Advanced Flame Treatment

New opportunities for roll-to-roll functionalization of polymer films

Andreas Holländer, Stefano Mancinelli

Introduction

Many technically important polymer materials are characterised by a small value of surface free energy. The surfaces are therefore activated in order to be able to print, laminate or bond them, for example. Electrical discharges such as corona (barrier discharge) are widely applied industrially for this purpose. Flame treatment is also used in a number of applications [1]. In all cases, the aim is to oxidise the surface of the polymer material as efficiently as possible. Highly reactive substances such as radicals are generated in the electrical discharges and also in flames. They cause this oxidation.

Unfortunately, the effects of activation are not stable. Depending on the polymer type, the activation effect diminishes over a shorter or longer period of time. In the past, various approaches have been pursued to mitigate or even eliminate this problem:
a) Treatment in low-pressure plasma (with non-polymerisable substances) [2]
b) Glow discharges instead of filamentary corona discharges by using nitrogen, argon, helium instead of air, different design of the treatment unit (remote treatment) [2]
c) Addition of aerosols of non-polymerisable substances to corona treatment processes [3]
d) Deposition of layers
   – by low pressure processes (PECVD) from gaseous or vaporisable substances
   – atmospheric pressure deposition from gaseous or vaporisable substances
   – addition of aerosols of polymerisable substances to corona treatment processes [4]
   – Addition of gases and vapours to flames [5]

(a), (b) and (c) can reduce, but not completely eliminate the problem of degrading activation effects. The deposition of layers (d) can lead to stable properties,

Source: Fraunhofer IAP

but brings with it a whole range of other problems such as adhesion of the layer to the polymer and much greater efforts in process control. When using flames for layer deposition, oxide layers have been described, especially with siloxane precursors. Some first reports on the application of functional polymers aerosols in combination with flame treatments were published recently [6].

In the experiments reported in this paper, the opportunities of combining flame activation and aerosol exposure were explored. The flame produces reactive species, which result in a coupling of organic molecules to the surface. This approach provides the opportunity of producing surfaces with new chemistries, which are not available with simple activation treatments. The nature of the flame treatment limits the aerosols to aqueous solutions (or possibly other non-flammable solvents) for all practical purposes. However, this still leaves a lot of opportunities.

2 Experiments

A flame treatment unit from esseCI was modified to realize the flame treatment of polymer films with the deposition of nanometer thin polymer layers via aerosols. In laboratory tests, the flame treatment unit was mounted over a linear

SUMMARY

Flame treatments are applied on large industrial scale for the surface activation of polymers. The process of flame treatment of polymers can be improved by combining it with the treatment with an aerosol of a solution of a functional polymer. It was shown that it results in the covalent binding of the polymer molecules at the surface. This approach was demonstrated with PP and PET films as substrates and with poly(acrylic acid) (PAA) and poly(ethylene imine) (PEI) as a functionalizing polymers in continuous processes at up 50 m/min. PAA introduces carboxylic acid groups and PEI gives rise to amino groups at the surface. This approach opens up a completely new range of functionality, which is not accessible with a flame treatment only. The amino groups allow improved properties for the adhesive joining with epoxy or urethane resins, in lamination processes, or for metallization. The functionalization was found to be stable for at least one year of storage and it resists washing with water and isopropanol.
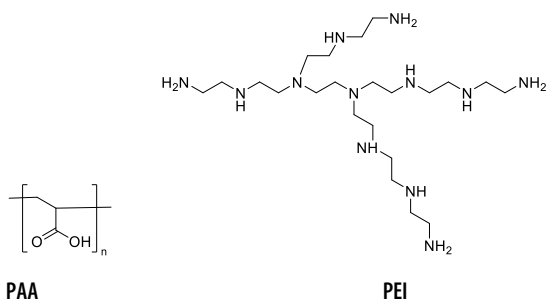
FIGURE 1: Schematic structures of Poly(acrylic acid) (PAA) and poly(ethylene imine) (PEI).

transport system that can move the film to be treated at speeds of up to 5 m/s. The movement can be programmed in a way that the exposure times for the flame treatment and the aerosol deposition are different. With this set-up, fast experiments were performed for the screening of treatment parameters. For continuous treatments, the flame treatment unit was installed in a pilot scale film converting system (R2R) above a water cooled chilling roll. In this system, webs up to a width of 30 cm can be treated at speeds up to 80 m/min (1.3 m/s).

The flame treatment unit was fed with a propane air mixture (1:10).

For the aerosol generation an ultrasound nebulizer was used in the laboratory experiment at low speed. For higher speed treatments and on the R2R equipment spray nozzles were used.

Poly(acrylic acid) (PAA) and poly(ethylene imine) (PEI) were used as aqueous solution (**Fig. 1**).

For the determination of the surface free energies of the functionalized surfaces, the contact angles of three test liquids (water, formamide, tricresylphosphate) were measured. The data were processed according to the van Oss acid-base model [7] and, alternatively, the Fowkes model [8].

3 Results

There are several possible approaches for using flames for producing reactive species for initiating coupling reaction to the surface. The feeding of the additives to the flame is the approach mostly applied in the case of CCVD. In order to minimize the oxidation of the additive, an approach is preferred, which adds the chemical after the flame treatment and utilizing its reaction with the surface

functional groups. This approach is suitable with e.g. amine functional chemicals. In cases where small-scale oxidation is acceptable, the chemical can be applied to the surface as a nanometre coating before the flame treatment.

In any case, the combination of flame treatments with the addition of other substances increases the number of process parameters considerably. An implementation of experiments for the elucidation of the influence of each parameter on a continuous R2R equipment requires large efforts in time and materials.

Narrowing down the parameter ranges by laboratory scale experiments would be very beneficial.

3.1 Lab-scale treatments

In order to carry out laboratory experiments under similar conditions like the R2R treatments, an equipment was set up using a high-speed linear motion system for transporting the sample with short exposure times to the flames. The equipment uses the same flame treatment unit as in the continuous treatment system and similar (or even higher) substrate speeds can be applied. The acceleration and the speed profile along the transport track were computer controlled. They can be adjusted to a variety of treatment parameters for the flame treatment and for the exposure to other chemicals separately. For experiments
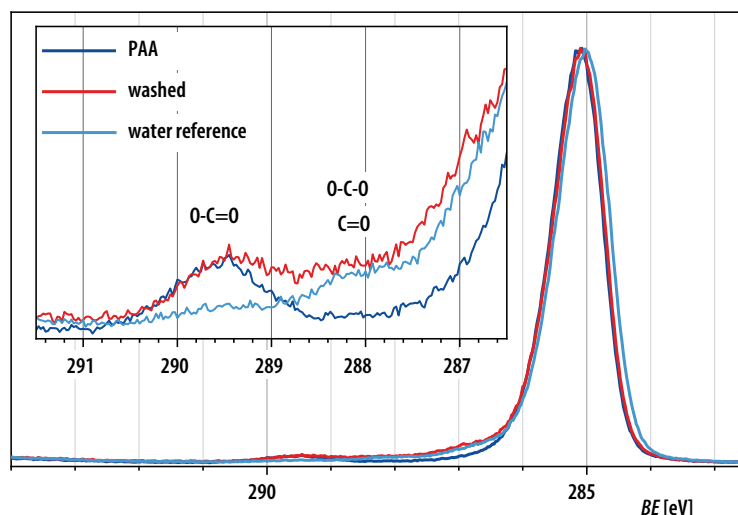

FIGURE 2: C1s spectra of a PP film sequentially treated with an aerosol of PAA and a flame. The spectra of pure PAA and a sample prepared with water instead of a PAA solution are shown as references.

ZUSAMMENFASSUNG

Moderne Flammbehandlung – Neue Möglichkeiten für die Rolle-zu-Rolle-Funktionalisierung von Polymerfolien

Flammenbehandlungen werden in großem industriellen Maßstab zur Oberflächenaktivierung von Polymeren eingesetzt. Der Prozess der Flammbehandlung von Polymeren kann verbessert werden, indem er mit der Einwirkung eines Aerosols einer Lösung eines funktionellen Polymers kombiniert wird. Es wurde gezeigt, dass dies zu einer kovalenten Bindung der Polymermoleküle an der Oberfläche führt. Dieser Ansatz wurde mit PP- und PET-Folien als Substrate und mit Polyacrylsäure (PAA) und Polyethylenimin (PEI) als funktionalisierende Polymere in kontinuierlichen Prozessen mit Geschwindigkeiten von bis zu 50 m/min demonstriert. PAA führt Carbonsäuregruppen ein und PEI führt zu Aminogruppen auf der Oberfläche. Dieser Weg eröffnet einen völlig neuen Bereich der Funktionalität, der mit einer reinen Flammenbehandlung nicht zugänglich ist.

Die Aminogruppen ermöglichen verbesserte Eigenschaften für die Verklebung mit Epoxid- oder Urethanharzen, in Laminierungsprozessen oder für die Metallisierung. Es wurde gezeigt, dass die Funktionalisierung mindestens ein Jahr lang stabil ist und dem Waschen mit Wasser und Isopropanol standhält.

v m/s	additive	d(p) nm	d, mm: 4 [N] at%	5 [N] at%	7 [N] at%	9 [N] at%
0,20	PEI	17	3,1	2,8	2,7	0,0
0,20	PEI	20	2,6	1,2	0,0	0,2
0,20	PEI	34	4,0	5,9	5,1	2,4
0,20	PEI	41	3,5	3,5	2,5	0,6
0,40	PEI	10	0,5	1,4	1,1	0,2
0,60	PEI	7	0,9	1,2	1,7	0,4
delta:						
0,20	PEI	17	-0,7	0,7	0,1	0,0
0,20	PEI	20	0,5	0,5	1,0	1,9
0,20	PEI	34	1,7	0,8	-0,5	-1,2
0,20	PEI	41	1,1	-0,4	1,7	0,3
0,40	PEI	10	1,3	0,9	1,5	0,1
0,60	PEI	7	0,4	-0,7	-1,3	-0,4

TABLE 1: XPS data for flame-PEI treatment of a PP film. (*d*: distance between burner and film, d(p): nominal PEI thickness, *v*: speed of the film, delta: differences of concentration values before and after water washing).

v m/min	fresh	[N], at % 4 weeks	washed
15	13.8	13.1	12.0
31	10.5	7.0	6.4
49	7.3	4.2	4.6

TABLE 2: Nitrogen concentration (XPS) at the surface of a PP film after flame treatment followed by a treatment with an aerosol of a PEI solution measured directly, after storage, and after washing.

with polymer coatings deposited right before the flame treatment an aqueous solution of PAA was used to coat a polypropylene (PP) film. The radicals generated in the flame were supposed to initiate reactions resulting in the creation of bonds with the surface and in a cross-linking of the PAA. The coating was performed with a 0.1 % solution and an ultrasound nebulizer. Mass balance calculation gave a thickness of the PAA coating of ca. 20 nm. The film was moved at a speed in the range between 0.2 m/s and 1 m/s. The sample was washed with water in order to remove not bonded PAA. X-ray photoelectron spectroscopic (XPS) analysis showed a small but well detectable amount of carboxylic acid groups in the C1s spectra (**Fig. 2**) after the washing step. As a reference, a sample was prepared with an aerosol from pure water instead of a PAA solution.

Oxygen functional groups prepared by flame treatment of a polyolefin are well suited for coupling amino functional molecules. PEI was used functionalize a PP film right after a flame treatment. In the result of this treatment, nitrogen can be found at the surface by XPS analysis. (**Table 1**)

For these experiments, the films were mounted on a cylinder segment allowing the assessment of the burner-film distance influence in a single experiment. The PEI coating thickness was estimated from the mass balance of the aerosol generator. A part of the samples was analysed directly after the treatment, others after washing with water for the removal of the not bonded PEI.

The nitrogen concentration was found to be in the order of some at%. Most of it was covalently bonded to the surface and was not washed away with water for samples prepared at a small distance between the flame and the film. At larger distances (> 5 mm) the surface oxidation by the flame is less pronounced and consequently less of the PEI is covalently bonded to the surface.

3.2 Roll-to-roll treatments

Rolls of 30 cm wide PP film and PET films were used for the experiments with the continuous treatments. The flame treatment unit was equipped with a spray coating system for applying the polymer solutions. After the flame treatment and the coating the film was fed through a 1 m long air drying oven, which was kept at 60 °C. Parameters were altered in an experiment run and the film was labelled with adhesive paper strips at these locations. After the experiment, samples were taken from various spots of the film. These samples were analysed for homogeneity of the treatment along the treatment direction and perpendicular to it. In most of the experiments, the homogeneity was found to be very good along the film run. The following data were obtained by averaging 10 samples from the middle of the film over ca. 2 m running length. The samples were analysed as taken from the film roll, after washing with water, and after storage for a defined period of time.

In experiments with a variation of the speed of a PP film it was found that at 15 m/min the saturation concentration of nitrogen was measured (13 at%). The nitrogen functionality was virtually completely stable against washing with water and storage. The higher the web speed the less nitrogen is found to the surface and the less of it is covalently bonded. However, even at 49 m/min
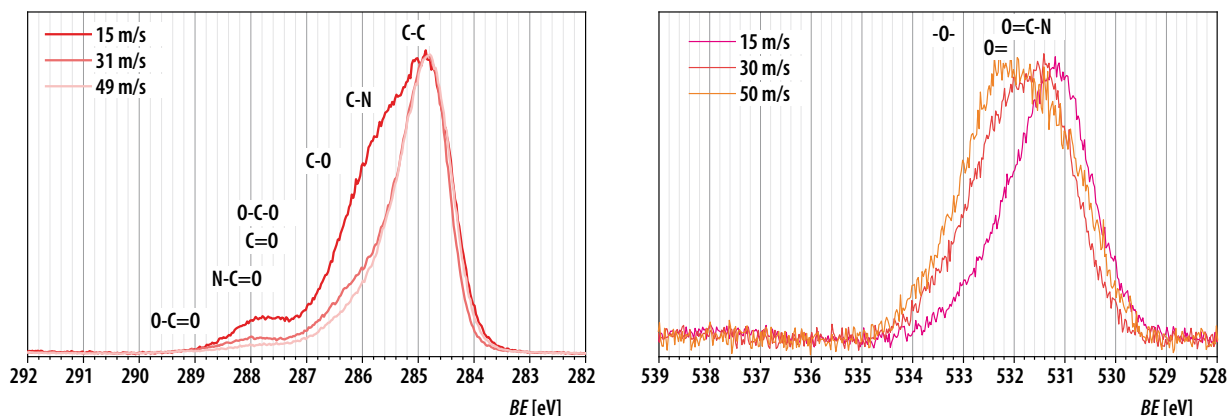
speed m/min	SFE(AB), mJ/m²				SFE(DP), mJ/m²		
	γ(a)	γ(b)	γ(LW)	γ(tot)	γ(pol)	γ(dis)	γ(tot)
20	2.0	14.2	40.9	51.6	17.7	30.9	48.6
38	2.3	11.8	41.1	51.6	15.1	34.0	49.1
51	2.3	9.3	40.9	50.2	12.3	35.7	48.1

TABLE 3: Surface free energies of PET film treated with flame and PEI aerosol at various web speeds. (*SFE*(AB): calculated according to acid/base model, *SFE*(DP): calculated according to Fowkes dispers-polar model).

	SFE(AB), mJ/m²				SFE(DP), mJ/m²		
sample	γ(a)	γ(b)	γ(LW)	γ(tot)	γ(pol)	γ(dis)	γ(tot)
fresh	1.4	47.6	38.9	55.1	52.4	15.2	67.6
after 4 weeks	1.1	40.5	37.2	50.8	45.1	14.9	60.0
after 1 year	2.5	26.6	35.6	52.0	30.1	23.7	53.9

TABLE 4: Surface free energies of PP film treated with flame and PEI aerosol measured right after the treatment and after storage in lab atmosphere. (*SFE*(AB): calculated according to acid base model, *SFE*(DP): calculated according to Fowkes dispers-polar model).

FIGURE 3: C1s spectra (left) and O1s spectra (right) of a PP film treated with a flame and a PEI aerosol at various web speeds.

some 4 at% nitrogen remain stable and bonded to the surface. (**Table 2**)

The carbon C1s photoelectron spectra provide further details of the PEI coupling to the PP surface (**Fig. 3**). The signal at a binding energy (*BE*) of 285.9 eV can be attributed to C-N bonds of the PEI. At a *BE* of 288.0 eV the carbon atoms in amide groups contribute to the spectrum. The corresponding amide oxygen atoms show a characteristic signal at a *BE* of 531.3 eV supporting the information from the C1s data. As expected from the elemental concentrations, the signals originating from the PEI and its coupling groups to the surface are most pronounced in the samples from the 15 m/min experiments.

The surface free energy of the polymer films is increased remarkably as a result of the introduction of these nitrogen functional groups. Some examples are given for a PET film treated with flames and with a PEI aerosol (**Table 3**). As the Fowkes model (*SFE*(DP)) occasionally gives unreasonable results with nitrogen functional surfaces, the contact angle data were also processed according to the acid/base model (*SFE*(AB)). The results are quite similar for all the samples. *SFE* values of about 50 mJ/m^2 were observed even for the treatment at 51 m/min.

Similar data were obtained with a PP film (**Table 4**). As for PP the long term stability of a surface treatment is a critical issue, the contact angle measurements were repeated over an extended period of time. The surface, which was covalently functionalized with large molecules of PEI was found to be stable for at least one year.

4 Conclusions

The process of flame treatment of polymers can be improved by relatively simple modifications. The exposure to an aerosol of a solution of a functional polymer was shown to result in the immobilization of the polymer molecules. This approach works well with PP and PET films as substrates and with PEI as a functionalizing polymer. PEI gives rise to amino groups at the surface and, by this, opens up a completely new range of functionality, which is not accessible with a flame treatment only.

The amino groups allow improved properties for the adhesive joining with epoxy or urethane resins, in lamination processes, or for metallization. The functionalization was found to be stable for at least one year of storage and it resists washing with water and isopropanol.

Acknowledgement

References

[1] *S. Farris, S. Pozzoli, P. Biagioni, L. Duó, S. Mancinelli and L. Piergiovanni:* Polymer **51** (2010) 3591. DOI: 10.1016/j.polymer.2010.05.036

[2] Plasma Processes and Polymers (ed. *R. d'Agostino, P. Favia, C. Oehr, M.R. Wertheimer*) Wiley-VCH, Weinheim, 2005. E. Kang, K. Neoh. Surface Modification of Polymers in Encyclopedia of Polymer in Science and Technology. Wiley 2009 DOI:10.1002/0471440264. pst358.

[3] *K. Kalwar:* DE 102009044638, Verfahren zur Oberflächenbehandlung eines Substrats und Vorrichtung zur Durchführung des Verfahrens

[4] *R. Mix, J. F. Friedrich and N. Inagaki:* Permanence of Functional Groups at Polyolefin Surfaces Introduced by Dielectric Barrier Dis-charge Pretreatment in Presence of Aerosols in Atmospheric Pressure Plasma Treatment of Polymers: Relevance to Adhesion, *Michael Thomas* (Editor), *K. L. Mittal* (Editor), ISBN: 978-1-118-74751-3, June 2013)

[5] *V. J. Eigenbrod, C. Hensch, A. Kemper:* Combustion chemical vapor deposition, Vakuum in Research and Practice **27** (2015) 30-34. doi: 10.1002/vipr.201500581

[6] *A. Holländer:* EP 3 620 301, Verfahren zur Modifikation und Beschichtung von Oberflächen von Polymermaterialien, Polymermaterial und Vorrichtung

[7] *C. J. van Oss, M. K. Chaudhury, R. J. Good:* Chem. Rev., **88** (1988) 927; *R. J. Good, M. K. Chaudhury*: in „Fundamentals of Adhesion", S.137, Ed. L. H. Lee, Plenum Press, New York, 1991

[8] *F. M. Fowkes:* Ind. Eng. Chem. **56** (1964) 40; *D. K. Owens, R. C. Wendt:* J. Appl. Polym. Sci., **13** (1969) 1741

AUTHORS

Dr. Andreas Holländer
Senior scientist at Fraunhofer IAP, Diploma in Chemistry, PhD in polymer science, more than 30 years work in surface science, technology, and analysis of polymers.

Dr. Stefano Mancinelli
Master's Degree in Materials Engineering, with more than 20 years on field experience with flame treatment process applications. esseCI Process Manager and pilot line responsible. esseCI s.r.l., Narni, Italy, s.mancinelli@essecinet.net.

Dr. Andreas Holländer, Fraunhofer-Institute für Angewandte Polymerforschung IAP, Geiselbergstr. 69, 14476 Potsdam, Germany, andreas.hollaender@iap.fraunhofer.de