

Plasma Makes for a Strong Bond

Multi-component Processing. In-line activation of polymer surfaces by plasma treatment directly in the injection mould enables positive-joint composites to be made from polymer combinations that were hitherto unable to adhere to each other, markedly improves adhesion of compatible combinations and can be easily integrated into a process chain.

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Major growth is still being forecast for multi-component processing [1, 2]. It will depend to a large extent on the development of combinations of processes for the production of complex, highly integrated composite parts. Combining established technologies, such as injection moulding, foaming and injection compression moulding with gating, in-mould decoration and back-compression moulding of metallic and polymeric preformed inserts offers promising prospects for new applications [3, 4, 5].

Adhesion Problem

The desire for high integration potential presupposes not only further developments in the established multi-component injection moulding but also reliable bonds between different materials. The quality of the adhesion between the polymer adherends thereby becomes a key issue of parts design. A positive joint depends critically on the tendency of the material pairing to enter into adhesion. However, only a limited number of combinations achieve the level of bond strength needed for technical applications. Compatibility matrices offer a means of describing the basic adhesive potential of material combinations [3, 6, 7]. But the usefulness of matrices rarely extends as far as polymer-related influences (e. g. miscibility, formation of adhesive bonds) and process set-up (type and location of gate, flow distance, machine parameters, pressure, melt temperature). They provide only average values

and say nothing about the level of scatter, which is often considerable. The development of adhesion forces depends heavily on the thermal and rheological conditions obtaining during injection moulding in addition to the inherent thermodynamic properties of the material [7, 8]. Alternative strategies that are deployed in practice to resolve this problem adopt both a design approach involving positive joints, such as undercuts and breakthroughs, and modifications to the materials, such as changes of adhesion, or the use of surface-treatment processes, such as priming, flame treatment, corona or plasma pre-treatment.

However, these alternative solutions frequently require additional handling capability and higher material costs. Moreover, they are often unsuitable for performing localized, flexible surface treatment. Additional constraints concern the joining of large-area surfaces and ease of processing.

In-line Plasma Activation as a Potential Alternative

An alternative way of activating a surface with a view to improving adhesion in its subsequent area of contact is to treat it with plasma in a normal atmosphere and thereby improve fine cleaning and adhesion. The plasma is generated by means of a high-voltage discharge in the plasma source. Targeted air flow along the dis-

charge zone separates parts of the plasma and transports the activated particles (mostly ions, electrons, free-radicals, photons) of high speed through a plasma nozzle onto the surface of the work piece (Fig. 1).

The plasma treatment takes place after the first component has been injection moulded. A robot introduces the plasma head into the open mould, localized acti-

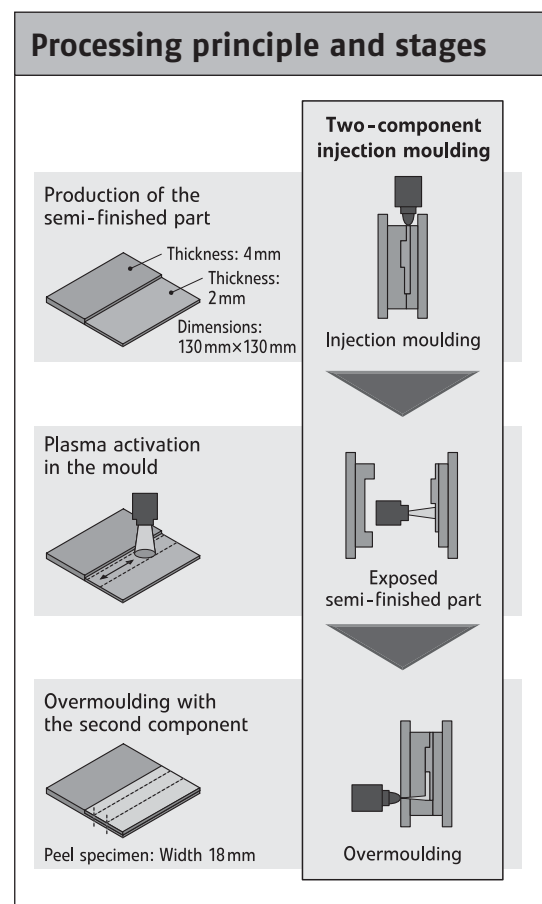


Fig. 2. In-line plasma activation in multi-component injection moulding

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Collaborative venture

The studies commenced to establish this technology in the field of multi-component injection moulding are currently being continued in a collaborative venture between the companies Krauss-Maffei Kunststofftechnik GmbH, PlasmaTreat, Neureder AG, Neue Materialien Fürth GmbH and the Institute of Polymer Technology. Basic and application-oriented trials are performed on an appropriate experimental setup in the pilot plant of Neue Materialien Fürth GmbH that consists of a two-component injection-moulding machine, a 6-axis buckling-arm robot and a variable plasma laboratory machine.

Companies who wish to follow the studies and participate in the results may do so within the context of an industrial group called "In-Line Plasma Treatment In Multi-Component Injection Moulding".

vation is performed, the mould is then closed and over-moulding with the second component occurs. Introduction of the robot arm, together with the start and finish of plasma pre-treatment, are controlled directly by means of an add-on in the machine control system (Fig. 2).

The plasma beam can activate widths ranging from several millimetres to approx. 25 mm, the exact figure depending on the power and geometry of the nozzle. Similarly, the level of treatment can be varied – the beam can be moved at a height of 10–40 mm above the surface and at a rate of 6–900 m/min over it [9].

The resultant short exposure time is conducive to gentle but effective heat treatment and triggers rapidly occurring physico-chemical processes on the surface that manifest themselves as a change in surface topography and molecular structure and as improvements in the wetting and adhesive bonding mechanisms to other materials at the interface [9].

The key processing advantages of in-line plasma treatment in multi-component injection moulding stem from

- the mobility and directionality of the plasma source,
- partial and localized treatment of the contact areas of large-surface parts
- material-specific treatment of the semi-finished part directly before contact with a mating partner, and
- incorporation into production or directly into the process chain, e.g. multi-component injection moulding.

The plasma treatment, which is necessary (unlike the case for standard multi-component processing), will prolong the over-

all cycle time, but the amount of extra time needed can be reduced to a few seconds by making adjustments to the mould.

Experimental Results

The Institute of Polymer Technology, together with Krauss-Maffei Kunststofftechnik GmbH, Munich/Germany, and PlasmaTreat GmbH, Steinhagen/Germany, has made preliminary studies of the improvements effected in the adhesion of polymer composites (Table 1). For this, a panel measuring 130 by 130 mm² was injection moulded and a strip 25 mm wide was treated with a rotating plasma nozzle. The surface of the treated area was over-moulded and a peel specimen (130 mm long, 18 mm wide) was removed for adhesion tests in a realistic climbing drum peel test.

Polyamide 6/TPU Composite. For a composite composed of polyamide 6 (PA6) and thermoplastic elastomer based on polyurethane (TPU1) the semi-finished PA6 parts were plasma-activated immediately after injection in the mould, as shown in Fig. 2, and then over-moulded at once with the second component.

Three injection-moulding settings were chosen, each featuring different melt temperatures for both the first and the second component. These were low (cold), medium (standard) and high (hot) and were selected so that rising process-

ing and contact temperatures at the interface would specifically lead to higher composite strengths (Fig. 3). In-line plasma activation of the first component improved the attainable level of adhesion at all three settings. In addition, a second course of treatment was found to have a favourable effect. The best composite adhesion was obtained at high processing temperatures.

PBT/TPU Composites. Conducted on polybutylene terephthalate (PBT) and TPU, the semi-finished PBT parts were removed from the injection mould, cooled to room temperature, and, after approx. 1 hour with or without activation, were inserted back into the injection mould and over-moulded with the TPU component. Plasma activation improved the composite strengths of various PBT and TPU combinations from <1 N/mm (practically no adhesion) to very good adhesion levels of between 7 and 12 N/mm (Fig. 4). This can be seen for both ester-based (TPU2) and ether-based (TPU3) TPUs, with the level of adhesion for the ether grade being approx. 25 % higher for a comparable Shore hardness.

The PBT/TPU2 combination was subjected to a second series of experiments in which the semi-finished PBT parts were produced and then plasma-treated. They were stored at ambient conditions for various periods from 2 hours to 15 days and then over-moulded. The results of the peel

Material combination		Process	Plasma parameter	
1st component	2nd component		a	v
PA 6 (Ultradid B3S)	TPU1 (Elastollan C78A)	2-cpt	8 mm	2.4 m/min
PBT (Pocan B1505)	TPU2 (Desmopan 385S)	Insert	10 mm	16 m/min
PBT (Pocan B1505)	TPU3 (Desmopan 9385)			
PBT (Pocan B1505)	TPU4 (Elastollan S60A15 SPF)			

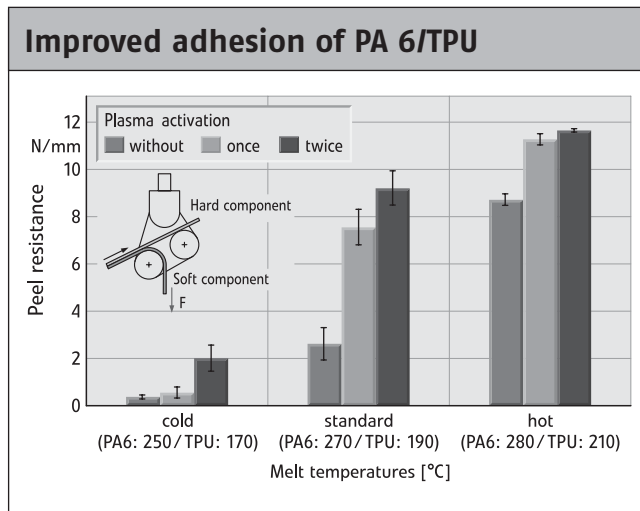
Table 1. Material combinations and plasma parameters employed (a = distance between nozzle and material surface; v = traversing speed of plasma nozzle)

Surface tension of semi-finished part [mN/m]		Before plasma activation	After plasma activation
		after Neumann	39.1 ± 0.7
after Wu		37.8 ± 0.7	54.3 ± 2.8
	d: 26.6 ± 0.6		d: 37.4 ± 2.2
	p: 11.2 ± 0.4		p: 16.9 ± 1.7
after Owens/Wendt		40.3 ± 2.4	54.7 ± (-)
	d: 36.3 ± 2.3		d: 41.7
	p: 4.0 ± 0.6		p: 13.0

1) Evaluation not possible due to stick-slip effects
 2) Angle on receding not measurable due to good wetting

Table 2. Surface tension of semi-finished PBT parts before and after plasma activation (p: polar fraction; d: disperse fraction of surface tension)

Fig. 3. Peel resistance of the combination PA 6/TPU1 for different injection moulding settings (melt temperature: component 1/ component 2) and as a function of the number of plasma treatments (v: 2.4 m/min; a: 8 mm)



tests are shown in Fig. 5. It may be seen that plasma activation can greatly increase the adhesive strength of the PBT/TPU2 composite. The effect is down slightly by about 15 % after one day and about 35 % after six days. Nevertheless, this still corresponds to an adhesive strength of about 7 N/mm. The increase in composite adhesion provided by plasma activation and the drop in peel resistance during storage correlate well with the marked increase that was determined in surface tension after plasma treatment and the decrease that accompanied increase in storage.

The stability of plasma activation demonstrated for the PBT/TPU2 combination is not generally translatable to other material combinations. Thus, activation of cold, semi-finished PA6 parts for insert moulding with the TPU1 employed here, as opposed to direct in-line plasma activation in the two-component process, only lead to a slight improvement in composite adhesion.

Why Does In-line Plasma Activation Work?

Apart from the measurable increase in composite adhesion, all plasma-treated samples showed improved wetting. The adhesion and the wetting potential of the adherends can be characterised in terms of their surface tension.

Whereas the surface tension of liquids and melts can be measured unequivocally, the surface tension of solids can only be determined indirectly by determining the advancing and receding contact angles with the aid of defined test liquids. The contact angle is determined by the surface roughness in addition to the surface tensions of the polymer and the test liquid. The lower the surface tension and the rougher the surface of the polymer, the greater is the angle of contact on advancing; the higher the surface tension and the rougher the surface, the smaller is the angle on receding until coherent stick slip is

no longer possible. In this case, the surface tension is determined from the angle of contact on advancing. In principle, the surface tension of a polymer is the same in the solid and liquid states, but it falls uniformly with rise in temperature, e.g. $\sigma_{PBT} = 34.5 - 0.036 * T$ mN/m in the range 20 to 250 °C [10, 11].

Table 2 shows a substantial rise in the surface tension of the semi-finished PBT part as a result of plasma activation. In particular, there is a strong increase in the polar fractions. The adhesion work, which is the sum of the surface tensions of PBT and TPU minus the interfacial tension between the two, rises substantially (Table 3).

Since the surface tension of the semi-finished part is increased by activation, but the surface tension of the TPU used for over-moulding remains the same, the contact angle becomes smaller, the computed spreading power increases and so wetting during over-moulding is improved. As an example, the contact angle for formamide is less than half (21.4° relative to 55.0°) after activation; with ethylene glycol, complete wetting occurs.

Further improvement in wetting comes from the fact that the surfaces of the activated semi-finished parts are smoother than those of unactivated samples, as revealed by photographs of PA6 samples taken under the atomic force microscope (AFM; Fig. 6). Unlike the rough contour of the moulded cavity surface of the slide before activation, plasma treatment produces a softer surface contour that surely promotes surface wetting.

Both the results of the IR measurements and the ESCA measurements essentially confirmed that the expected enrichment with oxygen and nitrogen and incorporation of the oxygen proceed mostly in the form of polar hydroxyl and carbonyl groups.

By way of example, the IR spectrum shown in Fig. 7 for the untreated semi-finished PA6 parts shows the highest transmission in the region of OH and CO bands (wavelength: 3500 cm⁻¹ and 1720 cm⁻¹). OH and CO groups formed by plasma activation absorb some of the incorporated radiation, which is why the transmission reading is lower.

The ESCA spectrum also clearly shows significant enrichment with oxygen in the activated PBT sample compared with the untreated semi-

Composite		PBT	TPU2	PBT	TPU4
PBT _{unactivated} / TPU	Surface tension (σ [mN/m]) ¹⁾	39.1 ± 0.7	21.0 ± 1.4	39.1 ± 0.7	33.2 ± 0.7
	Adhesion work (W_{ad} [mN/m]) ²⁾	55.0		71.7	
	Spreading pressure (p_{Sp} [mN/m]) ³⁾	13.0		5.3	
PBT _{plasma-activated} / TPU	Surface tension (σ [mN/m]) ¹⁾	54.3 ± 2.8	21.0 ± 1.4	54.3 ± 2.8	33.2 ± 0.7
	Adhesion work (W_{ad} [mN/m]) ²⁾	58.8		80.3	
	Spreading pressure (p_{Sp} [mN/m]) ³⁾	16.8		13.9	

¹⁾ Evaluation of static contact angle

²⁾ $W_{ad} = \sigma_{PBT} + \sigma_{TPU} - \sigma_{PBT/TPU}$

³⁾ $p_{Sp} = \sigma_{PBT} - \sigma_{TPU} - \sigma_{PBT/TPU}$

Table 3. Adhesion work, calculated after Dupre and Neumann, and spreading pressure of a PBT/TPU combination

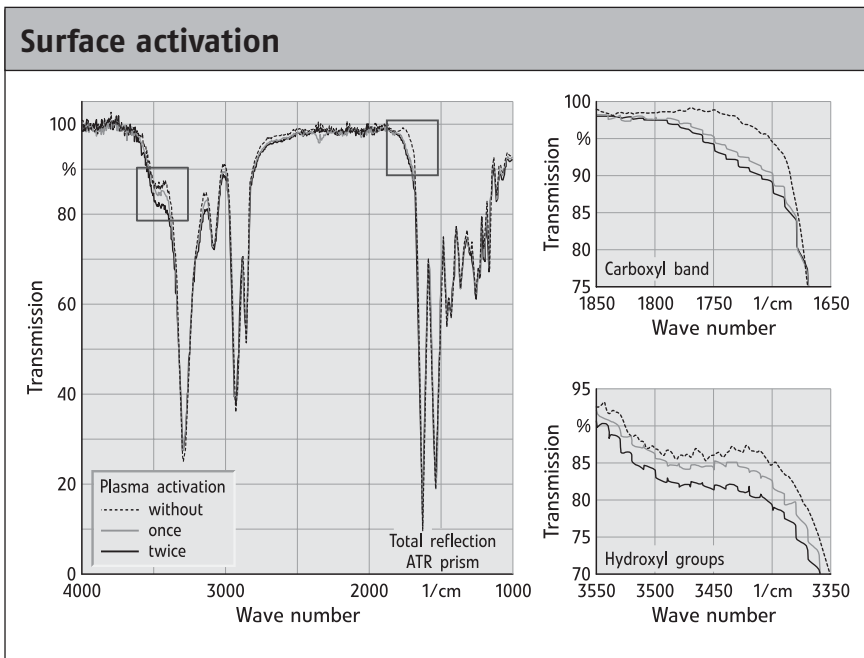


Fig. 7. IR measurements of activated and unactivated, semi-finished PA 6 parts

finished part. There is almost twice as much oxygen as carbon in the activated sample. Since ESCA cannot measure more than a few nanometres into the sample and since clearer changes in the molecular composition can be resolved better relative to the case for IR measurements, it is likely that the plasma only has a surface effect. The surface-analysis methods employed give some indication of the relationships between plasma activation, the resultant surface effects and the attainable composite properties.

Summary

In-line plasma activation coupled with the open-air process enables targeted, direct treatment of the composite surface in the production process of multi-component injection moulding. Thus, it is possible to achieve positive-joint composites from combinations that up to now adhered moderately or not at all, along with higher absolute adhesive strengths, and a reduction in the influence of adhesion-reducing processing settings in an economically attractive production process.

At the moment, it is not possible to estimate the extent to which the adhesive strengths attainable by the in-line process for a chosen material combination can be translated to insert moulding, and separate studies on this are needed. Important information about this could be obtained by measuring changes in surface properties, such as surface tension. ■

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REFERENCES

The comprehensive list of references can be accessed on the Internet under www.kunststoffe.de/A004

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Fig. 1. In-line plasma activation of the semi-finished polybutylene terephthalate (PBT) part in the injection mould directly before over-moulding with the second component. The plasma source is located on the robot and can perform directional activation
Vorspritzling = Semi-finished part; rotierende Plasmadüse = Rotating plasma nozzle; Plasmaquelle = Plasma source

Fig. 4. Improved adhesion of PBT/TPU: Peel resistance of composites made from PBT as first component and TPU as over-moulding, soft component (v: 16 m/min; a: 10 mm)

Schälwiderstand = Peel resistance; Plasmavorbehandlung = Plasma activation; mit = with; ohne = without; Hartkomponente = Hard component; Weichkomponente = Soft component

Fig. 5. Plasma stability: Peel resistance of the PBT/TPU2 combination as a function of selected storage time after plasma activation and over-moulding with TPU component (v: 16 m/min; a: 10 mm)

Schälwiderstand = Peel resistance; Zeit zwischen Plasmabehandlung und Aufspritzen der 2. Komponente = Time between plasma activation and over-moulding with second component; Oberflächenspannung = Surface tension; keine Haftung = no adhesion

Fig. 6. Surface roughness: Surface topography of PA 6 samples as determined by atomic force microscopy (AFM). Left: unactivated surface; Right: after plasma activation (v = 2.4 m/min; 2 treatments)

Fig. 8. Enrichment with oxygen: ESCA spectrum of activated and unactivated, semi-finished PBT parts

Intensität = Intensity; Bindungsenergie = Bond energy; behandelt = activated; unbehandelt = unactivated; Silizium = Silicon