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Parametric study of hot-melt adhesive under accelerated ageing for automotive applications

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Abstract

The mechanical properties of commercially available hot-melt adhesive, HMA, which is mostly used in automotive applications, have been studied under different environmental and loading conditions, paying particular attention to the ageing effects. Three laboratory accelerated ageing processes were applied to single lap joints (SLJs) of two polypropylene substrates in order to replicate the least favourable environmental conditions in automotive usage. Experimental parametric studies were performed on virgin and aged specimens, investigating the influence of two design factors, the overlap length and adhesive layer thickness, on the load carrying capacity and mode of failure of the SLJ. FT-IR was used to perform qualitative HMA polymer composition analyses. The DSC test was also performed to obtain the thermal behaviour, and the phase transition temperatures of the HMA. In addition, the sliding temperature test was performed in an electronically controlled climatic chamber to understand, by means of tests on SLJs, the temperature resistance of the HMA/polypropylene bonded systems. Results clearly show that depending on the type of ageing process, the strength of SLJ based on HMAs varies, this enhances a relevant difference with respect to the strength of SLJ based on conventional thermosetting adhesive. Furthermore, the parametric study performed revealed the correlation between the strength of the SLJ and its geometry, which might be taken as a design guideline for this kind of flexible adhesive joints.

Keyword: hot-melt adhesive, ageing effects, mechanical strength, sliding temperature, experimental tests

1. Introduction

In the automotive industry, vehicles are being made increasingly more lightweight with the aim of reducing both fuel consumption and environmental pollution. Moreover another relevant issue is vehicle end of life and material recyclability. In Europe, particularly, for the automotive sector the Directive 2000/53/EC on end-of-life vehicles (ELV Directive) has set targets aiming to increase the reusability, recoverability and recyclability of vehicle materials and components, and promotes the distribution of information necessary for sustainable and safe vehicle treatment. Some of the materials, complex vehicle components and joint technologies employed in vehicles do not make it easy to separate and recover materials before the shredding treatment. The development of new, simple, fast and cheap disassembling technologies could provide automotive companies with a new approach for the easy and immediate reuse and recycling of

automotive parts before the shredding process. For the non-metal elements, the portion of ELVs is estimated at between 25% and 35% of ELV weight [1]. As an order of magnitude it can be assumed that over 500,000 ELVs are processed annually by shredders, and the average weight of an ELV is estimated at 1,300 kg, equivalent to 195,000 tons of shredder flock waste per annum. Therefore, it is undoubtedly necessary to look for appropriate recyclable materials, such as thermoplastic materials that could be useful for the design of vehicle components [2].

The application of an adhesive bonded joint is frequently adopted to join similar and dissimilar materials in order to achieve optimized structures and manufacturing processes. [3, 4]. Hot-melt adhesives (HMAs) are one-component systems which consist of a non-volatile thermoplastic polymer and a non-aqueous carrier for the active adhesive components. HMAs provide several advantages, such as a rapid setting time and the elimination of volatile organic compounds [5-8]. HMAs also have long shelf life and can usually be disposed of without special precautions, except those needed to meet the present legislative directives.

HMA, due to the thermo-chemical properties, is more preferable among other types of adhesives for joining and repairing plastic components, for instance one can replace just one trim of a dashboard without replacing the entire part. For the re-configurability (e.g. in terms of style) of a car, HMA, due to its reversibility, is an ideal solution because of the easy of detaching a component and replacing it with a new one.

HMAs have, however, some disadvantages compared to traditional structural adhesives; HMAs exhibit lower strength and heat resistance compared to conventional thermosetting adhesives such as epoxies or cyanoacrylate because HMAs are thermoplastic materials that cannot react or cure to form crosslinks [9].

Various polymer materials and thermoplastic, such as poly (ethylene co-vinyl acetate) copolymers (EVAs), polyolefins, polyamides, polyurethane and polyesters, have formed the bases for HMAs [10]. Basically, the composition of a HMA includes a thermoplastic polymer backbone and a diluent system. Since HMAs need to be applied in the molten state, polymers with adequate resistance to heat degradation, such as polyethylene, polyvinyl acetate or EVA, are typically used as the backbone polymer. The diluent system in a HMA can include materials such as wax, tackifier, plasticizer, antioxidants, and other fillers [11].

In order to obtain the desired performances and optimum design life, HMAs need to be selected carefully and applied to their intended engineering applications: EVA adhesives for general purpose bonding [6, 12], polyolefin adhesives for difficult-to-bond plastics, polyamide adhesives for severe environments, and reactive urethanes for elevated temperatures or high flexibility requirements.

However, in addition to the chemical, thermal and mechanical behaviours of HMAs, the durability and ageing behaviour of HMA bonded structures are critical in determining their usability for replacing structural adhesives and mechanical fastening systems.

Several studies have attempted to correlate the change in the mechanical properties and strength of adhesive joints with exposure to a controlled humidity and temperature [13-28]. A change of environment can have both an effect on change over time of the physical properties of the adhesive and on the strength of the substrate-adhesive interface [29, 30]. For instance, John et al. [29] exposed double lap joints to high humidity and temperature and measured the change in joint strength. They used these data together with a shear strength criterion in a finite element model to predict the strength of the joints in these environmental conditions [24]. Zhang et al. [17] exposed adhesively-bonded single lap-shear joints (SLJs) of thin panel sheets to various specifically designed accelerated, constant and cyclic, hygrothermal environments. The residual

strengths of SLS joints with different adherends were compared to assess their durability. It has been observed that the joints of electro-galvanized steel (EGS) panels have a significant loss of strength at 80°C constant exposure, while the joints of aluminium alloy (AL) panels exhibit a relatively stable durability in the same scenario. Moreover, the ageing of SLS joints with dissimilar substrates was determined by the weaker adhesive–substrate interface, which was the adhesive–zinc interface of the EGS/AL panel joint under hot-wet conditions. The history effect of temperature-path on residual strengths of SLS joints was also investigated. Zhang and co-workers deduced that the durability of SLS joints under long-term exposure may be estimated by some short-term hygrothermal ageing with appropriate scenarios. Wylde and Spelt [31] used the open-faced method to measure the steady-state critical strain energy release rate, G_c , of brittle epoxy adhesives that had been aged in hot-wet environments. They tested the adhesive in both wet and dry states (i.e. with and without water in the adhesive layer), and found that the strength of the dry specimens decreased monotonically with ageing time while that of the wet specimens increased in the initial stages of ageing due to the reversible plasticization effect of water. In a related work, Kinloch [7] concluded that the rate of degradation increases with increasing temperature and the strength and durability of the joints. However, the above mentioned papers focused on structural adhesive, in particular epoxies, while to the authors' best knowledge, few articles can be found in the open literature which address the issue of environmental effects on HMA joints.

Several researchers have studied the effect of the geometry profile of SLJ using experimental and numerical methods. Da Silva et al. [33] investigated the effect of the materials, geometry and surface treatments on the SLS joints. They concluded that the shear strength increases with the overlap length, substrate thickness and substrate yield strength. Seong et al. [32] also investigated the effects of various parameters, such as the bonding pressure, overlap length, adherent thickness, and material type on the failure load and failure mode of joints with dissimilar materials. They conclude that the maximum stresses were close to the weak substrate surface in the bond thickness direction. Mazumdar et al. [35] studied the static and fatigue behaviour of adhesive joints with sheet moulding compound composite adherends. The joint failure load was shown to increase with the overlap length or with the adhesive layer thickness that was increased up to 0.33 mm. As a design parameter, the adhesive layer thickness has an important effect on the joint strength. As well illustrated by different researchers, the lap joint strength increases as the bond layer becomes thinner [36,37]. Several arguments have been proposed in the literature to explain the influence of the bond layer thickness. Adams and Peppiatt [36] attribute the joint strength decrease with the increase of the adhesive layer thickness to the fact that thicker bond layers contain more defects, such as voids and micro-cracks. Conversely, Crocombe [38] stated that as the adhesive layer becomes thicker, the plastic spreading of the adhesive along the overlap occurs more rapidly. Gleich et al. [39] and Da Silva et al. [37] illustrated that interface stresses result to be higher for thicker bond layers. Grant et al. [40] explained the influence of the adhesive layer thickness with the bending moment. However, most of the above mentioned papers focused on structural adhesive, i.e. epoxies, polyurethane, and polyamide, to address the influence of the joint geometrical dimensions, such as the layer thickness and overlap length.

Even though HMAs are traditionally associated with non-structural applications (e.g. packaging, sealing and footwear) in many literatures, the properties, that these materials give to the joint, has resulted in an expansion of their use in structural applications, such as in automotive vehicles, as well as in other non-structural applications, such as kitchen utensils. A

safe and effective design of bonded structures using HMAs, as with structural adhesives, depends on the availability of assessed materials models and failure criteria to properly describe their deformation and failure behaviour. In the absence of suitable failure criteria, an alternative approach is undoubtedly necessary to relate joint strength to the strength properties of the adhesive under corresponding test conditions.

Polyolefin based HMAs are widely used for automotive applications, both for interior and exterior parts, and among them in the bumper subsystems [41]. Like other adhesive formulations, polyolefin-based HMAs require a delicate balancing of constituents to enhance their performance and processing properties. [42, 43]. Polyethylene and polypropylene are usually used on their own or with just a small amount of additives, such as tackifier resins and waxes; they are important constituents as they can significantly affect both cost and performance properties [44]. The molecular weight of the polyolefin generally influences the properties of the adhesive. In general, as the molecular weight increases, the decrement of adhesive strength with increment of the working temperature is improved, making the adhesive strength less sensitive to the temperature. Additionally, as the molecular weight is increased the hot tack and melt viscosity properties are also increased. Conversely, as the molecular weight is decreased the stiffness and low temperature performance properties are increased [45]. When compared with other HMAs, polyolefins based adhesives provide a large combination of desirable properties including a wide service temperature range, good thermal stability and extended open times, good barrier against moisture and water vapour, and new solutions for difficult-to-bond applications [46]. In fact polyolefins are generally not thought as adhesives because as a substrate they are so hard to bond; however, polyolefin resins make excellent hot-melt adhesives because they do have a low surface energy and wet most polymeric and metallic substrates [47]. For the above-mentioned reasons, the use of polyolefin based HMA is expected to continue growing in automotive industry (applications in bumper subsystem, door panels, overhead system, seat subsystem, package trays, instrument panels, ..). Polyolefin based HMA is used for assembling products where a long open time and excellent cohesive strength are required [48]. Long open time allows for slower manufacturing setting time and typically requires longer compression time that, in turn, leads to slower machine production paces. Polyolefin based HMA offers excellent resistance to high (135 °C) and low temperatures. It is also able to easily bond flexible plastics (polypropylene, acrylic, nylon, PVC), rubber (natural, synthetic, neoprene), metals (aluminum, steel), fibers, and porous materials (leather, textiles, ceramics, cardboard, paper, wood). Another advantage in using this adhesive is its high thermal stability and excellent resistance to ageing and peeling.

Hence, in the present work a high strength polyolefin HMA was chosen and characterized to study the influence of the adhesive layer thickness, overlap length, and accelerated environmental exposure on the shear strength of the SLJs. The thermal behaviour and chemical composition of the chosen HMA were preliminary identified. To develop the accelerated ageing, three different hygrothermal environment conditions were chosen, taking into account the specific interest for automotive applications: (a) elevated constant temperature, (b) high humidity, (c) cyclic ageing at extreme temperature and humidity.

Regarding the capability of easy disassembly, particularly relevant for the automotive applications, specific tests according to the sliding temperature technique have been adopted. A number of SLJ specimens were loaded with a specific constant applied force (by means of a weight) and subjected to gradually increasing temperature inside a temperature controlled chamber, until the joint separation took place.

2. Materials

A commercial HMA was considered, some relevant material characteristics are reported in Table 1.

Table 1. Material data of the considered polyolefin based HMA [53]

Softening point (test method: BA QA102)	153 ° C-161 ° C
Viscosity at 180 °C (S. 27 / 5 rpm) (test method: BA QA102)	22,000 – 28,000 cP
Color	White
Duration of opening time	30 seconds
Capacity of adhesive to melt	High
Temperature resistance (test method: BS 5350 Part H3)	135 ° C

3. Experimental Detail

3.1 FT-IR analysis

A 5 mg portion of adhesive sample was taken from the bulk adhesive and placed between the heated plates (100°C) of a manual press to obtain a thin layer of adhesive was easily made.

For these samples, Fourier Transform Infrared (FTIR) spectra were recorded on a Perkin Elmer Spectrum 100 instrument in the attenuated total reflectance (ATR) mode with a diamond crystal, using 32 scans per spectrum and a resolution of 4 cm⁻¹ and a spectral range of 4000-600 cm⁻¹.

3.2 Thermogravimetric analysis

Thermogravimetric analyses (TGA) were carried out on a TA Q500 model from TA Instruments by heating samples contained in alumina pans at a rate of 10 °C/min from 50 to 800 °C in N₂ atmosphere. The instrument records the weight and the weight loss rated with the temperature increment as function of the temperature.

3.3 DSC Analysis

A differential scanning calorimeter (DSC Q200, TA Inc.), provided with a cooling system RCS90, was used to collect DSC thermograms. The DSC measurements were performed with standard aluminium pans and lids under nitrogen atmosphere (50 cm³/min) and with a 10 °C/min heating rate, from -80 °C up to 200 °C..

3.4 Mechanical properties

To achieve the required mechanical properties of bulk flexible HMAs, specimens were moulded using a Teflon mould, as shown in Fig. 1. The following procedure has been adopted for the adhesive specimen preparation: the adhesive has been poured into the mould at about 190°C, to fill the mould it takes about 5 s. Then the mould has been closed and maintained closed up to solidification. After some minutes, not less than 2, the mould can be open and the specimens can be taken out. The specimens were considered ready for characterisation tests not before 24 hours. Special inert lubricant was used during specimen preparation to facilitate the specimen removal from the mould. An appropriate opening time was also considered to eliminate uneven cooling rate which might affect the mechanical behaviour of the hot-melt

adhesive. To characterize the adhesive bulk material, the ASTM D638-03 standard test procedure was adopted. Tensile tests were performed with an Instron 5544 universal testing machine with electromechanical actuation, computer control and acquisition of transducer signals through a standard signal acquisition board. The load cell has a capacity up to 2 kN. To avoid specimen damage around gripping areas, trial tests were preliminarily undertaken by varying the gripping pneumatic pressure and finally for the chosen hot-melt adhesive type, a 0,2 MPa gripping pressure was used.



Fig. 1. Bulk adhesive samples: (a) Teflon adhesive mould; (b) sample of hot-melt adhesive specimens

Fig. 2 shows the stress-strain curve of a polyolefin based HMA that has been used for automotive bumper subsystem application. As shown in the figure, polyolefin based HMA exhibited quite low strength values, less than 1 MPa, but, as usual for many polymeric materials when submitted to low loading rate tests, very high deformations: in our case engineering strain reached values up to $\sim 700\%$. Based on the results obtained from these uniaxial tests one can conclude that HMAs are not recommended when high load carrying capacity and strict dimensional tolerances are required. In some cases, when moderate dimensional tolerances are needed, the stress-strain curve of the HMAs can be altered by modifying their chemical constituents, in order to decrease the fracture deformation [49].

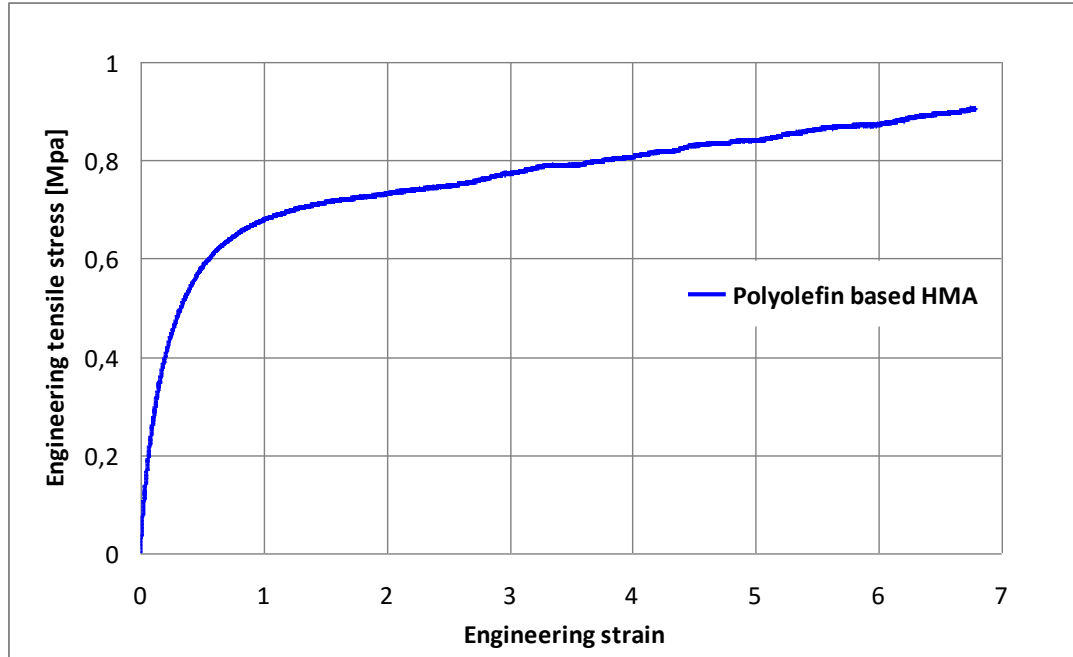


Fig. 2. Sample tensile test results for the Polyolefin based HMA

The mechanical properties of the substrate, polypropylene (PP), were also found experimentally, ISO 527 and 604 standards have been applied. Results are summarized in Table 2, [50].

Table 2. Mechanical properties of the PP material, test has been conducted at a crosshead velocity of 5 mm/s [50]

Initial yield (MPa)	Max. tensile stress (MPa)	Max. compressive stress (MPa)	E (GPa)	ν_{elastic}
6	16.8	25.2	2.44	0.4

3.5 Experimental set-up and SLJ specimen fabrication

The chosen polyolefin based HMA, which was supplied in granular solid form, was melted using a portable adhesive oven. The inside temperature of the furnace was controlled to maintain the desired temperature, in order to avoid degradation of the adhesive performance at elevated temperature and/or inadequate wetting characteristics at lower temperature. To apply HMA at a targeted substrate, an electric hot glue gun was assembled with the adhesive oven. An electric pump was used to push the HMA through a pistol dispenser by a mechanical trigger mechanism. The pistol dispenser utilized a continuous heating element to maintain the HMA temperature, in the range of 15 °C higher than the internal oven temperature.

A special layer controller device, as shown in Fig. 3a, was used to prepare SLJs having accurate layer thickness and aligned substrates. As shown in Fig. 3a, the two substrates, upper and lower substrates, were placed in their positions and, in order to control the adhesive layer thickness, a standard sheet metal spacer with thickness equal to the intended adhesive layer thickness was inserted between them. Then, turning a screw, the vertical displacement limit of the arm was adjusted.

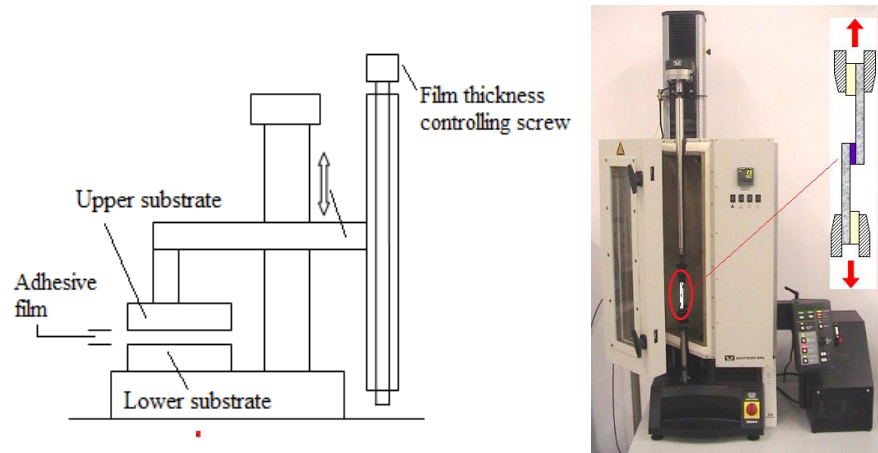


Fig. 3. Experimental set-up: a) the assembly device for SLJ preparation, b) the uniaxial tensile testing machine, Instron 5544, with temperature chamber

To avoid adhesive failure because of improper surface preparation, the substrates were previously cleaned with isopropanol. Then the HMA was applied on the lower substrate and within 10 seconds the upper substrate was moved downward until it touched the HMA. For about 2 minutes of the cooling period both the substrates were kept together by the fixture under a compressive force of 35 N to obtain the green strength and then they were removed from the assembly device. Finally, tabs were bonded at the ends of the specimens to ensure a correct alignment during the uniaxial tensile test, as shown in Fig. 3b.

The SLJ tests were performed with the already mentioned testing machine Instron 5544 at room temperature and in displacement control mode (according to ASTM test procedure for SLJ). In this work, five tests were carried out for each test configurations, and the average shear strength of the joint was calculated by dividing the maximum load of each test with the bonded area.

3.6 Accelerated ageing procedure

In this study three types of laboratory-controlled hygrothermal ageing procedures were applied to the SLJ specimens, they intend to represent the worst environmental conditions in which the actual bumper subsystem might be exposed during vehicle working life: two constant hygrothermal ageing (A1 and A2) and one cyclic hygrothermal ageing A3. Ageing 1, A1, consists in the exposure of the SLJ at a temperature of 90 °C for 500 hours without humidity control; ageing 2, A2, consists in the exposure of the specimens for 500 hours inside the environmentally controlled chamber at a temperature of $40 \pm 2^\circ\text{C}$ and relative humidity of 95-100%. In the case of ageing 3, A3, a cyclic mode of hygrothermal conditioning was applied. This means that the specimens were exposed at a temperature of $80 \pm 2^\circ\text{C}$ for 24 hours without humidity control, then at a temperature of $40 \pm 2^\circ\text{C}$ and a relative humidity of 95-100% for 24 hours and finally at a temperature of $-40 \pm 2^\circ\text{C}$ once again without humidity control. This entire sequence was repeated three times in order to complete the ageing process.

3.7 Sliding temperature test

There are basically two types of shear tests that are used in the adhesive industry to characterize HMA shear strength. In the first type, the temperature is held constant while the load is increased until bond failure; the failure is characterized by the failure load. In the second

type, which is named the sliding temperature test, the load is held constant while the temperature is increased until bond failure; in this case the failure is characterized by the failure temperature.

As different literature has described, the sliding temperature test has a fundamental relevance in investigating the performance of HMAs for a wide range of applications, such as in packaging, automotive and electronic product industries [51]. In particular, if the HMA based adhesive joint is susceptible for high temperature applications, it is worth investigating its temperature resistance and failure mode at a predefined preload. In this research, a parametric study through sliding temperature tests was also performed to understand the effect of adhesive layer thickness and overlap length on the failure temperature.

Prior to the sliding test, the SLJ specimens were stored at room temperature for 7 days. Before the sliding temperature tests, relevant experimental factors were identified and their values defined to control the climatic chamber during the test execution. At one extremity of each SLJ a 0.5kg mass was hung for constant loading, while the other extremity was fixed to the chamber support frame. The climate chamber was conditioned at relative humidity of 0% and heated at a rate of 50 °C/hr to reach a temperature of 190 °C which is greater than the melting temperature of the polyolefin based HMA. Adhesive joint failure is expected to take place before reaching this final temperature.

3.8 Experimental modelling of Single lap Joint (SLJ)

Based on the design of experiment procedure, the main factors and their levels were identified to develop a mathematical relationship for determining the SLJ strength. A full factorial plan was prepared for the experimental tests of the SLJs. Table 3 shows the factors and levels used in the test full matrix. In this work, the main geometric parameters were the adhesive layer thickness, overlap length and substrate thickness, designated by T, L and S, respectively. The substrate thickness was then omitted following the results of a preliminary case study, which showed limited substrate thickness variation in the chosen bumper subsystem application.

Based on the specified parameters, N=9 tests were performed according Table 4, for each of them there were r=5 replications, therefore a total amount of 45 tests have been performed. For all the specimens substrate length and width are equal to 100 mm and 20 mm, respectively.

Table 3 Full matrix of experiments for failure load predictions

	Main factors		Interactions
	Adhesive thickness T_n	Bond length L_n	$T \times L$
1	T1 = 0.5 mm	L1 = 12.5 mm	T1xL1
2	T1	L2 = 25 mm	T1xL2
3	T1	L3 = 50 mm	T1xL3
4	T2 = 1.0 mm	L1	T2xL1
5	T2	L2	T2xL2
6	T2	L3	T2xL3
7	T3 = 2.0 mm	L1	T3xL1
8	T3	L2	T3xL2
9	T3	L3	T3xL3

4. Test results and discussion

4.1 Material composition

FT-IR spectrum of the polyolefin based HMA is shown in Fig. 4. A stretching peak of CH_2 and CH_3 groups appears with great evidence at 2916 cm^{-1} surrounded by other peaks between 2800 and 3000 cm^{-1} . At 1459 and 1376 cm^{-1} , two other peaks are observed that can be interpreted as deformation of C-H links in CH_2 and CH_3 groups. Other absorption peaks are visible with lower wavenumber and lower intensities that are related to isotactic polypropylene.

The peaks at 1163 and 971 cm^{-1} are peculiar to the amorphous polypropylene (PP) [51] while the others at 997 and 838 cm^{-1} are related to the crystalline polypropylene [51-53]. In addition to the peaks related to isotactic PP, there are two other absorption peaks at 720 cm^{-1} and 730 cm^{-1} , both related to polyethylene (PE) [51]. From these results it can be concluded that polyolefin based HMA is a PP/PE copolymer. Specifically, peak at 720 cm^{-1} is related to both amorphous and crystalline PE phases, while the other at 730 cm^{-1} is associated only to PE crystalline phase [51]. The presence of a crystalline phase of PE means that the copolymer can have long chains of PE, which are able to be crystallized.

Absorption peaks in the region around 1700 cm^{-1} , in particular at 1778 cm^{-1} , could be related to the presence of a partially hydrolyzed anhydride group (peak at 1710 cm^{-1} refers to carbonyl acid $\text{C}=\text{O}$). The existence of these groups could be related to a treatment carried out in the copolymer in order to increase the polarity and consequently the adhesive properties.

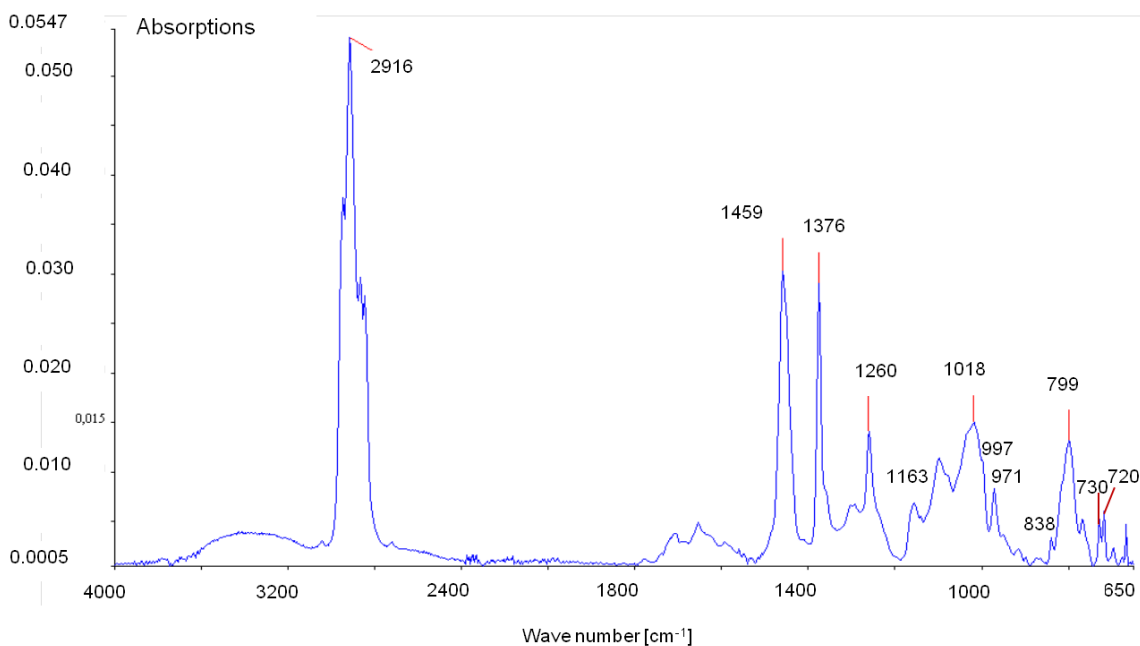


Fig. 4 – FT-IR spectrum of the Polyolefin based HMA .

4.2 TGA results

In Fig. 5 the result of TGA of polyolefin based HMA is reported. As can easily be seen in the figure, the polyolefin based HMA adhesive is subjected to a thermal degradation that takes place through only one step. Degradation in inert atmosphere starts at about 200 °C and ends almost at 480 °C with a maximum degradation rate at 450 °C. Higher temperatures do not cause any further degradation process. The carbon residue is 0.68% of the original sample weight.

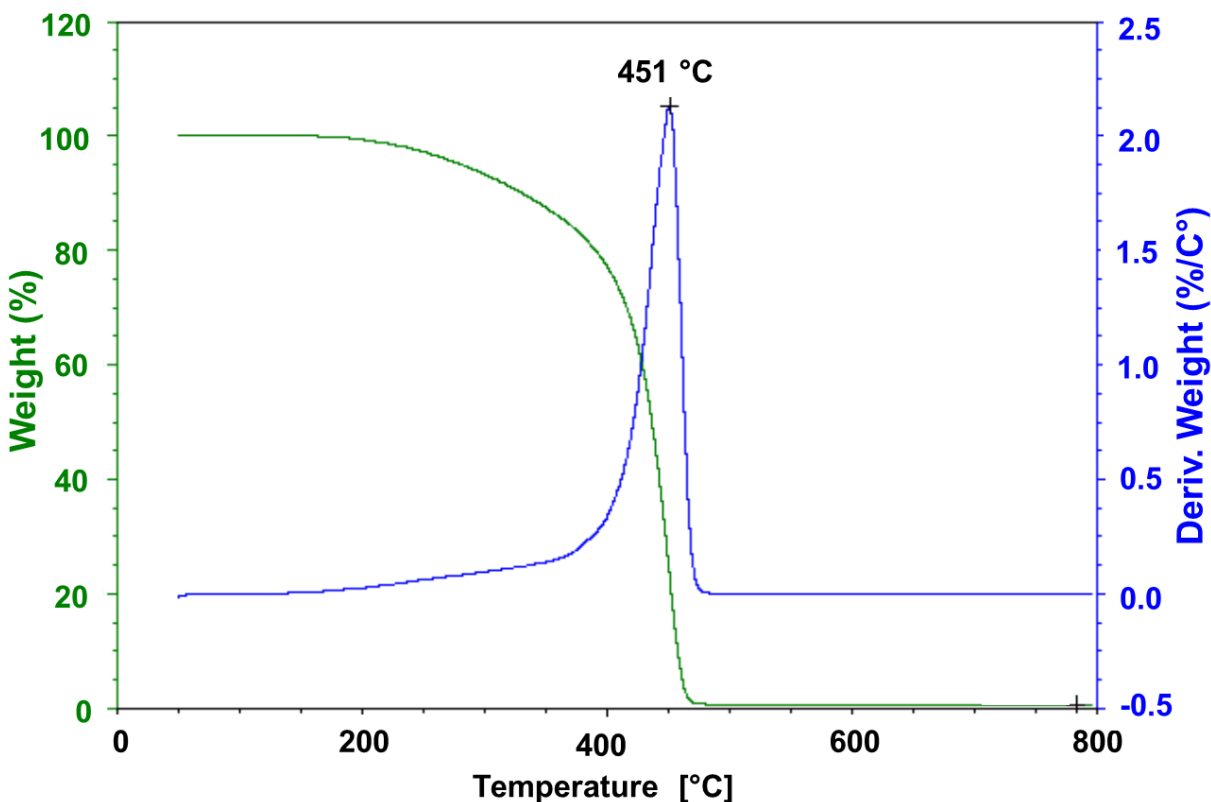


Figure 5 – TGA thermogram of the Polyolefin based HMA .

4.3 DSC results

As can clearly be seen in Fig. 6, polyolefin based HMA exhibited a sharp phase change peak with a combination of shallow and broad peaks. In the heating curve the endothermic peaks at about 120 °C and 155 °C could be associated to the melting point of polyethylene and polypropylene respectively. In fact, as for FTIR results, a crystalline phase of PE and a crystalline phase of PP are present in HMAs.

As can be seen in Fig.6, only a glass temperature is exhibited at (-16 °C) and this is correlated to a copolymer PE/PP. This means that the polyolefin based HMA is more susceptible to becoming brittle and easily loses its toughness at this temperature.

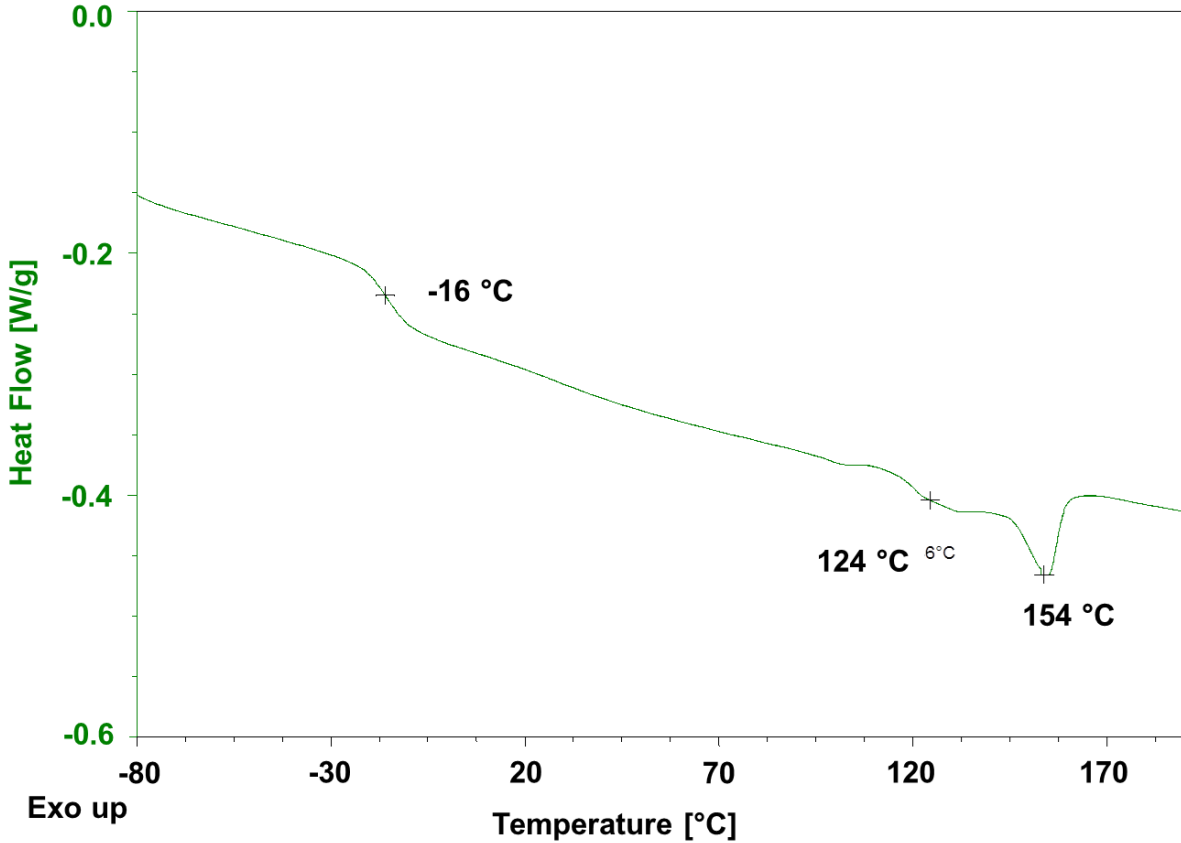
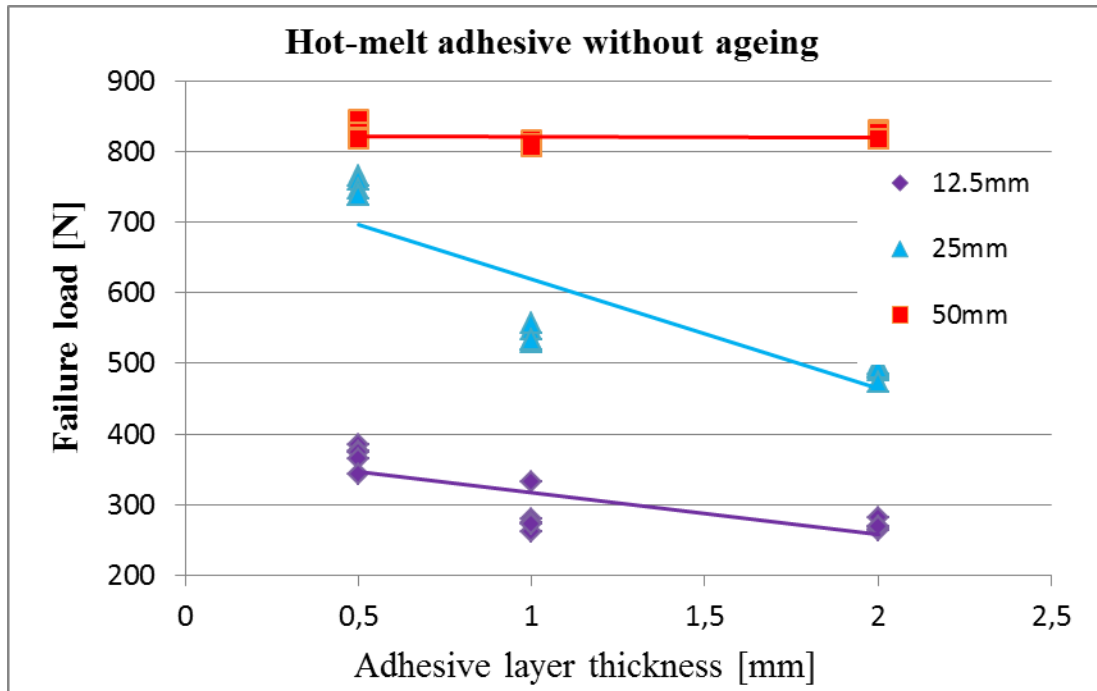


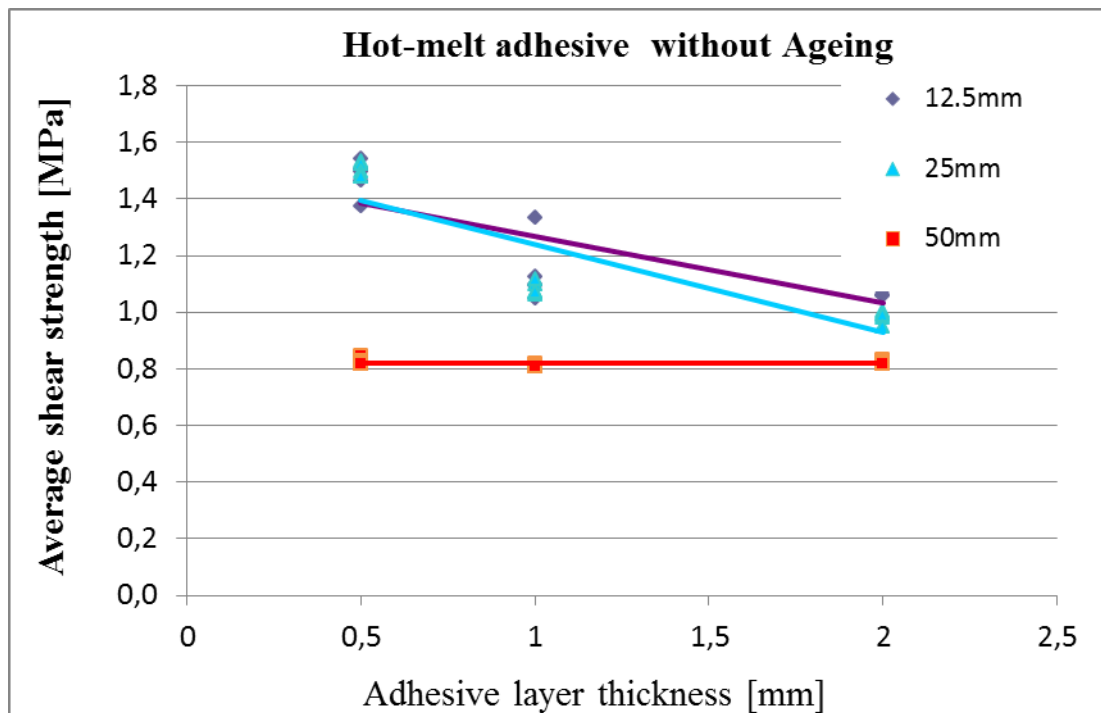
Fig 6. DSC test results of the Polyolefin based HMA

4.4. SLJ shear test under room environmental conditions

Fig. 7a shows results of the failure loads of SLJ at different overlap lengths and adhesive layer thicknesses. As is shown in the figure larger adhesive layer thickness generally leads to lower failure loads, while longer overlap leads to higher failure loads. It should be noticed that the failure zone for the highest values of the overlap lengths are in the substrate and not in the joints. Fig.7b shows results of the average shear strengths of the SLJ calculated by rating the failure load to the adhesion area. Shear strengths have similar descending trends with respect to adhesive layer thickness for the two overlap lengths of 12.5 and 25 mm, while for the overlap length of 50 mm we can see a completely different trend and values for the above mentioned reason. The results of the performed ANOVA analysis confirm that the two considered factors and their interaction have influence, with more than 99% of confidence, on both the considered performance. This influence is confirmed also if, for the average shear strength results, we perform the analysis just for the two overlap lengths of 12.5 and 25 mm.



(a)



(b)

Fig. 7. Test results of the SLJ tests of the Polyolefin based HMA; a – tensile failure load and b – average shear strength as functions of the adhesive layer thickness and joint overlap length;

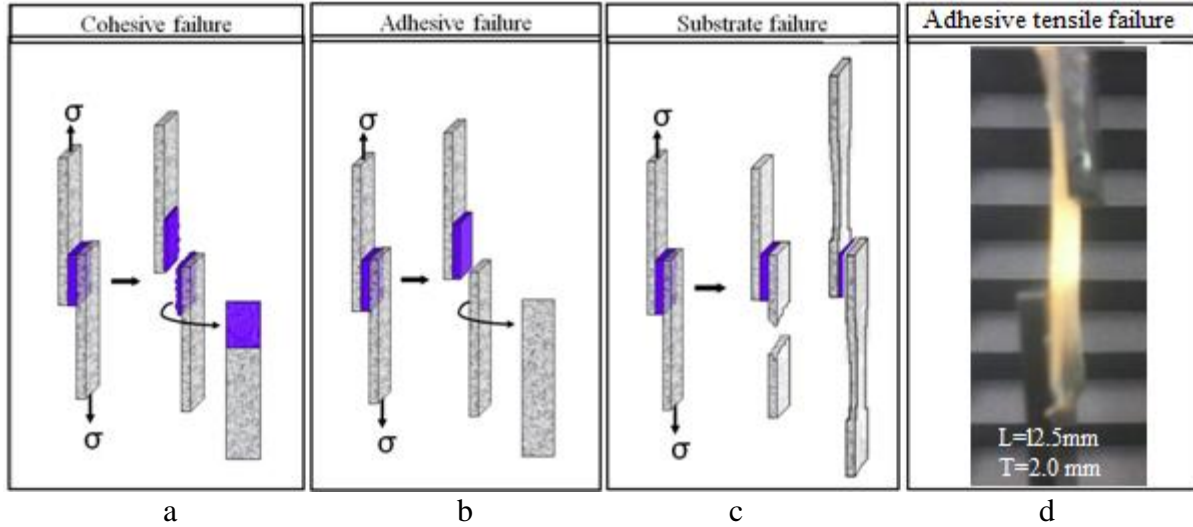


Fig. 8. Failure mode of SLJ specimen

Visual inspection shows that the most dominant failure type was cohesive failure (see figure 8a) for overlap length up to 25mm. Indeed, for the 0.5 and 1 mm adhesive layer thickness, 12.5 mm overlap SLJ exhibited cohesive failure and equivalent shear strength as with 25 mm overlap, however for the 2 mm adhesive layer thickness, the most dominant failure type observed, was adhesive failure at tip followed by adhesive layer tensile failure, as shown in Fig. 8b. Finally 50 mm overlap length specimens show insignificant failure load variation with adhesive layer thickness and generally exhibit substrate failure, as shown in Fig. 8c.

The subsequent investigation of the load-displacement diagrams of the tested specimens leads to an understanding of the contribution of substrate and SLJ response to the type of failure mode for given geometry changes. The load-displacement curves expected from the SLJ shear tests are different in the case of 12.5 and 25 mm overlap length specimens with respect to 50 mm ones. This expectation is confirmed by the curves that are shown in Fig 9. The curves that are visible in figures 9 a and b have similar trends: after the elastic linear phase, a non linear phase is visible, the maximum load is reached and then the curves have a quite sharp decrease. On the contrary the curves that are visible in figure 9c have completely different trends with respect to those in figures 9 a and b. After the elastic phase a maximum is reached quite rapidly and then the curves have a slow decrease while the displacement reaches quite large values. For this latter type of specimens the dominant plastic deformation of the PP substrate is responsible for this wide range of displacement after yielding. It is of interest to observe the curves reported in Fig. 10 where one of the characteristic curves of the SLJ and the tensile curve of the PP are superimposed. The SLJ curve is just a little bit lower than the PP curve, confirming that the structural behaviour of this type of joint is dominated by the substrate (as depicted in Fig 8 c). The shear stress-displacement curve for 50 mm overlap, shown in Fig. 9d, therefore, does not represent the actual adhesive curve, but the reported stress-displacement values represent the substrate deformation.

Finally in order to explain the differences that are visible between the two curves reported in Fig. 10. It is important to remember that the SLJ test introduces a bending moment in the substrates due to the eccentricity of the applied load and uneven stress distribution near the joint

extremities, thus the substrate experiences higher stress values than those induced by simple tensile tests.

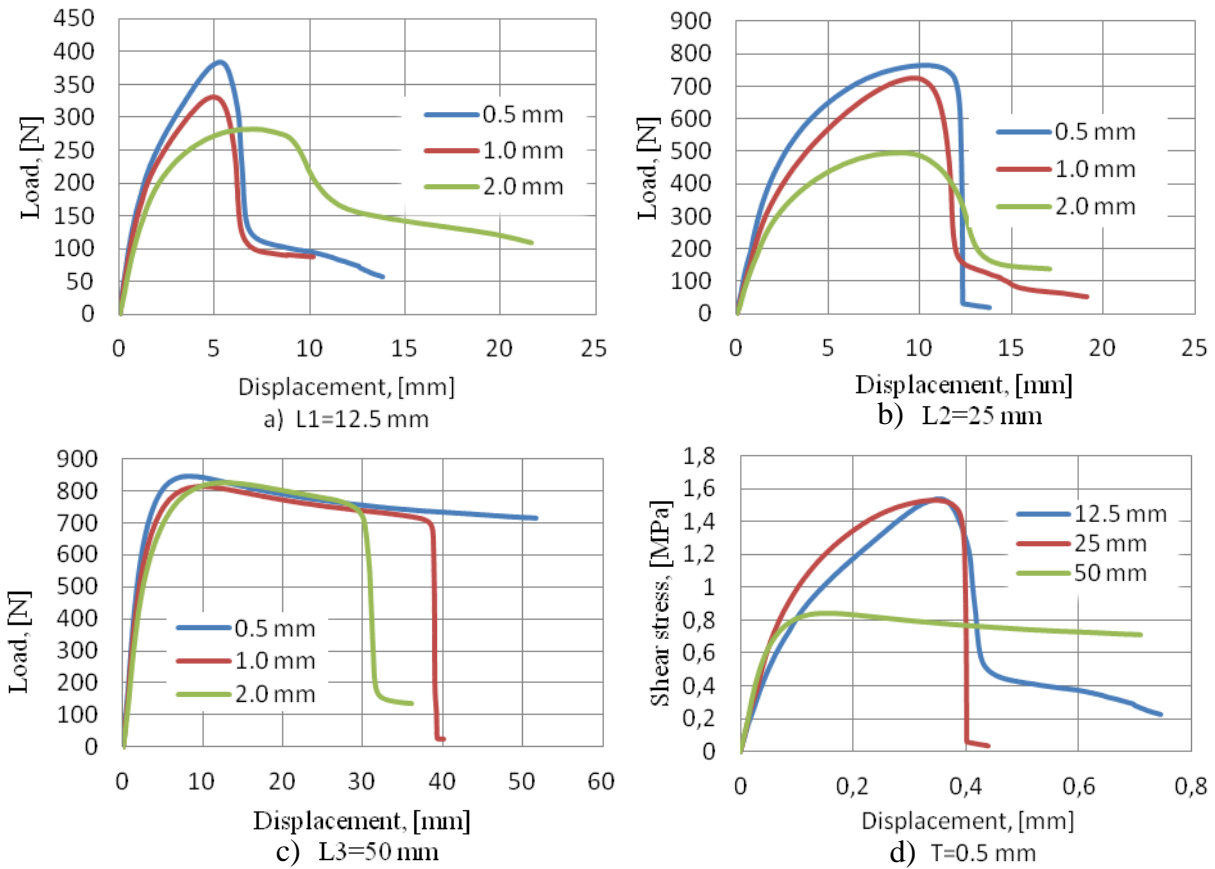


Fig. 9. a,b,c Load versus displacement curves of SLJ for different bond lengths and adhesive layer thickness, d average shear stress versus displacement curve for one adhesive layer thickness and different bond lengths.

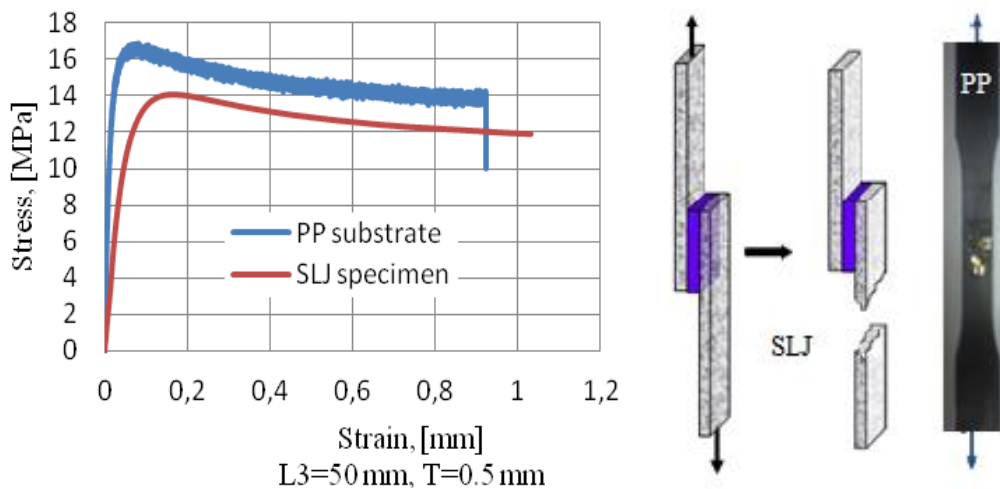


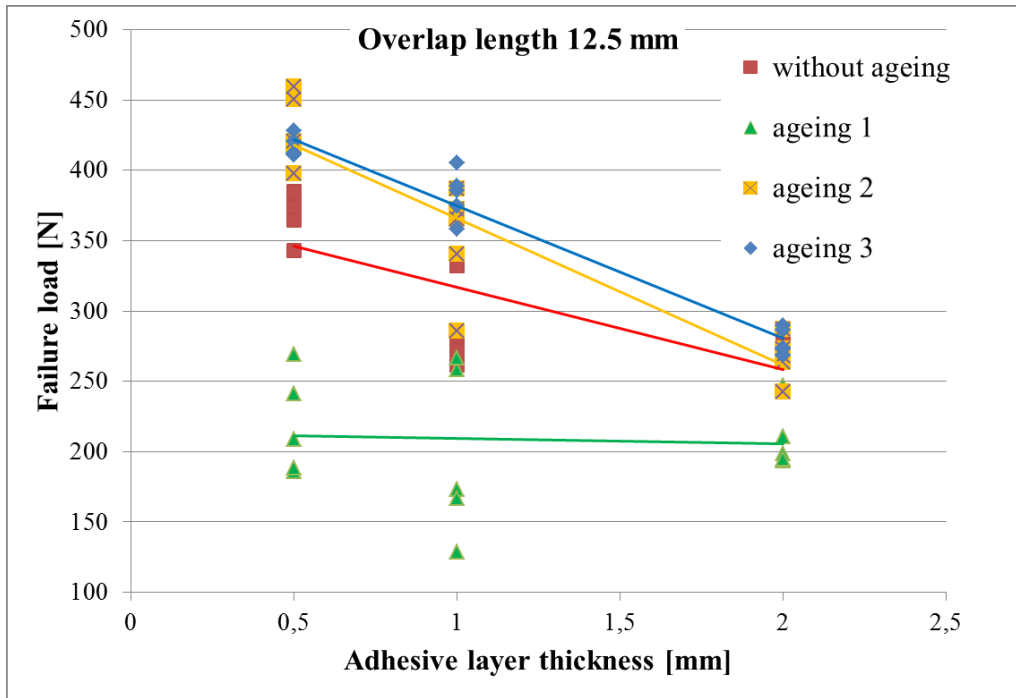
Fig. 10. Typical stress-strain curve for SLJ and PP substrate test.

Fig. 11 shows the results of the failure load and shear strength of environmentally conditioned (with ageing) and unconditioned (without ageing, WOA) SLJs. As can be clearly seen in the figure, for both the cases the failure load and shear strength decrease substantially while the adhesive thickness increases from 0.5 mm to 2 mm. Particularly, as shown in Fig. 11a, which is dedicated to the specimens with 12.5 mm overlap length, ageing A1 induces a relevant detrimental effect on the failure loads while small changes, that become negligible if the average strength values are considered, are visible with variation of the adhesive layer thickness. On the other hand A2 and A3 ageing generally improve the failure load values with respect to the results obtained with the unconditioned specimens, even though less considerable effects are visible for 2 mm adhesive thickness.

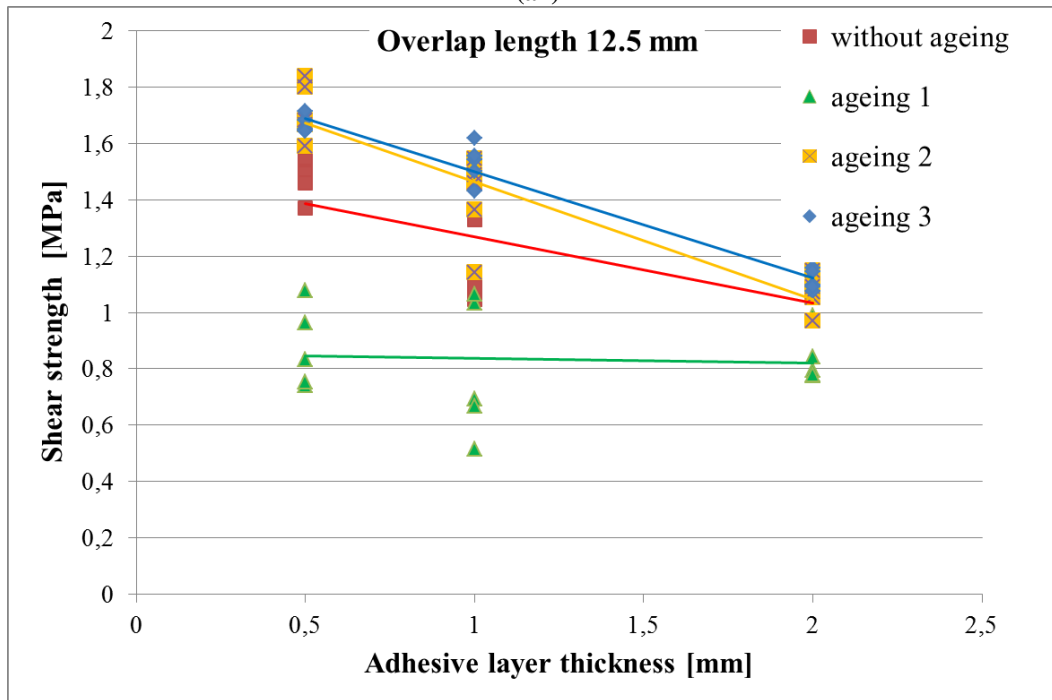
For 25 mm overlap length, as is shown in Fig 11b, an improvement of the failure load values for the conditioned specimens is visible in the case of adhesive layer thickness of 1 mm, while for the other two cases of adhesive layer thickness the results are substantially grouped. However the linear interpolation lines put in evidence a diffuse increment of the failure load and of the shear strengths after ageing treatments 2 and 3, while for ageing treatment 1 this is more evident for the smaller value of the adhesive thickness and is negligible for the higher one.

For 50 mm overlap SLJ, as is shown in Fig. 11c, an improvement to the failure load and of the shear strength values for the conditioned specimens is visible in all the cases except for adhesive layer thickness 2 mm and A1 ageing where a decrement is visible. However, for the cases of 0.5 mm and 1 mm adhesive layer thickness, these changes are not due to the ageing effect in the adhesive because of substrate dominant failure during the test. Only for the case of 2 mm adhesive layer thickness, probably due to the combined effect of high temperatures and higher layer thickness, adhesive layer failures were found in all tests.

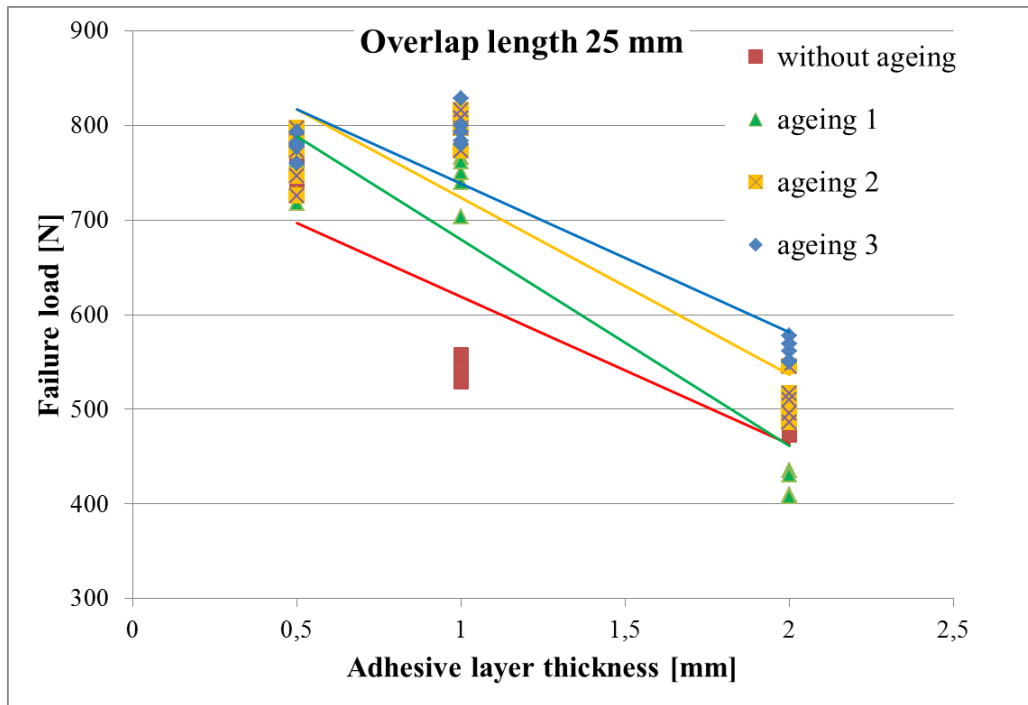
For the whole sets of data ANOVA analysis have been performed to evaluate the effectiveness of the two types of factors, the ageing treatment and the adhesive layer thickness, on the failure loads and on the shear strengths. Obtained results confirm that the two considered factors and their interaction have influence, with more than 99% of confidence, on both the considered performance.



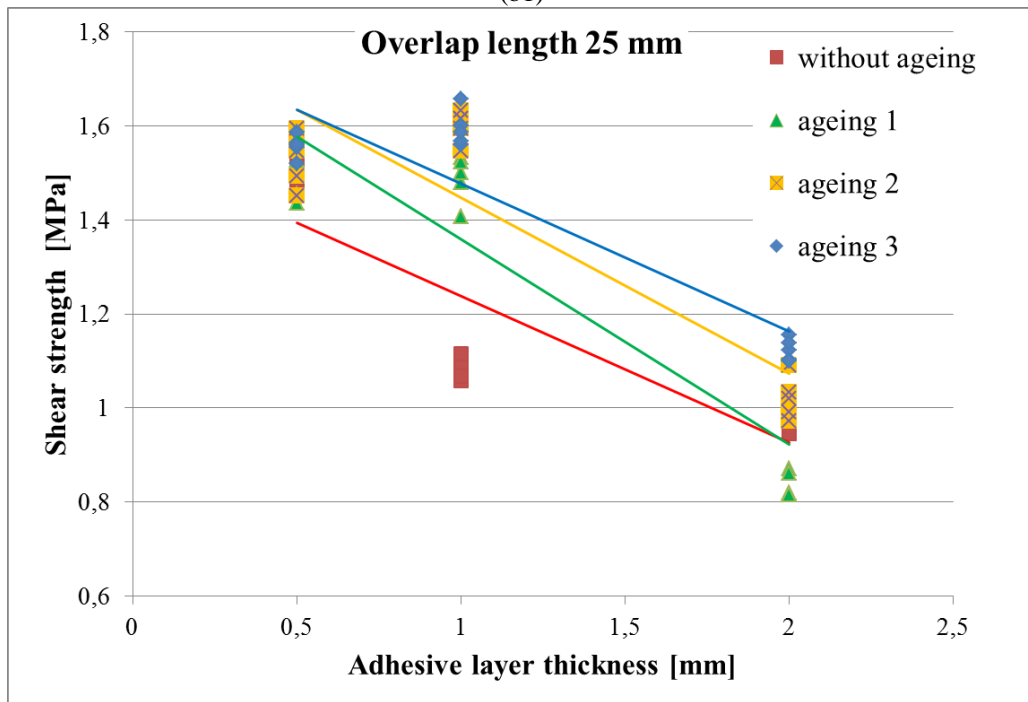
(a1)



(a2)



(b1)



(b2)

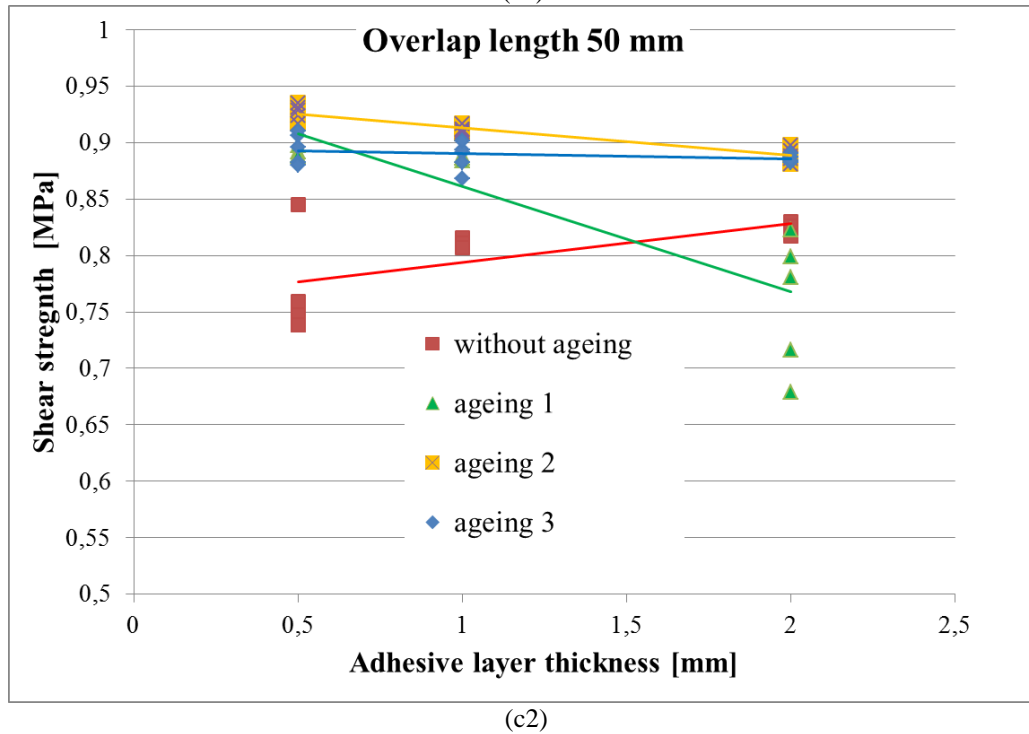
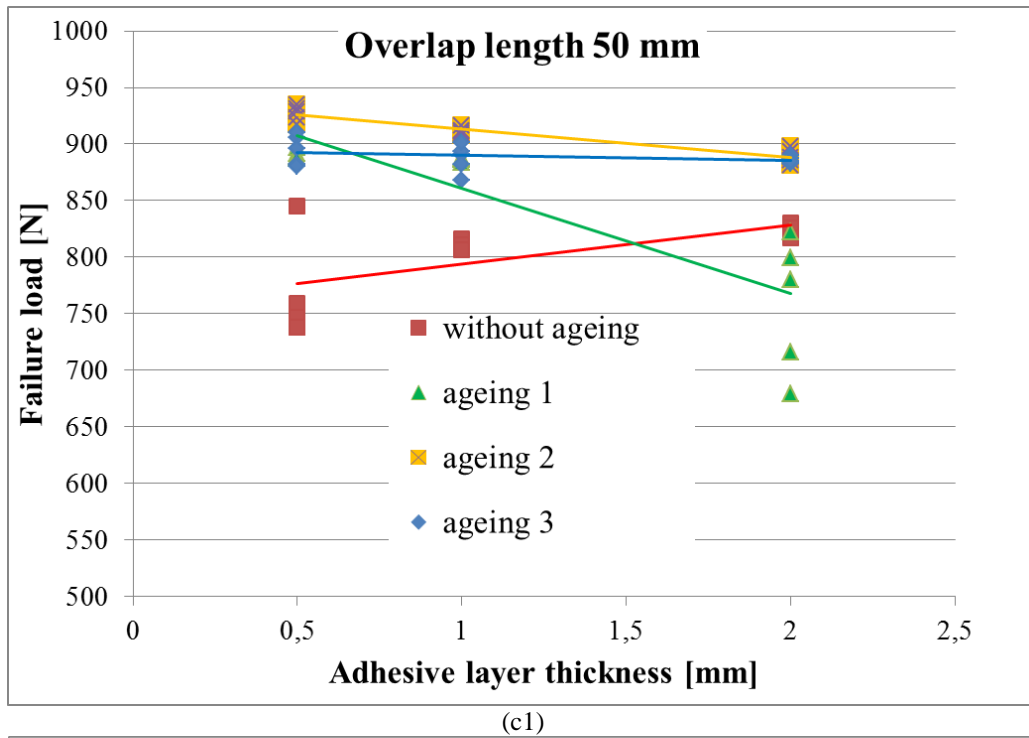
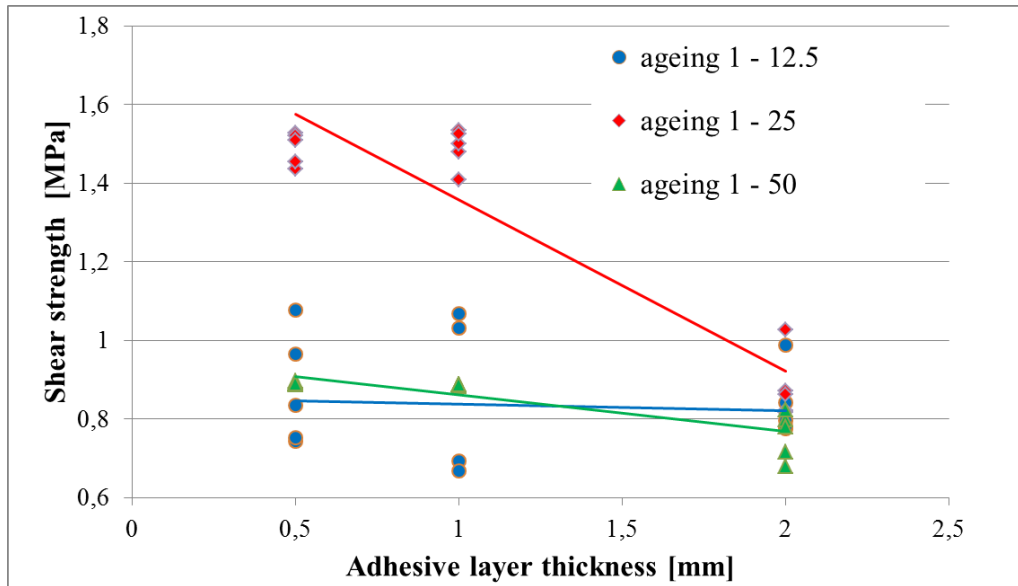
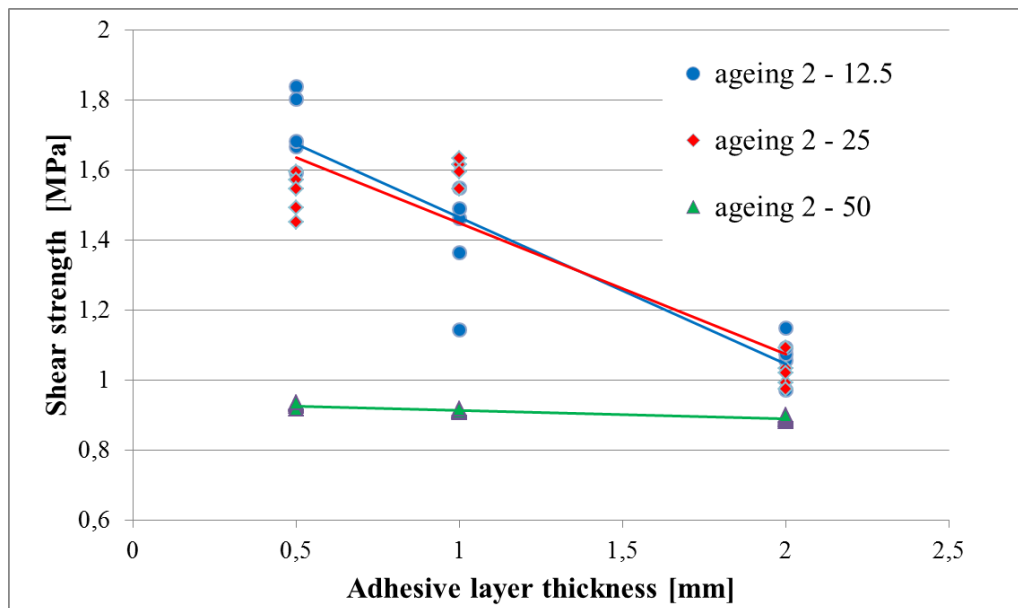


Fig. 11. Comparison of the failure loads (1) and shear strengths (2) for the different ageing conditions and geometry parameters: (a) 12.5 mm overlap length; (b) 25 mm overlap length; (c) 50 mm overlap length.



(a)



(b)

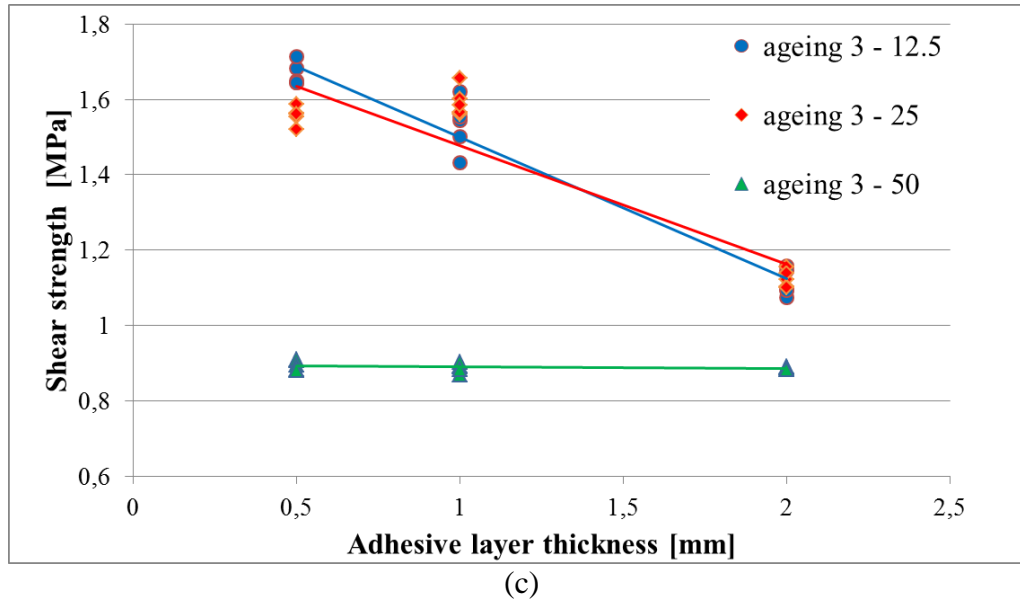


Fig. 12. Comparison of the shear strengths for the different ageing conditions and geometry parameters: (a) after ageing 1; (b) after ageing 2; (c) after ageing 3.

A companion analysis has been performed with the diagrams of figure 12 that are aimed to put in evidence the effect of the three different ageing procedures, on the basis of the tests performed on the specimen with the same set of geometrical dimensions (overlap length and adhesive layer thickness). These results can also be compared with those already shown in Fig.7b.

Figure 12a puts in evidence the increment in the shear strength that is consequent to the ageing 1 treatment for the case of 25 mm of overlap length, while for the case of 12.5 mm overlap length a relevant decrement in shear strength is well visible.

Figures 12b and c put in evidence the increment in the shear strength that is consequent to the ageing 2 and 3 treatments for the cases of 12.5 and 25 mm of overlap lengths. While for the case of 50 mm overlap results are slightly affected by the ageing treatments since the failure type is generally concentrated in the substrate.

Also in this case an ANOVA analysis has been performed to evaluate the effectiveness of the two types of factors, the overlap length and the adhesive layer thickness while the ageing treatment is considered constant for each set of data, on the shear strengths. Obtained results confirm that the two considered factors and their interaction have influence, with more than 99% of confidence, on the considered performance.

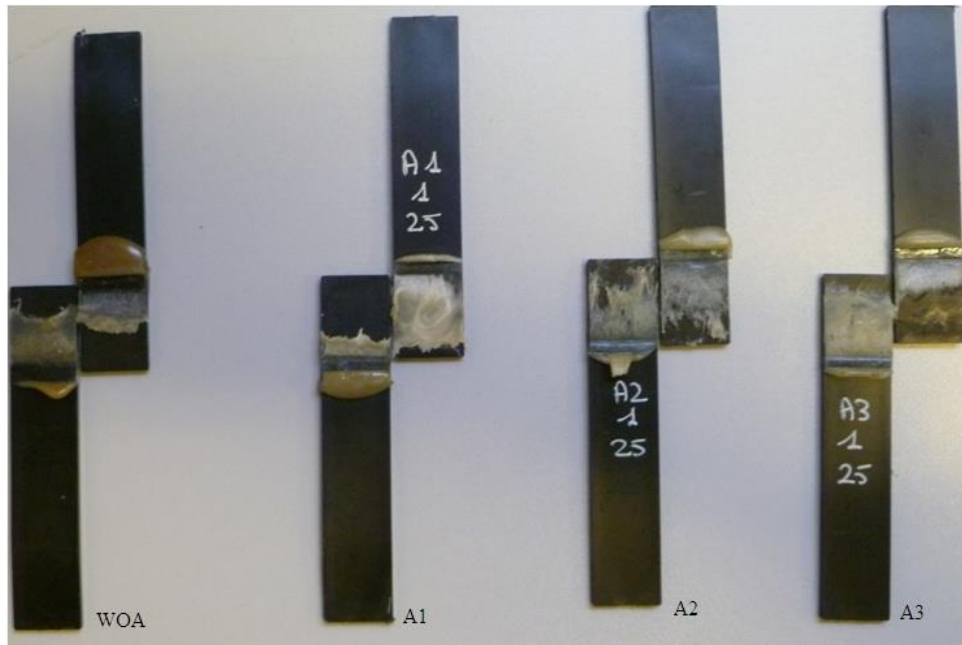


Fig 13. Mode of failures for the different environmental conditions.

To comprehend the results of sustained or/and higher failure load in the A2 and A3 ageing types it is worth looking for a common factor that might exist in A2 and A3 but not exists in A1 and WOA configurations. In this regard, the common factor is the high percentage of controlled relative humidity, in the range of 95-100%. It is therefore likely that the presence of moisture could improve the strength for HMA based SLJs, unlike what is generally obtained for thermosetting adhesive based SLJs, such as epoxy [2]. Besides, an important point that should be addressed here is the influence of the temperature on the strength of these HMA/polypropylene SLJs. In the absence of moisture, the detrimental effect of high temperatures on the strength of SLJ is clearly shown in Fig. 11a and b. This phenomenon has been hindered by the presence of moisture content in A2 and A3. Conversely, the results of lower failure load found with A1 can be explained as follows: due to the fact that temperature can increase the kinetic energy of molecules, developing different values of thermal strain in both the adhesive and substrate, it is reasonable to expect that interfacial adhesive failure and joint degradation could be more pronounced with rising temperature. In A3, unlike other common types of thermosetting and thermoplastic adhesive based SLJ, HMA based adhesive joints showed improvements of the joint strength after performing cyclic ageing. This phenomenon can be explained by the combined effect of the wide range of temperature and humidity variation. It is likely that with A3 ageing treatment the detrimental temperature effect inferred by the 1st cycle was hindered by applying the 2nd and 3rd cycles. These phases of the ageing process could help to recover the joint strength because, as reported in Table 2, they are characterized by lower temperature values and, for the 2nd cycle, by high relative humidity.

The analysis of the failure modes of the aged and un-aged SLJs revealed the existence of different failure modes, such as cohesive and adhesive failures. As can be clearly seen in Fig. 13, where pictures of the failure modes of four specimens, i.e. three types of aged specimens and one type of WOA specimen, are shown, different modes of failure resulted. The WOA specimen exhibits adhesive dominant failure but not as much as A1. Regarding A2 and A3, cohesive dominant and complete cohesive failures, respectively, are exhibited. These phenomena are

responsible for significantly enhancing the failure load: the larger the cohesively failed area in the joint is the higher the failure load. For instance, in Fig. 13, the entire overlap surface area of A3 is covered by the cohesive failure mode: this indicates that the expected failure load in A3 is greater than that of the other test configurations.

Figure 14 collects three diagrams of the load-displacement results for the cases of overlap length L_2 25mm. Each diagram is related to one of the adhesive layer thickness values and includes four curves related to the four different environmental conditioning processes considered.

In Fig. 14 it is possible to observe that, due to the enhancement of adhesive bond strength after A2 and A3 ageing treatments, considerable amounts of plastic elongation of the PP substrate are found ahead of bond failure. Lower adhesive layer thickness (figures 13a and b) gives higher failure load and elongation.

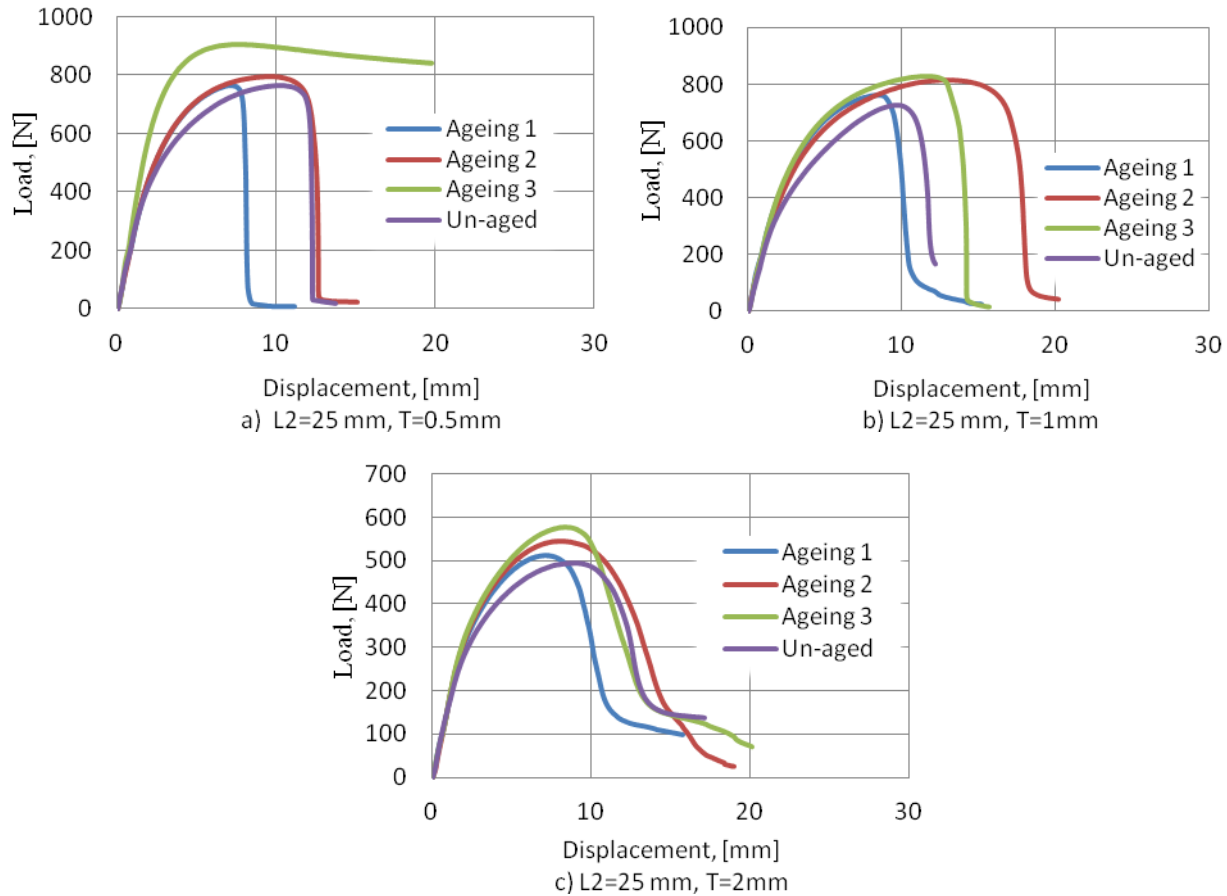


Fig. 14. Load versus displacement diagrams of aged and un-aged specimens, $L_2 = 25$ mm.

4.5. The Sliding temperature in the Single lap shear test

Fig. 15 shows the correlation between the failure temperature and the overlap length of SLJ at different adhesive layer thicknesses, for the considered HMA/polypropylene system. It can be clearly seen that the highest values of the sliding temperature are for the larger overlap length. Moreover, for the adhesive layer thicknesses 0.5 and 1 mm, the results are substantially superimposed and the failure temperature goes up linearly with the increment of the overlap

length. Therefore, it is possible to write an equation to predict the value of failure temperature as a function of the overlap length. On the other hand, at 2 mm adhesive layer thickness, even though an increment of the failure temperature as a function of the overlap length is found, the results show that the failure temperature is lower than the corresponding values at 0.5 mm and 1 mm layer thicknesses. It must be evidenced that HMAs are polymeric materials with a viscoelastic behaviour. A part of the energy is dissipated by the movement of chain (viscous flow) when a stress is applied to the polymer. These viscous losses are time dependent and temperature dependent [52]. This implies that increasing an adhesive thickness (volume), the failure temperature and joint strength is reduced, since the adhesive layer is exposed to an elevated temperature for a given period of time under constant load.

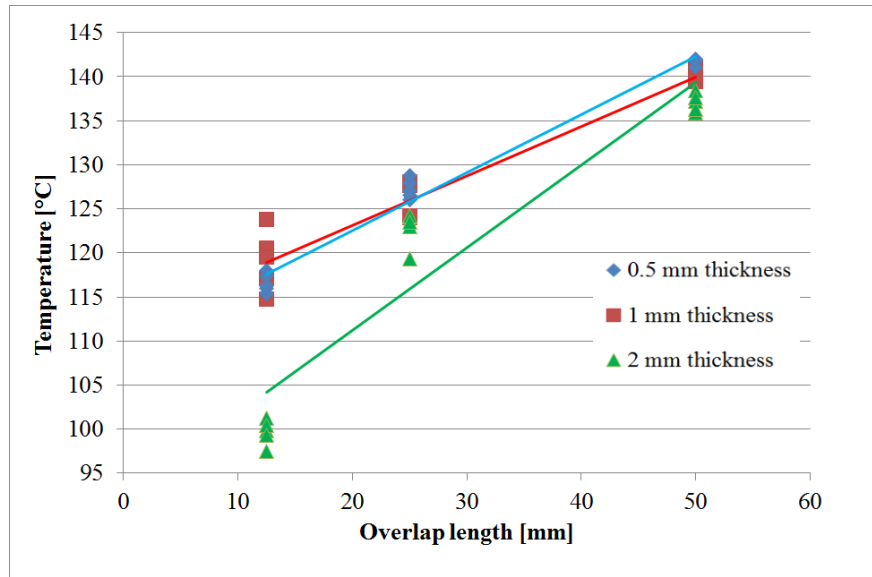


Fig. 15. Relationship between the Sliding temperature and overlap length

The ANOVA analysis has been performed to evaluate the effectiveness of the two types of factors, the overlap length and the adhesive layer thickness, on the sliding temperature. Obtained results confirm that the two considered factors and their interaction have influence, with more than 99% of confidence, on the considered performance. However if in the ANOVA analysis we neglect the data related to the 2 mm thickness, we obtain that the adhesive layer thickness has no more influence on the sliding temperature, while both the overlap length and the interaction between the overlap length and the adhesive layer thickness still have influence on the sliding temperature.

Fig. 16 shows pictures of the failure surfaces of polyolefin based HMA for two different overlap lengths and adhesive layer thicknesses. In most cases, an increasing extension of the area required for cohesive failure to occur with both increasing overlap length and adhesive layer thickness is visible.

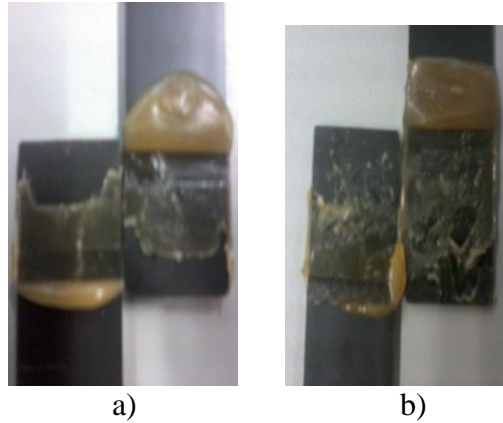


Fig. 16 Mode of failure surface: a) 0.5×12.5 mm; b) 1 mm×25 mm.

4. Conclusions

HMAAs are a class of flexible thermoplastic adhesives whose use can be considered for a wider range of uses both in automotive as well as in other mechanical engineering applications, Being based on thermoplastic materials, they offer better recyclability and easier part detaching technology performance with respect to thermosetting ones.

In this study, an experimental approach has been developed to investigate the influence of joint geometry parameters and accelerated ageing procedures on the strength and durability of SLJs used for joining two parts, made of a polypropylene, in one specimen. Further analysis related to the sliding temperature has been done. The following conclusions can be drawn:

1. FT-IR, DSC, and TGA tests revealed that the polyolefin based HMA considered is a HMA mainly composed of polyethylene and polypropylene copolymers.
2. The failure load increases with overlap length; however, a critical value of the overlap exists, which for the case considered is larger than 25 mm, above which the failure load no longer increases because of a change in the failure location: instead of the adhesive joint the substrates fail. Also the shear strength has been calculated and analysed. It comes out that there is a small, however significant, difference between the values obtained for 12.5 mm and 25 mm of overlap lengths, while the case of 50 mm of overlap length gives nearly constant values of the shear strength, because of the different type of failure. The performed ANOVA analysis has confirmed the effects of the studied parameters and of their interaction with 99% of confidence.
3. The failure load decreases as the adhesive layer thickness increases: at 2 mm adhesive layer thickness, the most dominant failure type observed initiated as adhesive failure at tip followed by adhesive layer failure with high plastic elongation, unlike thermosetting structural adhesive which generally shows a brittle behaviour. Also the shear strength has been calculated and analysed. It comes out that there is an evident decrement in shear strength while passing from 0.5 mm to 2 mm of adhesive layer thickness for the cases of 12.5 mm and 25 mm of overlap lengths, while for the case of 50 mm of overlap length, nearly constant values of the shear strength are obtained, because of the different type of failure. The performed ANOVA analysis has confirmed the effects of the studied parameters and of their interaction with 99% of confidence, even when the data for the 50 mm of overlap are neglected.

4. The hygrothermal experimental tests showed that, depending on the type of ageing condition, the SLJ shear tests give different results; unlike other conventional thermosetting adhesives, HMA, after A2 and A3 ageing treatments, showed steady or/and increased failure load regardless of the presence of humidity and of temperature variation within a range of -40 and +80 °C for a given period of time. On the other hand, after A1 ageing treatment, in the absence of humidity and at elevated temperature, +90 °C, the failure load decreased. Also for these cases the shear strength values have been calculated and analysed. A part for the cases related to the 12.5 mm of overlap length where the ageing 1 treatment gives a relevant decrement in failure load and shear strength values, for the 25 mm of overlap we obtained an increment of the failure loads and of the shear strengths for all the three ageing treatments. This trend is also visible, although with small differences, for the case of 50 mm of overlap length. The performed ANOVA analysis has confirmed the outlined effects of the studied parameters and of their interaction with 99% of confidence.
5. Cyclic ageing revealed that the strength of SLJ exposed to high temperature could be recovered because of the presence of high relative humidity and a low working temperature.
6. The sliding temperature test revealed that increasing the overlap length proportionally increases the sliding temperature. There is no significant difference between 0.5 and 1 mm of adhesive layer thickness, while for greater adhesive thickness (volume) the failure temperature and joint strength is reduced with respect to thinner adhesive layers, since the thicker the HMA exposed to high temperature, the more energy is dissipated by the movement of the chains (viscous flow).

5 . References

- [1] Wylde J.W., Spelt J.K. Measurement of adhesive joint fracture properties as a function of environment degradation, *Int J Adhes Adhes* 1998;17: pp. 237–46.
- [2] Altshculler A., Automobile Recycling Alternatives: Why Not?, for Neighbors Organized to Stop the Hazards of All Metal Shredders!(NO SHAMS!),
- [3] Smith C. A., The Future of Packaging Adhesives, *Proceedings of the Institution of Mechanical Engineers, Conference Proceedings* 1966; 181: pp. 61-68.
- [4] Roberts B. C., Hot-melt Adhesives and Machinery Design Requirements for Their Application, *Proceedings of the Institution of Mechanical Engineers, Conference Proceedings* 1966; 181: pp. 69-80.
- [5] Cagle, C.V., *Handbook of Adhesive Bonding*, McGraw-Hill, United States, 1973.
- [6] Park Y. J., Joo H. S., Kim H. J., Lee Y. K., Adhesion and rheological properties of EVA-based hot-melt adhesives, *Int. J. Adhesion & Adhesives*, 2006; 22:pp. 571-576.
- [7] Kinloch A. *Adhesion and adhesives—science and technology*. Chapman and Hall; 1994. pp. 175–80.
- [8] Skeist I. *Handbook of adhesives*. Chapman and Hall; 1990. pp.408–22.
- [9] Petrie, E. M., Reactive hot-melt adhesives for better structural bonding, *Metal Finishing*, 2008;106(5): pp. 39-43.
- [10] Shin H. H., Hamed G. R., Peel adhesion and viscoelasticity of poly (ethylene-co-vinyl acetate)-based hot melt adhesives. II. The influence of wax, *J. Appl. Polym. Sci.*, 1997; 63: pp. 333-42.
- [11] Li, W. et al., *Ind. Eng. Chem. Res.*, Vol.47, 2008, pp.7524-7532.

- [12] Park Y. J., Kim H. J. Hot-melt adhesive properties of EVA/aromatic hydrocarbon resin blend, *Int. J. Adhesion & Adhesives*, 2003; 23: pp. 383-392.
- [13] Schultz J, Nardin M. In: Pizzi A, Mittal KL, Keimel FA, editors. *Handbook of adhesives technology*, Chapter 2. Marcel Decker Inc.; 1994. p. 19.
- [14] Comyn J. *Adhesion science*. Cambridge: Royal Society of Chemistry; 1997 Chapter 1.
- [15] Kinloch AJ. *Adhesion and adhesives science and technology*. London: Chapman and Hall; 1987 Chapter 1.
- [16] Knox E.M., Cowling M.J., Durability aspects of adhesively bonded thick adherend lap shear joints, *Int. J. Journal of Adhesion & Adhesives*, 2000; 20: pp. 323-331
- [17] Zhang F. , Yang X, Wang H. P. , Zhang X., Xia Y., Zhou Q., Durability of adhesively-bonded single lap-shear joints in accelerated hygrothermal exposure for automotive applications, *Int. J. of*, 200; 44: pp. 130-137.
- [18] Bao L. R., Yee A. F., Effect of temperature on moisture absorption in a bismaleimide resin and its carbon fiber composite, *Polymer*, 2002;43: pp. 3987-3997.
- [19] Doyle G., Pethrick R. A., Environmental effects on the ageing of epoxy adhesive joints, *Int. J. of Adhesion & Adhesives*, 2009; 29: pp. 77-90.
- [20] Joshi N, Muliana A. Deformation in viscoelastic sandwich composites subject to moisture diffusion. *Comp Struct* 2010;92: pp. 254–64.
- [21] Karbhari VM, Zhao L. Issues related to composite plating and environmental exposure effects on composite-concrete interface in external strengthening, *Comp Struct* 1998;40: pp. 293–304.
- [22] Brewis DM, Comyn J, Raval AK, Kinloch AJ. The effect of humidity on the durability of aluminium-epoxide joints. *Int J Adhes Adhes* 1990;10: pp. 247–53.
- [23] Bowditch MR. The durability of adhesive joints in the presence of water. *Int J Adhes Adhes* 1996;16: pp. 73–9.
- [24] John SJ, Kinloch AJ, Matthews FL. Measuring and predicting the durability of bonded carbon fibre/epoxy composite joints. *Composites* 1991;22: pp. 121–7.
- [25] Saponara VL. Environmental and chemical degradation of carbon/epoxy and structural adhesive for aerospace applications: Fickian and anomalous diffusion, Arrhenius kinetics. *Comp Struct* 2011;93: pp. 2180–95.
- [26] Silva MAG, Biscaia H. Degradation of bond between FRP and RC beams. *Comp Struct* 2008;85: pp. 164–74.
- [27] Park Y-B, Song M-G, Kim J-J, Kweon J-H, Choi J-H. Strength of carbon/epoxy composite single-lap bonded joints in various environmental conditions. *Comp Struct* 2010;92: pp. 2173–80.
- [28] Hua P., Han X., da Silva L.F.M., Li W.D., Strength prediction of adhesively bonded joints under cyclic thermal loading using a cohesive zone model, *Int J Adhes Adhes*, 2013;41: pp. 6–15.
- [29] Sargent JP., Durability studies for aerospace applications using peel and wedge tests, *Int. J Adhesion & Adhesives* 2005;25: pp. 247-256
- [30] Ameli A., Datla N.V., Azari S. , Papini M., Spelt J.K., Prediction of environmental degradation of closed adhesive joints using data from open-faced specimens, *Composite Structures*, 2012; 94: pp. 779–786.
- [31] Wylde J.W., Spelt J.K. Measurement of adhesive joint fracture properties as a function of environment degradation, *Int J Adhes Adhes* 1998;17: pp. 237–46.

- [32] Seong M.S., Kim T.H., Nguyen K.H., Kweon J.H., Choi J.H. A parametric study on the failure of bonded single-lap joints of carbon composite and aluminum, *Composite Structures*, 2008, vol. 86, pp. 135–145 .
- [33] Da-Silva L.F.M., Carbas R.J.C., Critchlow G.W., Figueiredo M.A.V., Brow K. Effect of material, geometry, surface treatment and environment on the shear strength of single lap joints. *Int J Adhes Adhes* 2009;29: pp. 621–32.
- [34] W. R. Broughton, R. D. Mera, Environmental degradation of adhesive joint accelerated testing, NPL report CCM(197, 1999).
- [35] Mazumdar SK, Mallick PK. Static and fatigue behavior of adhesive joints in SMC–SMC composites. *Polymer Compos* 1998;19(2): pp. 139–46.
- [36] Adams, R.D. and Peppiatt, N.A. Stress analysis of adhesively bonded lap joints, *J. Strain Analysis*, 1974, 9, pp. 185-196.
- [37] da Silva LFM, TNSS Rodrigues, Figueiredo MAV, de Moura MFSF, Chousal JAG. Effect of adhesive type and thickness on the lap shear strength, *J. Adhes.* 2006;82: pp. 1091–115.
- [38] Crocombe, A. D. Global yielding as a failure criteria for bonded joints, *Int. J. Adhesion Adhes.*, 1989: 9: pp. 145–153.
- [39] Gleich, D. M.; Van Tooren, M. J. L.; Beukers, A., Analysis and evaluation of bondline thickness effects on failure load in adhesively bonded structures, *J. Adhesive Sci. Technol.* 2001; 15: pp. 1091-1101.
- [40] Grant LDR, Adams RD, da Silva LFM. Experimental and numerical analysis of single-lap joints for the automotive industry. *Int. J. Adhes. Adhes.* 2009;29: pp. 405–13.
- [41] Merrill N., Low-Molecular-Weight Polyolefins for Hot-Melt Adhesives part 2- Adhesives & Sealants Industry; May 2007, Vol. 14 Issue 5, p.28
- [42] Development Trends of hot-melt adhesive, <http://www.hnyake.com/english/newshow.asp?Cid=107&sid=107&pid=161>
- [43] Thomas P. Flanagan, Thomas P. Flanagan, Hot-melt adhesive composition based on ethylene-propylene copolymer – United States Patent Office 3,492,372 (January 27, 1970).
- [44] Petrie E. M., Member of SpecialChem Technical Expert Team - Tackifiers for Hot-melt Adhesives SpecialChem - Jan 15, 2003.
- [45] Rolando T.E. , Solvent Free Adhesives, iSmithers Rapra Publishing, 1998.
- [46] www.henkelna.com/us/content.../101492_MD_Nov._Appliance_Suppl..pdf (21/05/13)
- [47] <http://www.specialchem4adhesives.com/techcenter/formulation-guide/formulation.aspx?id=122> (20/05/13)
- [48] <http://www.beardowadams.com>
- [49] Chabert F., Tournilhac F., Sajot N., Tencé-Girault S., Leibler L., Supramolecular polymer for enhancement of adhesion and processability of hot-melt polyamides, *Int J Adhes Adhes*, 2010; 30: pp. 696–705.
- [50] Koricho E. G., Implementation of Composites and Plastics Materials for Vehicle Lightweight, Politecnico di Torino, Department of Mechanical and Aerospace Engineering, PhD Thesis, 2012.
- [51] Y. J. Park, H. J. Kim, H. J. Kim, M. Rafailovich and J. Sokolov, Viscoelastic properties and lap shear strength of EVA/aromatic hydrocarbon resins as hot-melt adhesives, *J. Adhesive Sci. Technol.*, 2003, Vol. 17, No. 13, pp. 1831-1845
- [52] S. Hummel, Atlas of Polymer and Plastic Analysis, vol. 2 part b/I, Carl Hanser, Weinheim, Germany, 1998.

- [53] R.Gallo, L. Brambilla, C. Castiglioni et al., “Environmental degradation of a novel ethylene-propylene copolymer in thick sheets,” *European Polymer Journal*, vol. 41, no. 2, pp. 359–366, 2005.
- [54] C. Hongjun, L. Xiaolie, M. Dezhu, W. Jianmin, and T.Hongsheng, “Structure and properties of impact copolymer polypropylene. I. Chain structure,” *Journal of Applied Polymer Science*, vol. 71, no. 1, pp. 93–101, 1999.
- [55] Guillemin J., Bistac S. and Schults J., Relation between polymer viscoelastic properties and adhesive behavior, *Int. J. Adhesion & Adhesives*, 2002; 22: pp. 1-5.