Surface modification of polymers for structural adhesive bonding – Surface characteristics and adhesion mechanism

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Physical pre-treatment methods for adhesive bonding of polymers, especially for thermoplastics as they often show poor initial adhesive properties, are commonly named as suitable to increase the adhesive bond strength. In particular, a chemical "activation" (creation of functional groups) as well as an increased polarity and wetting behavior was identified in literature by many authors as the main reason for good adhesion [1].

In this study, the need of a chemical surface functionalization after physical pre-treatment for polymers was investigated. Different pre-treatment methods e.g. vacuum blasting, low pressure plasma and vacuum-UV (VUV) light were used. After optimizing the plasma and VUV treatment processes, high bond strengths e.g. on PEEK substrates up to 65-70 MPa tensile strength (butt joint) with an epoxy adhesive were reached. In order to understand which surface properties led to the bond strength increase, the pre-treatment processes were further varied specifically through a variation of the used process gases (air, nitrogen, argon, fluorine) as well as a subsequent rinsing of the pre-treated samples. The results showed, that neither a chemical modification of the surface in the form of functional groups nor a good wettability was necessary to create bonds of highest strength. In addition, the investigations showed that physical pre-treatment processes create "Low Molecular Weigth Oxidized Material" (LMWOM), which covers the surface. However, LMWOM has no impact on the formation of adhesion forces. Therefore, analytically measured surface properties cannot be directly related to the adhesive bond strength, if LMWOM has not been removed beforehand. These results were successfully transferred from PEEK to several other thermoplastics as well as thermoset epoxy resins.

In contrary to the published textbook opinion and literature, the investigations showed that adhesion does not take place through the formation of covalent bonds, but mainly through Van der Waal's (VdW) interactions. According to this, neither the surface chemistry nor the wetting behavior or polarity, but rather the surface roughness determines the adhesive bond strength. In order to allow as much VdW interaction as possible by a corresponding surface enlargement, the scale of this roughness (molecular scale) is decisive. Although these results are not in accordance to the published textbook opinion, they do provide an explanation for the different models of the adhesion mechanism.

[1] M. D. Banea and L. F. M. da Silva; Adhesively bonded joints in composite materials: An overview, Proceedings of the Institution of Mechanical Engineers, Journal of Materials Part L (2016).