O. TRZASKA[1)], J.W. KACZMAR[1)], R. WRÓBLEWSKI[1)], M. NIEKRASZ[1)], Ł. KORNACKI[1)], V. CASALEGNO[2)], M. PERIOLATTO[2)], R. BONGIOVANNI[2)]

[1)] Wroclaw University of Technology, Faculty of Mechanical Engineering, Chair of Foundry Engineering, Polymers and Automation, Łukasiewicza 7/9, 50-371 Wrocław, Poland

[2)] Politecnico di Torino, Department of Applied Science and Technology (DISAT), Corso Duca degli Abruzzi, 24 – 10129 Torino, Italy

The effect of the filled epoxy resin interlayers on the adhesion in polymer-metal hybrid joints

***Abstract**: Two epoxy resin compounds were used as the adhesion interlayers at the interface between an injected glass fibre reinforced thermoplastic polymer PA6GF30 (polyamide 6 with 30% wt. of glass fibres) and steel sheet (DC01 steel, 0.5 mm thick). Both epoxy resins, Epidian62 and Epidian57, were filled with alumina particles (grain size of 3μm ± 1%) in a volume rate of 100:29 epoxy resin – alumina. Steel sheets with cured layer of epoxy resin compounds were placed in the injection mold, then the PA6GF30 was injected between them. Shear strength tests were basis for the evaluation of the adhesion of the manufactured polymer-metal hybrid joints. SEM and optical microscopy analysis were used to investigate the structure of joints after shear deformation. Conversion rates of epoxy compounds and heat of curing reactions were investigated by using of differential scanning calorimeter (DSC). It was found that the highest strength of these joints was achieved for epoxy compounds based on Epidian62.*
***Keywords**: epoxy resin, polymer metal hybrid composites, hybrid joints, adhesion promoters*

1. Introduction

The polymer-metal hybrid composites (PMH) have been applied for about two decades as the structural parts in the passenger and medium size cars. PMH elements are used in the instrument-panel, cross beams, the roof-panel-cross-support and the entire front-end vehicle modules [1-3]. They are characterized by the physical and mechanical properties of both components: the steel sheets ensure good mechanical strength and stiffness, and the thermoplastic polymers allow an easy forming of complicated shapes and a relatively low density. Polymer-metal hybrid elements improve the specific strength of the components effecting on the lower mass of the hybrid components and can also combine different functions, such as supporting of wires and pipes in the passenger and medium size cars [2,4,5].

One of the most relevant advantage of PMH applications in the car structures is the significant reduction of the vehicle weight (light weight engineering), which translates into the lower fuel consumption, better exploitation and therefore lower CO_2 emission [2-4].

The PMH composites made of steel sheets and thermoplastic polymers can be manufactured in different ways depending on the required final properties of the product and on the used materials.

A suitable processing is injection molding, which is mainly applied for the mass-production and is characterized by the excellent repeatability of the injected elements, the short time of the process cycle and the nearly full automation.

Between metals and thermoplastic polymers mechanical or adhesive joints can be formed. The production of the thermoplastic PMH is mainly based on injection molding technology and the main processes are: IMA (In Moulding Assembly) like „Insert" and „Outsert" technology, PMA (Post Moulding Assembly), MOM (Metal Over Moulding), Metal-GAIM (Metal-Gas assisted injection moulding) and Metal-WAIM (Metal-Water assisted injection moulding) [4,5]. They take advantage of the systems of polymer rivets in the metal elements formed during injection molding and/or the metal inserts edges over molding by injected thermoplastic polymer [4,5].

The direct metal-polymer joint usually shows poor adhesion as the metal is polar and the thermoplastic polymer is not. There are several possibilities in order to increase the adhesion of the thermoplastic polymer to the metallic surface:

— heating of the metallic surface just before the injection molding process, then the better mechanical micro-interlocking is obtained between the metal surface roughness and the injected polymer [6,7];
— the thermoplastic polymer modification, e.g. by the addition of the coupling agents like grafted polymers (e.g. polymer grafted maleic anhydride) to the bulk polymer [8];
— the metal surface modification: mechanical modifications (e.g. increasing of the surface roughness) and chemical modifications (e.g. the metal surface pre-treatment by plasma, etching, the metal surface covering with the adhesion promoters) [7,9,10].
— the introduction of an interlayer between metal and polymer.

From the above described methods of adhesion improvement the last one was chosen in this work: according to the excellent adhesion of epoxy resins to metallic surfaces, an epoxy layer was applied. The presence of the polar aliphatic hydroxyl and ether groups in the epoxy resin chains enable the creation of the strong secondary bonding with the metal surface [11]. The possibility of mecha-

nical and chemical modifications of the epoxy resins make possible the joining of hydrophobic (non-polar) materials like polyolefines: the acrylic-epoxy adhesive LESA is used for the joining of the polypropylene elements with metal stampings, this method of PMH manufacture was patented and used in the front-end-module prototype of some cars [6].

The properties of the epoxy resins, and consequently their performance as coupling agents, strongly depend on the conditions of the hardening process and are dependent on the kind of hardeners used and the technological parameters like the pre-treatment of the joined surfaces. Depending on the type of the curing agent (its chemical properties) and its mass ratio to the epoxy resin manufactured epoxy compound can exhibit different physic-chemical properties (e.g. flexibility and shear strength of the epoxy resin compound can be modified by appropriate choice of the curing agent) [12,13]. The curing parameters are also an important issue. The strength of the joints depends on both time and temperature of the hardening process. An important factor is also the post-curing process of the joint (in a definite temperature for the specified epoxy resin compound), which significantly improves the quality of the joints and resulting in increase of their flexibility [14]. The addition of appropriate fillers (such as SiO_2, Al_2O_3 or $CaCO_3$) can also modify the epoxy compounds. The mechanical characteristics of the obtained joints (based on the modified epoxy resins with fillers) are affected by both the size of the filler's particles, as well as the preparation of the metal surfaces [15,16].

In the case of metal inserts, which are applied as the part of PMH elements in the injection molding process, few steps of metallic surface pre-treatment are required: surface roughening, chemical etching, degreasing and refining. Method of the preparation of the steel sheet surface (depending on the type of metal) affects its geometry and, as a result, the adhesion of the epoxy compound layer. Research shown in [16] indicates that there is also a correlation between the geometric dimensions of the abrasive used for the sheet metal surface treatment, particle size of filler and the epoxy resin compound and the adhesion layer of the epoxy compound to the surface of the metal sheet.

The epoxy interlayer (epoxy resin compound) on the metal surface, suitable for the application during injection molding process, should be characterized in term of cohesion and adhesion to the metal surface and to the thermoplastic polymer. The adhesion between epoxy resin compound and the metal surface is formed during preliminary covering of this metal surface, and the adhesion between epoxy resin compound and the thermoplastic polymer is formed during injection molding process.

The aim of this work is the improvement of the mutual strength of the metal-polymer joints by the application of the epoxy resin compound interlayer strengthened with the alumina particles. In order to estimate the conversion rate of the epoxy resin compound interlayer (at the injection molding time) the thermal analysis (DSC) were applied.

2. Experimental

2.1 Materials

The hybrid joints were manufactured by using polyamide 6 reinforced with 30% glass fibers (Tarnamid T-27 GF30 which was kindly supplied by „Grupa Azoty S.A." from Tarnów, Poland) and steel sheets DC01 (cold rolled steel sheet for drawing and forming; the chemical composition specification according to the standard EN 10130 in maximum percentage content 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 hardener PAC (polyaminoamid) were kindly provided by "Ciech S.A." from Nowa Sarzyna (Poland).

The weight ratios of hardener to the epoxy resins were 65:100 (for both epoxy resins) – the weight proportions were suggested by manufacturer. The alumina particles filler, F1200 – P.P.U.H. „KOS" from Koło (Poland) with particle size of 3μm ± 1%, were mixed with epoxy resin and later the hardener PAC was added. The weight ratio of alumina F1200 to the epoxy resin was 1:1 (77,5% vol. of epoxy resin and 22,5% vol. of alumina particles). The obtained epoxy resin compounds were labelled appropriately as:

— Ep57/PAC/F- Epidian 57 hardened by PAC with alumina particles,
— Ep62/PAC/F- Epidian 62 hardened by PAC with alumina particles.

2.2 Preparation of metal-polymer joints

The metal sheets (DC01 steel, 0.5 mm thick) were sandblasted by using alumina F80 particles (the particle size ranges from of 180 to 212 μm, the angle of jet – 45°, the pressure of sandblasting: 6 Bar) and etched with a 15% orthophosphoric acid (V) (H_3PO_4) water solution by 30 minutes. The prepared metal sheets were then degreased with the ammonia solution, isopropyl alcohol and acetone (each step by 15 minutes). The etching, degreasing and refining solutions were performed at the room temperature (eg. 20°C).

The 20 mm × 20 mm metal surfaces were covered by 0.5 mm layer of the epoxy resin compounds (based on Epidian 57 or Epidian 62 hardened by PAC, containing alumina particles). Then they were hold at the temperature of 20°C from 90-200 minutes in order to start the curing process resulting in the increase of hardness and stiffness, the addition of alumina particles results in decreasing of epoxy layer shrinkage, increasing its strength and cohesion. This first step of curing is necessary to let the epoxy interlayer withstand the pressure of injected liquid PA6GF30 polymer, which is in the range of 80-100 MPa and could destroy the applied soft, uncured epoxy resin compound. The coated steel sheets were placed in the injection mould cavity (of a DEMAG ERGOtech 50-120 Compact injection molding machine) and then the

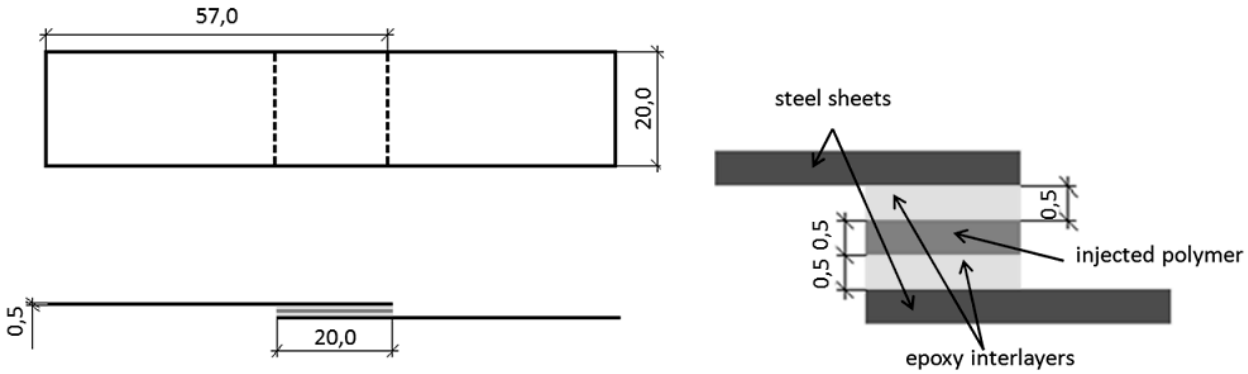


Fig. 1. The single shear lap specimen

PA6GF30 polymer was injected between metal sheets. The specimens in the shape of the single lap joints (Fig.1.) were heated for 120 minutes at 120°C after injection molding to involve the second step of curing of the epoxy resin compounds.

The samples were then tested by applying a tension rate of 1.5 mm/min, until failure (according to the standard PN-EN 1465:2009 "Adhesives – Determination of tensile lap-shear strength of bonded assemblies"), at a Tinius Olsen H25KT test machine.

The apparent shear strength (ratio between the maximum applied force and surface of the joined area) was used for the evaluation of the adhesion at the interface metal – epoxy interlayer and epoxy interlayer – thermoplastic polymer of the manufactured hybrid polymer-metal joints.

2.3 Epoxy layer characterisation by Differential Scanning Calorimetry (DSC)

Thermal analysis of the epoxy compounds were performed by differential scanning calorimeter DSC 1 (Mettler Toledo) in dry nitrogen with a heating rate of 10°C/min. Epoxy compounds used for DSC analysis have the same alumina content as those used to coat steel sheets.

In order to calculate the epoxy compounds conversion rates achieved after the first step of curing the uncured samples and the partially cured samples were investigated (curing process for the partially hardened specimens was proceeded at 20°C for 120 minutes to reflected the parameters of the first step of curing in the polymer-metal hybrid joints manufacturing process).

3. Results and discussion

3.1. Optical microscopy analysis of the lap joints

The cross-section of the single shear lap specimens permit to analyze the adhesion of layers of epoxy resin compounds and thermoplastic polymer between DC01 steel substrates. At Fig.2 one can see the joint made of Ep62/PAC/F and PA6GF30 between DC01 steel substrates. The strongest mechanical joints are obtained for a metal surface which is characterized by the "U" shaped structure which permits to interlock the epoxy resin compound inside the metal surface cavities (Fig.3 and Fig.4). The cross-section of the sample Ep62/PAC/F shows visib-

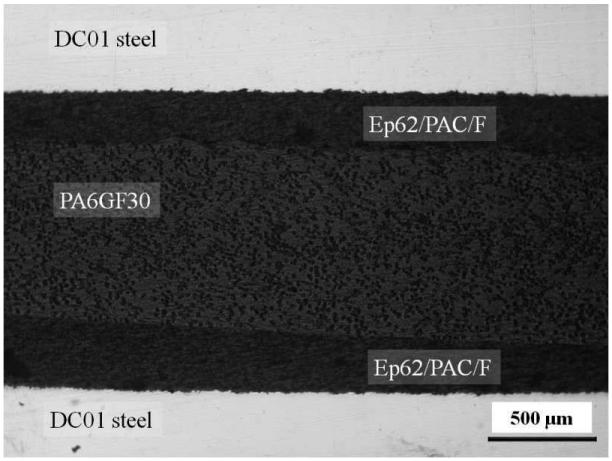


Fig. 2. Cross-section of the DC01 steel – Ep62/PAC/F – PA6GF30 joint

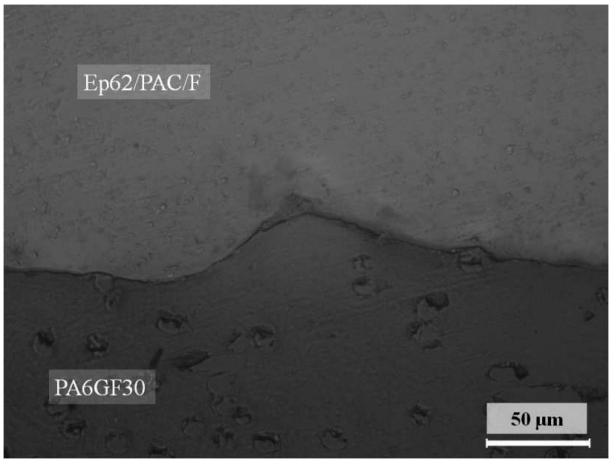


Fig. 3. Cross-section of the Ep62/PAC/F – PA6GF30 interface

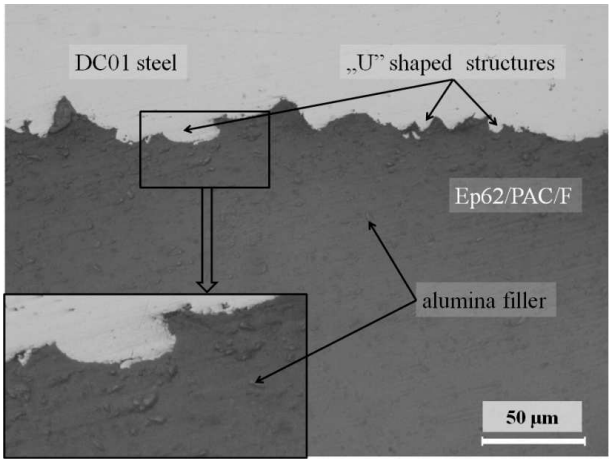


Fig. 4. Cross-section of the DC01 steel – Ep62/PAC/F interface

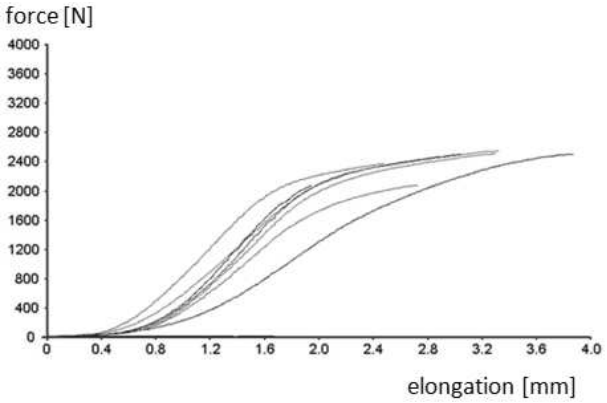


Fig. 5. The relationship force – elongation taken during shear testing for polymer – metal hybrid joints based on Ep62/PAC/F epoxy resin compound

le interface DC01 steel sheet-Ep62/PAC/F with the homogenous distribution of the alumina filler in the epoxy resin compound volume (Fig.4). There are also visible the agglomerations of alumina filler (5-7 µm of size) which are dispersed homogenously in the epoxy resin compound bulk.

The mechanical interlocking, to a lesser degree, is also present at the interface epoxy resin compound – thermoplastic polymer. The presence of the alumina filler, besides improvement of the epoxy resin compound cohesion, contributes to the development of a good interface between the injected thermoplastic polymer and the epoxy resin compound and enhance the mechanical coupling between them (Fig. 4).

3.2. The shear strength tests and SEM analysis

In the Table 1. the average values of shear strength of the hybrid joints are presented. The results are based on the strength investigation of 6 samples for each series. The higher values of shear strength for Ep62/PAC/F compounds are probably the effect of the presence of plasticizer in the Epidian 62. The highest elasticity of the epoxy interlayer enhances the shear strength of the joints during mechanical tests.

Table 1. The average shear strength of the PMH

Parameters	Ep62/PAC/F	Ep57/PAC/F
average shear strength [MPa]	5.93 ± 0,48	2.68 ± 1,30
average maximum shear force [N]	2370 ± 192	1073 ± 521

There were ascertained the relatively large differences in the values of maximum breaking forces (characterized by the relatively high value of standard deviation) for joints based on Ep57/PAC/F epoxy resin compounds which are probably the result of the chemical inhomogeneity of the epoxy resin compound volume. It could be explained by the constitution of the Epidian 57 resin (epoxy resin mixture with diluents- saturated polyester resin). The relationship force-elongation of the joints with the Ep62/PAC/F interlayer (Fig. 5) depicts similar shaped curves. Joints for this kind of epoxy resin compounds show elastic properties, the values of maximum shear strength are simultaneously to the values of breaking forces.

Lower values of mechanical strength in polymer-metal hybrid joints, based on Ep57/PAC/F compound, are probably due to presence of the diluents, which contribute a not homogenous distribution of alumina filler in the epoxy resin compound (Fig.6).

During injection molding, due to the partial curing of the epoxy resin compound, there was possible transport of the epoxy resin compound (containing alumina particles) inside the liquid PA6GF30 polymer. The mechanism is visible at Fig.7a and Fig.7b, where alumina particles surround the single glass fibres. It shows that mechanical

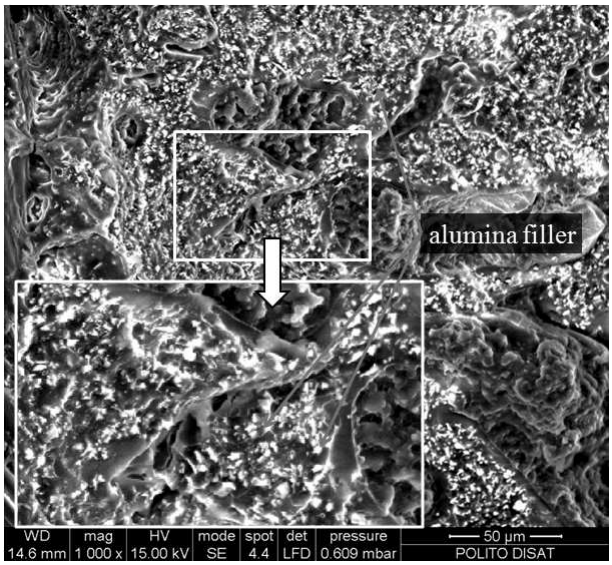
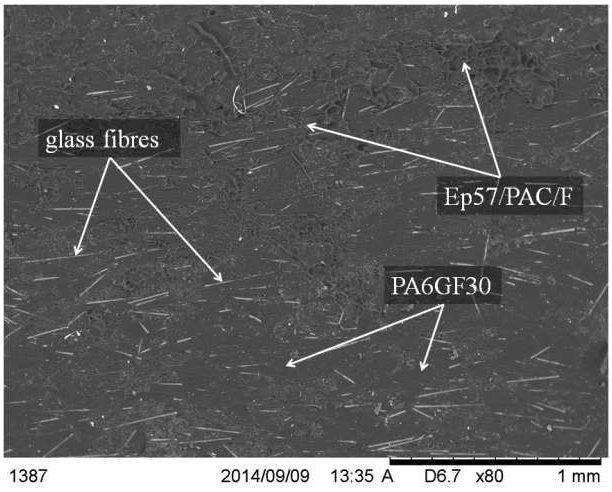


Fig. 6. SEM picture of Ep57/PAC/F epoxy interlayer after shear strength test

a)



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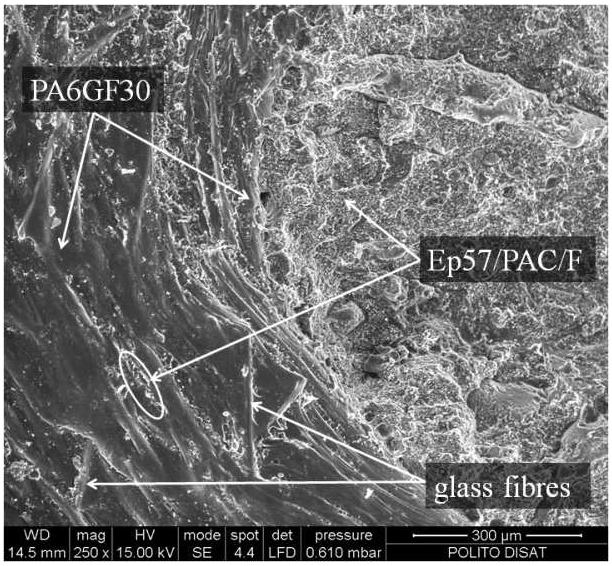


Fig. 7. SEM pictures of polymer – metal hybrid joints, based on Ep57/PAC/F epoxy resin compound, after shear strength test: a.) SEM picture of the thermoplastic polymer (PA6GF30) surface, from the DC01 steel – PA6GF30 interface, b.) SEM picture of sample showing the interface of the border: interface of injected PA6GF30 and epoxy resin compound

interlocking also occur at the interface of injected PA6GF30 and epoxy interlayer. The presence of glass fibres in the thermoplastic polymer volume foster the mechanical joining and facilitates mutual hitching.

Higher values of breaking forces of the Ep62/PAC/F and their similar character comparing to Ep57/PAC/F can be explained on the base of the relatively homogeneous dispersion of alumina particles in the epoxy resin compound volume in micro scale (Fig.8). The rest of epoxy resin compound containing alumina filler around the glass fibres is also visible. The border between epoxy resin compound and injected PA6GF30 is shown on Fig.9.

For both polymer – metal types of hybrid joints (with Ep57/PAC/F epoxy interlayer, Fig.10, and with Ep62/PAC/F interlayer) the fractures caused by poor

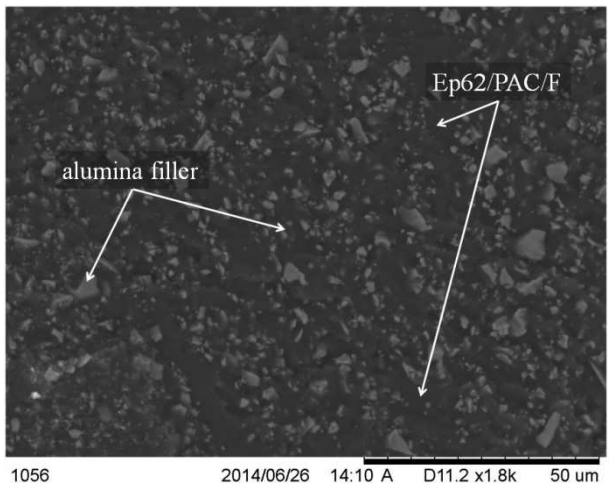
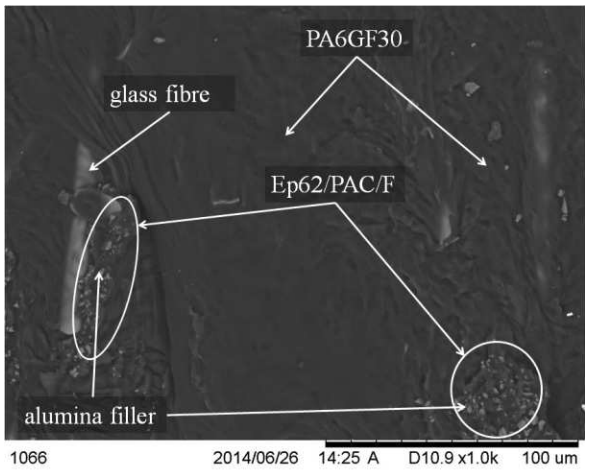


Fig. 8. Distribution of alumina particles in the Ep62/PAC/F epoxy interlayer after strength test

a)



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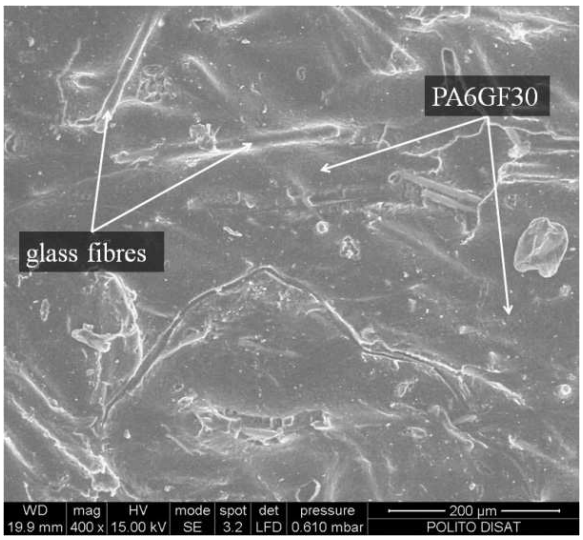

Fig. 9. SEM pictures of fracture surfaces of the Ep62/PAC/F – PA6GF30 border after shear strength test; a) SEM picture of sample prepared with use the conductive graphite layer; b) SEM picture of specimen prepared without conductive layer

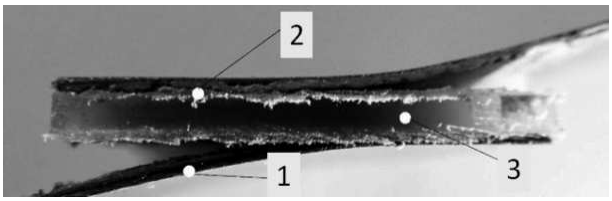

Fig. 10. Joint after failures during shear strength test. PMH with; 1 – DC01 steel sheet, 2 – Ep57/PAC/F epoxy interlayer, 3 – PA6GF30 polymer

adhesion between DC01 steel sheet and epoxy resin interlayer and epoxy resin layer and PA6GF30 polymer were ascertained. Moreover fracture caused by poor cohesion character in the epoxy resin interlayer were ascertained.

3.2.1. Thermal analysis

The DSC thermograms obtained during thermal analysis of the Ep57/PAC/F and Ep62/PAC/F compounds are shown at Fig.11 and 12. Heat of the curing process is generated by the exothermic curing reaction and is represented as the area under the peak. The black graphs illustrate the epoxy resin compounds after their preparation (uncured compounds). The heat of their curing reaction is treated as a total exothermic heat of curing (ΔH_T). The heat in the partially cured epoxy compounds (illustrated as the red graphs) is lower than ΔH_T, because the hardening reaction has already proceed and part of energy of curing reaction was emitted, and is treated as the residual exothermic heat of cure (ΔH_R) [18].

The conversion ratio of the epoxy resin compounds (x) is calculated from the quotient of the residual heat of cure to the total heat of cure [18]:

$$x = 1 - \frac{\Delta H_R}{\Delta H_T} \quad (1)$$

The conversion rates of epoxy resin compounds are listed in Table 2.

Table 2. The conversion rates of epoxy resin compounds (with alumina filler)

epoxy resin compound	residual heat of curing (ΔH_R) [J/g]	total heat of curing (ΔH_T) [J/g]	conversion, x
Ep62/PAC/F	157.68	198.28	0.20
Ep57/PAC/F	138.23	153.94	0.10

The low values of the conversion rates confirmed the participation of the epoxy resin compounds in the interaction with the injected polyamide 6. The conversion rate should be enough low to let the epoxy interlayer to interact with injected polyamide 6 and enough high to stabilize the epoxy interlayer at the metal surface.

The thermal properties of Ep57/PAC/F and Ep62/PAC/F epoxy compounds (with the alumina filler) were compared with thermal properties of the same compounds without alumina filler (Ep57/PAC and Ep62/PAC and are shown at Fig.13 and Fig.14). The conditions of their preparation and investigations were the same as for the filled epoxy compounds. Both Ep57/PAC and Ep62/PAC compounds have higher values of total heat of curing than their filled equivalents, what can be explained by the higher volume of epoxy resin in investigated sample. Samples with alumina filler have only 77,5% vol. of epoxy resin with hardener, hence their total heat of curing is appropriately lower.

The conversion rates of both compounds (Table 3) are higher comparing to their filled equivalents, what can be explained by the better access of hardener to the epoxy groups than in the filled compounds (due to the presence

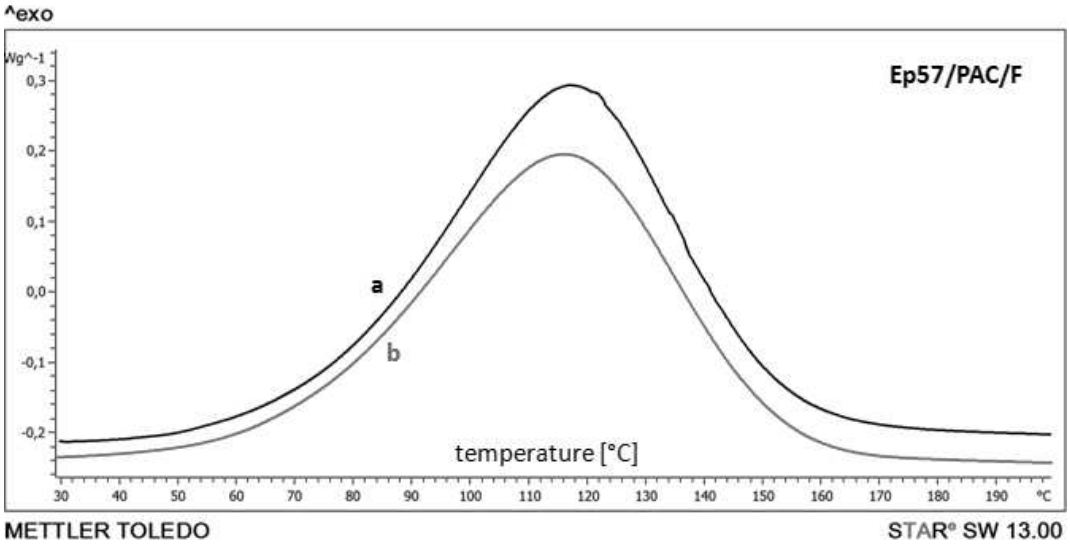

Fig. 11. DSC thermogram taken during the hardening process of the Ep57/PAC/F epoxy resin compounds (with alumina filler); the black graph (a) presents the uncured compound and the red graph (b) the partially cured compound (curing process proceeded at 20°C for 120 minutes)

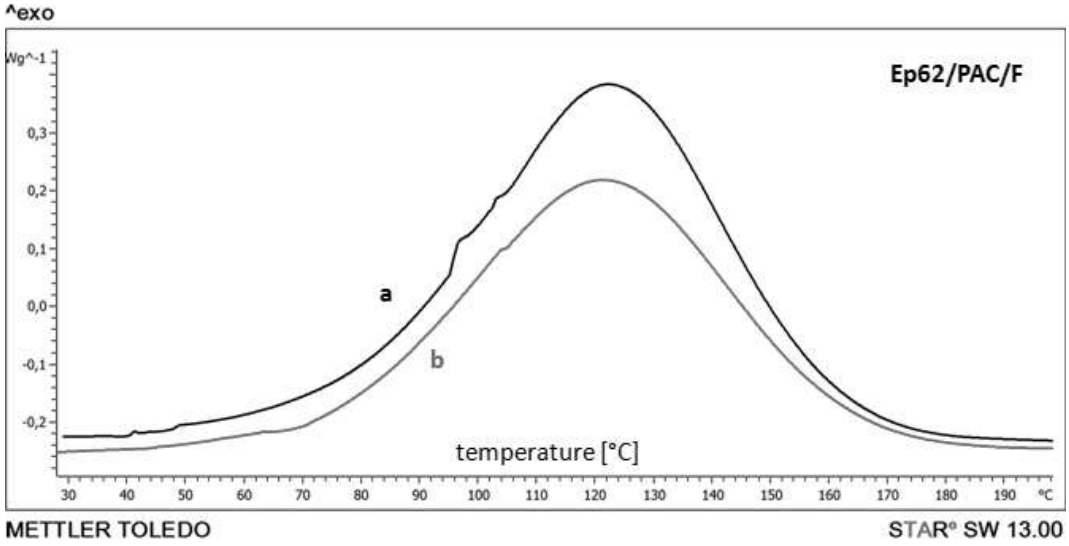

Fig. 12. DSC thermogram taken during the hardening process of the Ep62/PAC/F epoxy resin compounds (with alumina filler); the black graph (a) presents the uncured compound and the red graph (b) the partially cured compound (curing process proceeded in 20°C for 120 minutes)

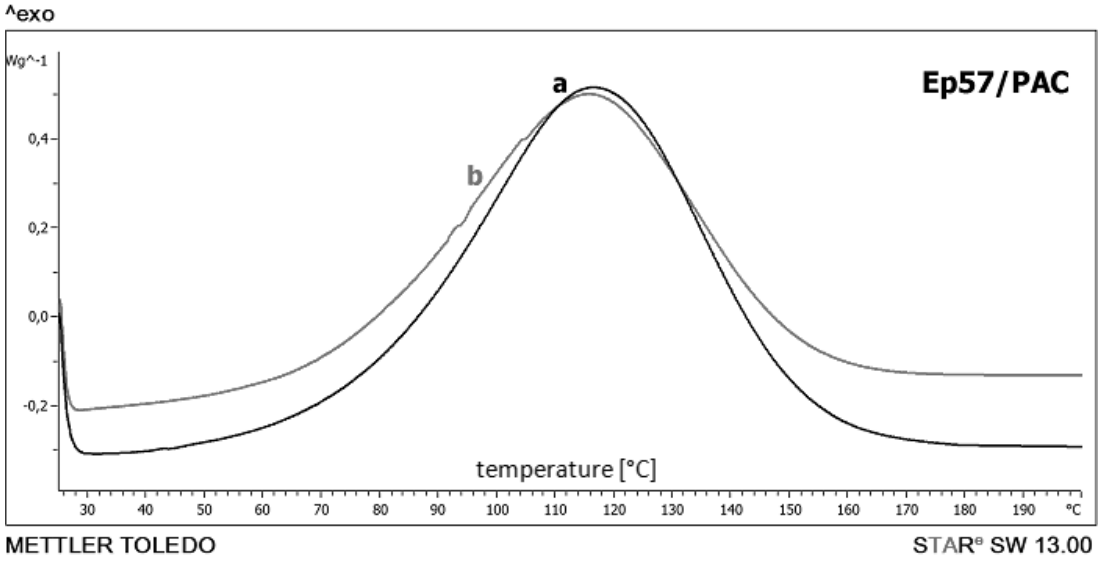

Fig. 13. DSC thermogram taken during the hardening process of the Ep57/PAC epoxy resin compounds; the black graph (a) presents the uncured compound and the red graph (b) the partially cured compound (curing process proceeded in 20°C for 120 minutes)

of filler the steric hindrance can be observed). The temperatures of curing peaks of unfilled and filled epoxy resin compounds are similar, hence the thermal parameters of first and second step of curing can be the same.

Table 3. The conversion rates of epoxy resin compounds (without alumina filler)

epoxy resin compound	residual heat of curing (ΔH_R) [J/g]	total heat of curing (ΔH_T) [J/g]	conversion, x
Ep62/PAC	77.41	288.72	0.73
Ep57/PAC	207.91	248.71	0.16

4. Summary

The shear strength of the polymer – metal hybrid joints with the application of Ep62/PAC/F epoxy as the interlayer on the surface of DC01 steel are higher (5.93 ± 0,48 MPa) than for the applications of Ep57/PAC/F epoxy interlayer (2.68 ± 1,30 MPa). In comparison with Ep57/PAC/F the Ep62/PAC/F compound includes the plasticizer, which increases the elasticity of the resin, effecting on the higher strength of the polymer – metal hybrid joints. Both epoxy resin compounds were cured using PAC hardeners, which contain in its structure the long

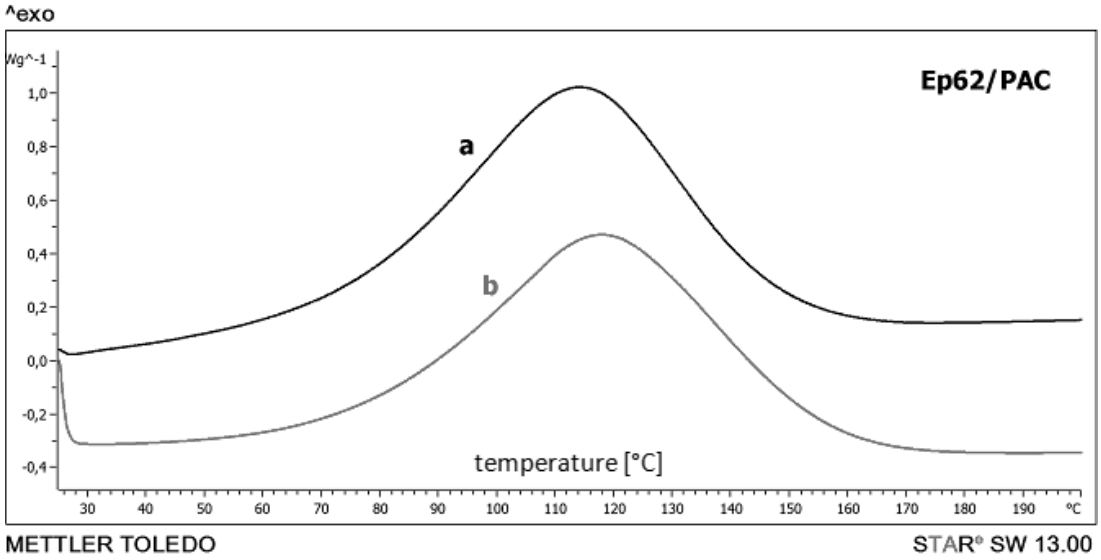

Fig. 14. DSC thermogram taken during the hardening process of the Ep62/PAC epoxy resin compounds; the black graph (a) presents the uncured compound and the red graph (b) the partially cured compound (curing process proceeded in 20°C for 120 minutes)

aliphatic chains. It causes the enhancement of the elasticity of joints caused the incorporating of aliphatic chains in the cured epoxy structure. However the additionally presence in Epidian 62 of the external plasticizer increases the elasticity of resin. The ready product Epidian 62 is more suitable for introduction of the alumina strengthening filler powder and point out the better properties for application in the thin pro-adhesive epoxy interlayers.

Thermal analysis of the epoxy resin compounds curing process shows that curing of the Ep62/PAC/F proceeded faster than of the Ep57/PAC/F compound. After the same time curing time the conversion rate of the Ep62/PAC/F was 0.20 and of the Ep57/PAC/F was only 0.10.

The SEM analysis has shown differences between structure of metal hybrid joints manufactured using Ep62/PAC/F and Ep57/PAC/F taking into account the alumina filler distribution. It is assumed that the areas in the Ep57/PAC/F without filler are result of the diluents presence in Epidian 57. The adhesive and cohesive failure during strength investigations of the epoxy interlayer at the interface with the injected thermoplastic polymer suggests the further necessity of enhancing of the adhesion effect at the mutual interface.

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