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Local Shear Strength of Hybrid Polymer-Metal Joints Produced During Injection Moulding

Abstract: *In the present work the application of proadhesion interlayers based on epoxy resin compounds as the coupling agents between injected polymer material and the metal insert surface has been proposed. Within the framework of the investigations the effect of the type of applied epoxy resin compounds and their modifications on the mechanical properties (shear strength) of produced hybrid joints have been analyzed. The joining of thermoplastic polymer with the metal sheets was achieved by injection molding of polyamide 6 with 30% of glass fibers (PA6GF30) between metal sheet surfaces (DC01 steel, 0.5 mm thick, cold rolled steel sheet for drawing and forming) covered by epoxy composition interlayers.*

INTRODUCTION

The number of applications of the hybrid elements composed of spatial metal alloy die stampings and polymer sub-assembly elements increases in the mechanical engineering and especially in the automotive and household industry. This increase of applications is connected with the relative simple manufacturing process, possibility of its automation, good mechanical properties and the relatively low price. The joints between metal die stamping and polymer sub-assembly are formed in the chosen places of the functional part, according to the desired mechanical strength and application of the element.

Among the manufacturing technologies of the hybrid polymer-metal joints, injection moulding, and pressing can be mentioned, as well as the mechanical solutions such as friction bonding used for the manufacturing of the composite systems [1]. The injection moulding technology includes the mass production technology, as well as the ability to produce parts with the large specific strength parameters and providing dimensional repeatability. It is possible to combine metal inserts made of the metal alloy die stampings with the injected polymer in one production cycle. In addition, this technology is used to integrate several components into a single component, that includes several functional elements. This reduces the number of assembly operations, what decreases the production time and costs.

The materials used for metal inserts are mainly die stampings made of steels, aluminum and copper alloys. Besides the relatively good mechanical properties of the hybrid elements, the important factors are their corrosion resistance, difference in the thermal expansion coefficients [2], as well as the relatively small entire density (especially for hybrid components for the automotive industry). Therefore, aluminum and copper alloy components are becoming increasingly popular (for example, replacement of the Audi TT steel front component with an aluminum component reduces the weight of the hybrid polymer-metal structure by 15% [3]). However, due to the price, steel alloys are still a competitive solution in comparison with the other materials.

Polymers used in hybrid composites should be characterized by good dimensional stability as well as adequate strength and elasticity. As the polymers applied in the hybrid elements can be mentioned polypropylene (PP), styrene / acrylonitrile copolymer SAN, acrylonitrile / butadiene / styrene (ABS) terpolymer, polyoxymethylene (POM), polyamide 6 (PA6) and polyamide 66 (PA66), polyphenylene sulfide (PPS) [4, 5]. In the automotive applications, due to the operation conditions and strength requirements, polyamides reinforced with short glass fibers (e.g. polyamide 6 with 30% glass fiber content - PA6GF30) are particularly very widely applied [3,6,7].

The main problem that occurs when combining polymeric materials with metal alloys is the different nature of both materials. Sometimes, according to the very poor adhesion at the polymer-metal interface, for joining of metals and polymers the mechanical solutions were applied [4, 8]. In order to improve the adhesion of the injected polymer material to the surface of the metal, a variety of solutions are used, such as modification of the surface of the metal elements, modification of the injected polymer material by the addition of the adhesion promoters or the application of intermediate adhesion layers on the surface of the metal inserts [9-11].

In the process of injection molding technology it is preferable to apply on the metal surfaces the coatings with the good adhesion to both components of the hybrid elements (metal alloy surface and the injected polymeric material). As the example the application of suitable polyolefin adhesive films for joining prepregs based on thermoplastics with metal sheets can be indicated [12-14]. Injection molding technology can be exemplified by PIF technology (Plastics Injection Forming), which utilizes metal inserts previously coated with an intermediate layer to bond the metal element to the injected polymeric material (both the intermediate layer and the injected polymeric material can be the same material) [15-18]. Examples of materials that meet the requirements of pro-adhesive intermediate layers are epoxy resins. The epoxy resins are characterized by the wide range of curing parameters (like temperature and curing time), good wetting properties of substrate surfaces, low shrinkage during crosslinking, good adhesion (e.g. to the metal alloys, glass, ceramics), high mechanical strength, chemical resistance, good dielectric properties and good thermal resistance [18-20]. The good adhesion properties of the epoxy resins and the high reactivity of the oxirane group have led to the application of these materials in many areas, including: the production of adhesives, the impregnation of prepregs [21-23], as coating materials [19], as compatibilizers in polymer blends [24, 25].

In this work, the application of epoxy composites as the pro-adhesive interlayers for the production of polymer-metal hybrids based on the injection molding technology is presented. The conditions of the crosslinking process of the epoxy systems, their composition and modification, as well as the method of surface preparation of the metal elements and the conditions of the injection molding process on the chosen mechanical properties of the polymer-metal joints were analyzed and discussed.

EXPERIMENTAL

MATERIALS

The hybrid joints were manufactured by using Polyamide 6 reinforced with 30% glass fibers (Tarnamid T-27 GF30, „Grupa Azoty S.A." from Tarnów, Poland) and steel sheets DC01 (cold rolled steel sheet for drawing and forming; the chemical specification according to the standard EN 10130 (content in %) is: C: 0.12, Mn: 0.60, P: 0.045, S: 0.045. The epoxy resins, Epidian 57 (liquid, low molecular weight epoxy resin mixture with diluents – saturated polyester resin), Epidian 62 (liquid, low molecular weight epoxy resin with plasticizer), and Epidian 5 (liquid, low molecular weight epoxy resin) and hardener PAC (polyaminoamid) were delivered by "Ciech S.A.", Nowa Sarzyna (Poland). The weight ratios of hardener and the epoxy resins were 65:100 (for Epidian 57 and Epidian 62 epoxy resins) and 80:100 (for Epidian 5) – and were suggested by the resins manufacturer. The alumina particles filler (from P.P.U.H. „KOS", Koło, Poland), F1200 – with particle size of 3 μm ± 1%, and F500 - with particle size of 12,8 μm ± 1%, were mixed with epoxy resins and later the hardener PAC was added. The weight ratio of alumina F1200 and F500 to the epoxy resin was 1:1 and 1:2 respectively. The obtained epoxy resin compounds were labelled appropriately as: 5PAC, 62PAC and 57PAC.

SAMPLES PREPARATION

The steel sheets were sandblasted by using alumina F80 particles (the particle size ranges from of 180 to 212 μm) and etched with a 15% orthophosphoric acid (V) (H_3PO_4) water solution during 30 minutes. The prepared metal sheets were then degreased with the ammonia solution, isopropyl alcohol and acetone (each step of 15 minutes at the temperature of 20°C).

The samples were the single-lap shear specimens for shearing strength tests (Fig.1).

The steps of manufacturing of polymer-metal joints are shown in Fig.2. The selection of parameters and conditions for performing individual stages of hybrid joints production are presented in the work [26].

The 20 mm x 20 mm area were covered by the layer of epoxy composition. The first step of curing process took place at 30°C in oven during 90 – 180 min. (time depended on the type of epoxy composition). Then the metal sheets (with partially cured epoxy composition layers) were placed in injection mould cavity (of a DEMAG ERGOtech 50-120 Compact injection molding machine) and the PA6GF30 was injected between metal inserts covered by epoxy compound layers. The hybrid samples were later placed in the oven at 120°C for 120 min. to involve the second step of curing. Shear tests were performed at a Tinius Olsen H25KT test machine, applying a tension rate of 1.5 mm/min, until failure of the joint (according to the standard PN-EN 1465:2009 "Adhesives – Determination of tensile lap-shear strength of bonded assemblies"),. The thermal properties of epoxy compounds were measured by differential

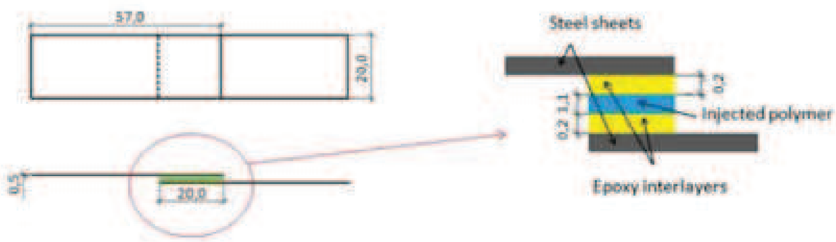

Fig. 1. The drawing of the specimen of polymer-metal joint of the single-lap type

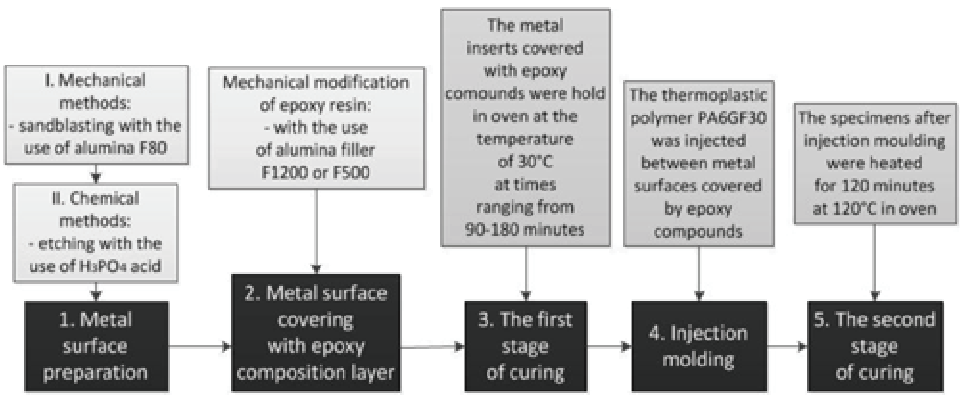

Fig. 2. Block diagram of technology of manufacturing thermoplastic polymer – metal joints

scanning calorimeter DSC 1 (Mettler Toledo) in dry nitrogen with a heating rate of 10°C/min.

RESULTS AND DISCUSSION

The thermal analysis has proved that the epoxy layers on the metal substrates, at the moment of the injection of thermoplastic polymer, were characterized by the degree of curing approximately between 16 – 30%. The constant curing time (120 minutes) applied during the thermal analysis confirms curing differences for individual epoxy compounds. For the 62PAC and 57PAC composition, the crosslinking degree was 16%. During the production of hybrid joints, the actual time of the first crosslinking step for epoxy based joints was from 90 to 180 minutes. By comparing the results of the thermal analysis with the actual times of the first crosslinking step used in the hybrid joints manufacturing process, it can be stated that the degree of crosslinking of the epoxy composite (at the time of insertion of the steel sheet into the injection mold cavity) is of the order of 20%. In Fig. 3. the DSC curves of the epoxy composites modified with F1200 filler (the weight ratio of alumina F1200 to epoxy resin was 1:1) compared with the curves for compounds of the same composition without the addition of powder filler are shown.

The enthalpy of the crosslinking reaction of the epoxy composition with the addition of F1200 powder filler is lower than the enthalpy of crosslinking of the non-filled compositions. For compositions based on Epidian 62, the enthalpy of crosslinking was lower by 32%, and for compositions based on Epidian 5 - 36% (relative to F1200 non-filled compositions). This is due to a decrease in the total weight of the resin - hardener system relative to the total weight of the sample. In terms of pure components enthalpy values (filled systems with respect to unfilled) are comparable. Higher temperatures at which filled compositions reached an exothermic peak (relative to analogous unfilled systems) indicate a decrease in their reactivity. This was also reflected in the extended time of their (filled systems) first crosslinking step, which positively influenced the stability of the injection moulding process and other necessary operations related to the production of hybrid joints. In both cases, the increase in temperature peak of the exothermic cure may also be noted by about 6% relative to the exothermic temperature peak of the crosslinking process of F1200 unfilled compositions.

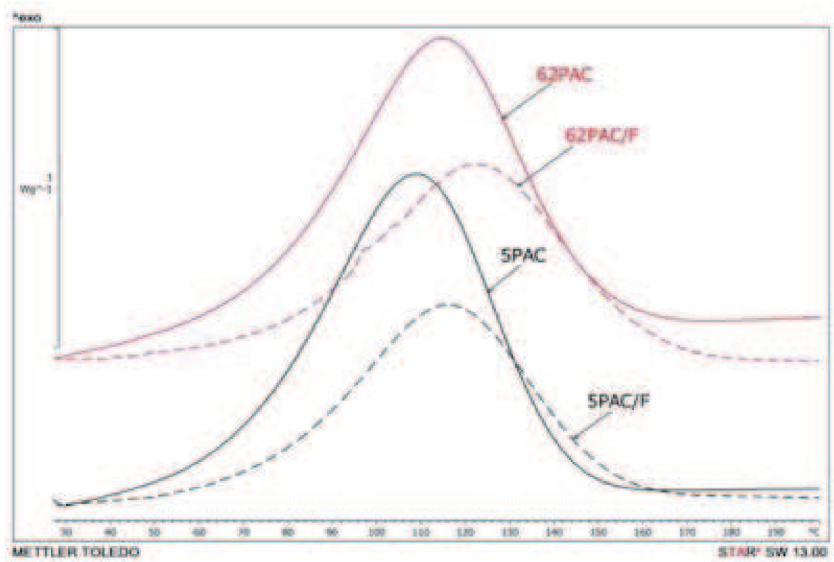

Fig. 3. DSC curves for 5PAC and 62PAC epoxy compounds; solid line - compositions without additives; the F1200 additive filler composition was designated as the dashed line (the weight ratio of alumina F1200 to the epoxy resin was 1:1) [27]

In Fig. 4. the results of shear strength test of polymer-metal hybrid joints according to the applied epoxy resin and the type and amount of alumina powder filled (in the form of F1200 and F500 alumina) are presented.

In the case of joints based on the filled 62PAC composition, the shear strength differences for the individual filling variations are relatively small and range between 5.1 ± 0.9 [MPa] and 5.9 ± 0.5 [MPa]. Only for compositions 57PAC / F500 (weight ratio 1: 2) and 57PAC / F1200 (weight ratio 1: 1) the decrease of shear strength of hybrid joints was observed, in relation to the hybrid joints based on the unfilled epoxy compositions. The reduction in shear strength was 30% and 18%, respectively. In most cases, the presence of powder fillers also positively influenced the reduction of the spread of standard deviations, which proves the increased repeatability of the properties of the produced joints. In Fig.5. the fractures of epoxy composition surfaces after shear strength tests are presented.

In other cases, the increase in shear strength of hybrid joints was noted after adding the powder filler to the epoxy composition (regardless of filler type). The highest increase in shear strength in comparison with the not filled compositions was observed for hybrid joints produced using:

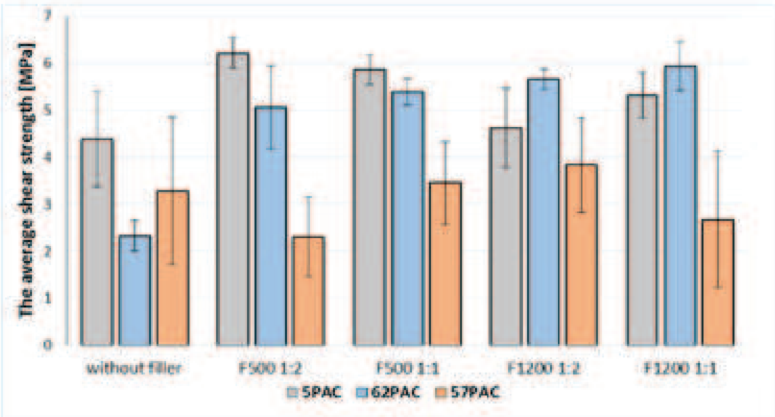

Fig. 4. The effect of type and amount of alumina filler addition into epoxy compositions on shear strength of PA6GF30 – DC01 steel (after alumina F80 sandblasting) hybrid joints

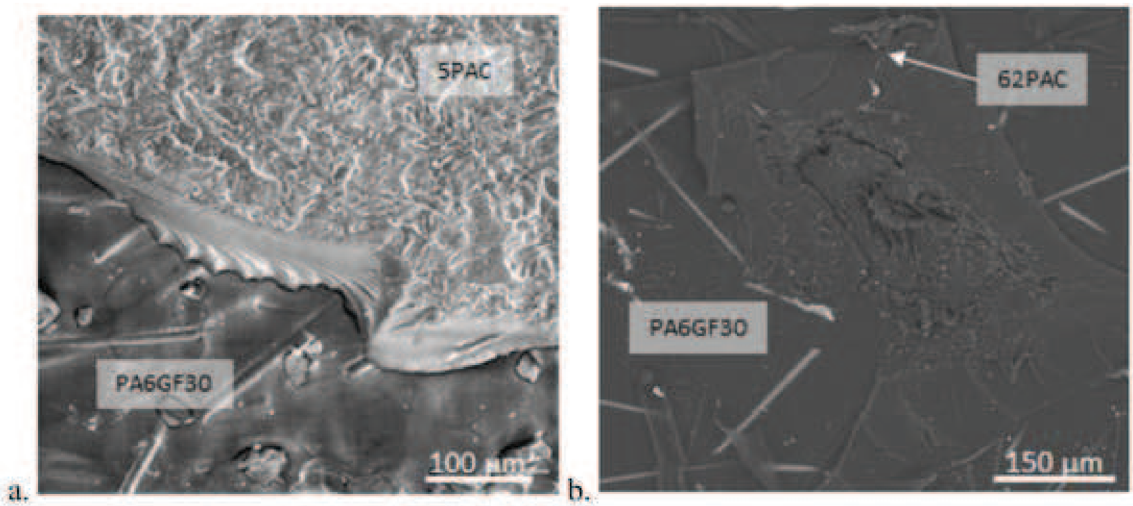

Fig. 5. SEM pictures of fracture surfaces after shear strength tests of the (a) – adhesive failure of 5 PAC non-filled resin and PA6GF30 (prepared without conductive layer) and (b) - adhesive failure 62PAC non-filled resin and PA6GF30 (prepared with conductive layer)

- 5PAC/F500 (weight ratio 1:2) - 42% increase;
- 62PAC/F1200 (weight ratio 1:1) - 155% increase;
- 57PAC/F1200 (weight ratio 1:2) - 17% increase.

It can therefore be concluded that, in addition to the type of filler, the shear strength of hybrid combinations is also influenced by:

- appropriate parameters of surface roughness of steel sheet, possibility of interlocking of alumina particles in the surface roughness and the viscosity of epoxy resin;
- the wettability of the steel surface by the epoxy systems;
- a suitable mass fraction of the filler in the epoxy composition.

The last factor depends on the type of epoxy composition and the physico-chemical properties of the filler itself (such as chemical composition, particle size, shape).

SUMMARY

The manufacturing of local joints at the polymer – metal interface during injection molding technology requires appropriate preparation of the metal insert surface to activate it to the physico-chemical interaction with the polymeric material. In order to produce the polymer - metal joints with the relatively good mechanical strength the application of pro-adhesive interlayers having affinity for both metal surfaces and the injected polymeric material has been the most effective. Important is also input of mechanical adhesion due to the interlocking of polymeric material in the surface roughness of the metal. As the pro-adhesive interlayers the epoxy compositions were applied. They are characterized by the good adhesion to the steel surface, moreover the oxirane groups of epoxy resins also react with amino groups present in the polyamide. In the case of injection molding of polyamide 6 with 30% glass fiber (PA6GF30) at the interface the mutual interactions of physico-chemical character between injected polymer and the epoxy compound take place.

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