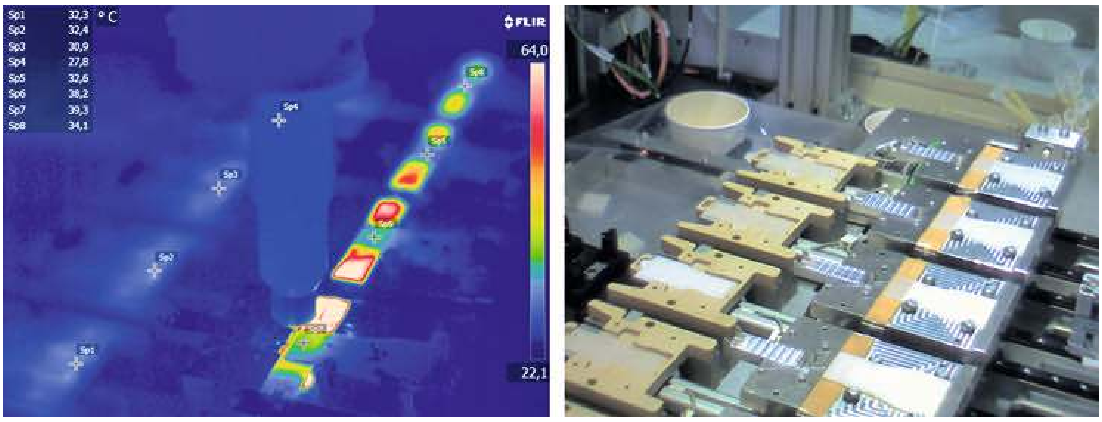

Fig. 1. Thermographic camera image (left) during plasma treatment of PP samples. View of the inside of the production cell in true colors (right) (figures: Kunststofftechnik Paderborn)

A Look Beneath the Surface

Plasma Treatment. Thermoplastic polymers change their properties after atmospheric plasma treatment. This effect is primarily used as a pretreatment to make targeted changes to surface energy. Such activation processes are accompanied by additional processes that are amongst other things responsible for a reduction in molecular weight. The question of whether these kinds of processes also affect the mechanical properties of the material was the subject of an investigation at the Department of Polymer Technology (KTP) at the University of Paderborn, Germany.

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In many cases the surface treatment of polymers is a necessary process step in order to achieve adequate bonding between composite components. An example of this is adhesive bonding, with which high added values can be achieved. The prerequisite for strong bonding between polymers is the appropriate adhesive, suitable adhesive bonding technology and optimal surface properties. Atmospheric plasma treatment is one of the key technologies for surface activation. Surface modification can take place inline before the joining process. This means that through the use of highly efficient, environmentally friendly bonding processes, low cost starting materials that were previously incompatible can be combined. The result is high bonding strengths and composites with long term stability. This technology is used for instance in the production of automobile headlamps or to improve the adhesion properties of EPDM profiles (Ethylene Propylene Diene Monomer elastomer) in combination with flock adhesives or bonded coatings [1, 2].

Alongside changes in surface energy it is known that the interaction of plasmas with polymer surfaces can lead to decomposition processes at the molecular level. These result for example in damage to the polymer chain and the formation of low molecular weight components which no longer bond strongly to the base resin. It therefore seems reasonable that beyond a certain level of surface damage a reduction in the mechanical properties, such as the modulus of elasticity, is to be expected.

This hypothesis was the subject of a study at the Department of Polymer Technology (Kunststofftechnik Paderborn – KTP) at the University of Paderborn, Germany. It was based on surface treating homo polypropylene films with an atmospheric pressure plasma nozzle (an RD1004 nozzle with an FG5001 generator from Plasmatreat GmbH, Steinhagen, Germany). To reflect different treatment parameters the speed of the plasma nozzle and the separation between nozzle and substrate were varied by two factor steps within the framework of a full factorial trial plan with four blocks and four center points. The mechanical properties were determined via tensile tests according to DIN EN ISO 527-1/2

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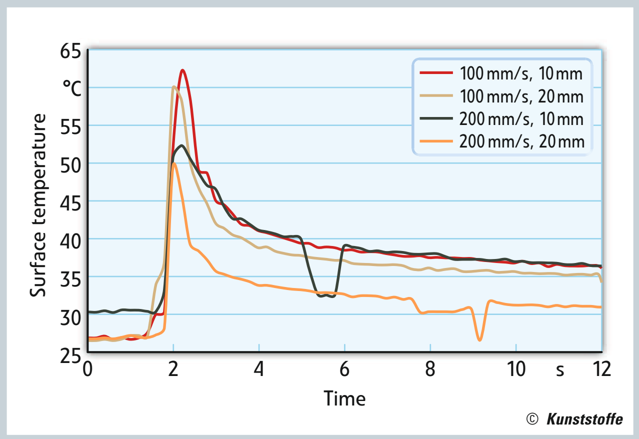

Fig. 2. Typical surface temperature curve of plasma treated polypropylene films for various treatment parameters

Fig. 3. Mechanical testing of the plasma treated films under tensile loading

[2]. The analysis of the surface energy of the plasma treated PP-H films was conducted using wetting angle measurements with an OCA35 optical video contact angle measurement system from Dataphysics Instruments GmbH, Filderstadt, Germany. During the plasma treatment inside the production cell the polymer samples were observed using a ThermaCAM SC640 thermographic camera from Flir Systems Inc., Wilsonville, OR/USA, in order to determine the end surface temperatures after plasma treatment **(Fig. 1)**. In this way it is possible to capture the maximum surface temperatures and the heating or cooling curves of the samples.

During intensive plasma treatment the surfaces of the samples reach temperatures of up to 62 °C. The greater the separation of the plasma nozzle and the substrate being treated and the higher the process speed the lower the maximum temperature and therefore the quicker the cooling of the surfaces **(Fig. 2)**. The steep temperature drops that can be seen in the cooling curve are due to the fact that the plasma nozzle moves through the camera's field of view so for this time a lower temperature is registered.

Possible changes to the emissivity due to surface changes stemming from the plasma treatment were ignored in this investigation since no significant changes in comparison to the initial levels are to be expected. The determination of the E-modulus was conducted using a 1446 universal tester from Zwick GmbH & Co. KG, Ulm, Germany **(Fig. 3)**.

The plasma treatment process is essentially defined by two primary parameters: The separation of the plasma nozzle and the polymer surface and the process speed of the plasma nozzle. This relationship has been previously demonstrated in many other investigations. As a rule, the more intensive the plasma treatment – that is the lower the process speed and separation – the higher the surface activation of the substrates.

Influences on Surface Energy

The investigations of the surface energies confirm that distance to the plasma treated sample has a larger influence on surface energy than process speed. Thus at constant process speed a reduction in the separation positively affects surface activation.

However, the distance over which treatment is effective is limited. When a separation of 23 mm is exceeded no increase in the polar share of the surface energy, which is primarily responsible for the magnitude of the surface activation, occurs **(Fig. 4)**. At higher process speeds the activation potential also reduces, however not so rapidly as for larger separations.

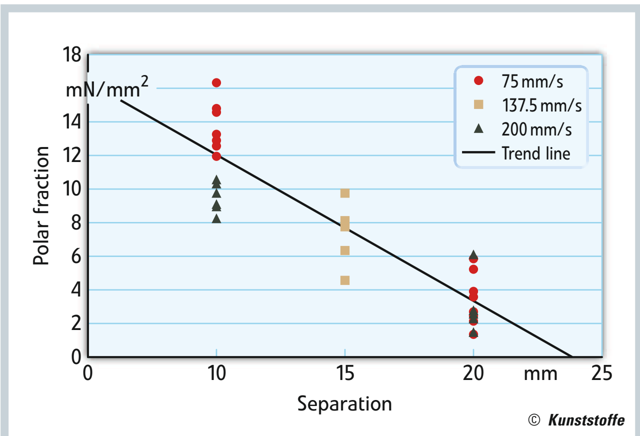

Fig. 4. The polar fraction of surface energy falls with increasing separation to the substrate during treatment

Effects on the Modulus of Elasticity

The modulus of elasticity, one of the important properties of a material, gives information about how much resistance the material offers during deformation. If a plasma treatment affects the E-modulus, then it must be expected that this change stems from the plasma treated surface and that the mechanical properties vary across the cross-section. In this investigation, however, only the measurable elastic modulus was considered that results from the E-modulus averaged over the cross-section.

Figure 5 shows that after plasma treatment the samples display a lower E-modulus. The resistance to deformation is reduced. Particularly with intense treatment (low separation and low speed) there is a significant change in E-modulus.

When the results are statistically analyzed a significant influence of both factors, that is treatment speed and separation between nozzle and substrate surface, on E-modulus can be seen. **Figures 5 and 6** show the relationship between the E-modulus values and the process parameters separately.

The results of the investigations show: An intensive plasma treatment reduces the E-modulus of the polymer by an average of up to 30 %. The larger the separation to the plasma nozzle and the high- →

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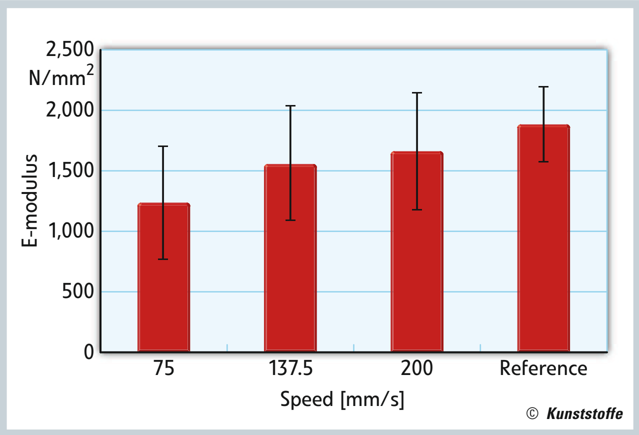

Fig. 5. Change in the E-modulus through various plasma processing profiles – effect of speed

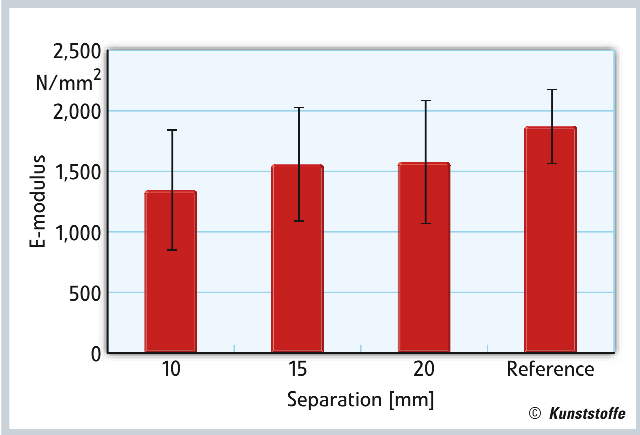

Fig. 6. Change in the E-modulus through various plasma processing profiles – effect of separation

er the processing speed the lower the reduction in E-modulus following plasma treatment. In these cases, however, the samples suffer a loss of surface activity.

The interaction between surface energy and E-modulus is shown in **Figure 7**. A high surface energy of the plasma treated sample is associated with a lower E-modulus. An intensive activation of the surface is therefore at the expense of a reduction in the mechanical properties.

Finding the Right Balance

The investigations have highlighted several interesting and remarkable aspects for industrial applications. It could be demonstrated that there is a direct and counteracting relationship in the competing objectives of a plasma treatment: High levels of surface energy, minimal changes in the mechanical properties and an economically viable selection of plasma treatment parameters (i. e. process speed) have mutually interacting effects on each other. For practical applications this means that for industrially economic treatment parameters (low separation to the substrate and high processing speeds) attention must be paid to achieving a balance between high surface energy and the lowest possible damage to the surface. If the surface energy has to be as high as possible after the plasma treatment then non-negligible changes in the mechanical properties will occur.

Where atmospheric pressure plasma treatment is used as a pretreatment, the user must consider possible changes in the mechanical properties. This applies in particular to situations where the mechanical design of composite parts is undertaken, such as structural adhesive bonding.

Conclusions and Outlook

The results presented confirm that the modification of mechanical properties of plasma treated thermoplastics is accompanied by a significant surface warming through the treatment process. In order to ensure a long lasting bond the plasma treatment should therefore not be too intensive. Often a moderate activation is all that is needed in order to achieve sufficient bonding whilst at the same time only causing a small change in mechanical properties.

In future by studying variously plasma treated sample material and geometries experimentally it will be possible to make concrete recommendations for the processing parameters of specific components. This offers the opportunity to guarantee the best possible activation with the lowest losses in mechanical properties. ■

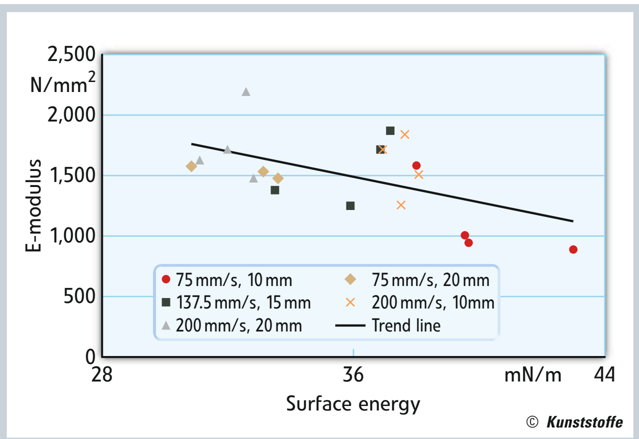

Fig. 7. Correlation between the E-modulus and the surface energy of the plasma treated film

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