N ₂ -atmosphere)	71.50	6.83	17.57	3.23

whether there is a relationship between the bonding strength and the nitrogen coverage of the surface. For this purpose samples of PVDF were functionalized with different process conditions and subsequently analyzed.

The results in Table 2 show that the oxygen-content has remained virtually unchanged, while the nitrogen-content increases with each step. They also show that the increase of the nitrogen concentration on the substrate surface correlates with the lap shear strengths of the adhesive bonds. This is an indication

that suitable functional groups could be formed on the surface, which can enter into a strong bond with the functional groups of the adhesive. But to verify this, further tests with other polymers are necessary.

4.4 Accelerated Aging

To investigate the aging resistance of the adhesive bonds samples of PC, PP and PA6 were subjected to an alternating climate test (PV1200) for 30 cycles. In this test the specimens were heated to 80 °C at high humidity and then cooled to -40 °C. One cycle takes 12 hours.

Although a decrease in the lap shear strength is observed, the value is still well above the initial level of

Fig. 6 Determination of aging resistance.

an untreated sample. The decrease is due to infiltration effects leading to a weakening of the adhesive layer.

5. Conclusions

The results show that the absence of oxygen in the functionalization of polymer surfaces has a significant influence on the surface properties. In particular, the plasma pretreatment with N₂/H₂-plasma in an N₂ atmosphere leads to a strong improvement in the bond strength. In addition, the pretreatment effect is long-term stable up to several weeks. But there is still potential for improvement in the production of nonaging compounds, since the strengths are currently affected by infiltration effects.

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