# A STUDY OF PHYSICAL AND MECHANICAL PROPERTIES OF A NANOMODIFIED THERMOPLASTIC ADHESIVE IN NORMAL AND ACCELERATED AGEING CONDITIONS

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**Abstract**

Bonding is one of the key aspects of recent vehicle design, especially when multi-material structures are considered to contribute to the lightweight trend. Some innovative technologies, based on magneto sensitive nanoparticles dispersed in hot melt adhesive (HMA), have been already studied in order to reduce the cycle time of a vehicle and to allow for the recycling at the vehicle end of life. In this research activity, the effect of a 180 days normal ageing and three different accelerated ageing cycles (currently used by vehicle industries) of a thermoplastic adhesive with Iron (II,III) oxide nanoparticles embedded in the adhesive matrix have been studied. Performed Single Lap Joint (SLJ) tests prove the variations of the mechanical properties and adhesion strength during both the normal and accelerated ageings. Thermogravimetric analysis (TGA) and Fourier Transform Infrared Spectroscopy (FTIR) have been used to reveal the different degradation levels among the various ageing cycles. Results have been conveniently compared and criticized in order to show the differences and the similarities between the normal ageing cycle and accelerated ones.

## 1. Introduction

In the last decades the use of the adhesive bonding is widely increased in many industrial sectors, especially in the automotive field. This increase is due to two reasons. The former is that the new emission rules, issued by European commission, have cleared the way to the lightweight design [1]. In this contest, the adhesive bonding assumes considerable importance because may offer a real contribution to weight reduction, for instance by substituting welding and bolts with adhesives. The latter is due to the high performances of the adhesives that can offer high mechanical proprieties, easy way to be applied and the possibility to join dissimilar materials. This latter property is particularly connected to the vehicle lightweight trend because it gives the possibility to join lighter components, such as composites material parts with plastic or metal parts.

In this area of interest, the complexity in disbonding when required and at the end of the life cycle can represent an obstacle [2]. Therefore some innovative joining technologies have been studied in order to set a viable solution to these problems. One of this joining technologies is induction welding or bonding, where adhesive layer heating is obtained by means of electro-magnetic waves [3]. The used inductor physical principle is described as follow. When alternating current (AC) is applied to the primary of a transformer, an alternating magnetic field is created. In a basic configuration, the power

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supply sends AC currents through an inductor, usually a copper coil, and the workpiece is placed inside the coil. The coil with the power supply works as the primary of the transformer while the workpiece is the secondary of the transformer. Essentially due to the hysteresis (high frequency phenomenon) and eddy current losses the workpiece increases its temperature.

In the last years, the principle of the induction heating has been used for welding hybrid components, such as plastic with metal, or taking advantages by the conductive material embedded into the matrix of a composite material. The study finalised to our automotive application is focused on a hot melt adhesive (HMA) additivated with electro-magnetic particles. In this way, the metallic nanoparticles can be used to warm up the HMA in order to reach its melting temperature and then bond the components. The use of this technology is intended to increase the recycling of more materials and the reuse of components according to the European specification about circular economy.

Ageing is one of the relevant issues for the use of adhesive for structural applications. In this work, the effect of a 180 days of normal ageing (i.e. at room temperature and humidity) and of three different accelerated ageing cycles (currently used by vehicle industries) of the considered HMA with magnetite nanoparticles embedded in the adhesive matrix have been studied. The objective of this study is to evaluate the chemical and mechanical properties of the nano-modified and pristine HMA at the end of ageing cycles. Furthermore some comparisons between the normal and the accelerated cycles have been done in order to understand the final conditions of the adhesive.

## 2. Materials and methods

The aim of this work is to assess the effect of different accelerated ageing cycles, currently used by automotive industries and normal ageing (i.e. at room temperature and humidity). In particular, the effect of the ageing cycles on mechanical and chemical properties has been investigated using SLJ tests, thermogravimetric analysis (TGA) and Fourier Transformed Infrared Spectroscopy (FT-IR). FTIR spectra were collected with a Perkin Elmer Spectrum 100 in the attenuated total reflectance (ATR) mode with a diamond crystal, using 16 scans per spectrum and a resolution of 4 $cm^{-1}$ and a spectral range of 4000-600 $cm^{-1}$. After ATR correction, at the peak at 1378 $cm^{-1}$ the spectra were normalised to an absorption of 0.1.
Thermogravimetric analyses (TGA) were carried out on a TA Q500 model from TA Instruments by heating samples in alumina pans at a rate of 10 °C $min^{-1}$ from 50 to 600 °C in a nitrogen flow.
For this work, two different compounds of HMA have been prepared: a pristine HMA and a HMA additivated with 5% in weight of magnetite (5 wt%). The standard SLJ specimens have been exposed to three different accelerated cycles in air atmosphere, that are summarised below:

**Cycle A**: Exposure at 90°C without the control of the Relative Humidity (RH) for 500 h.
**Cycle B**: Exposure at 40°C with RH set at 98% for 500 h.
**Cycle C**: Exposure at 80°C without RH for 24 hours,
Exposure at 40°C with RH set at 98% for 24 hours,
Exposure at -40°C for 24 hours.
**Cycle N**: Exposure at room temperature and humidity for 180 days.

In this work a HMA has been used to join the Single Lap Joint (SLJ) specimens. The mechanical properties have been evaluated with SLJ shear test, using an Istron 8801 material testing machine. The test velocity was set at 100 mm/s. Magnetite $Fe_3O_4$ purchased from Sigma-Aldrich with particle dimension <50nm was embedded in the HMA. The HMA is a polyolefin based thermoplastic adhesive, its main characteristics are reported in the paper [4]. In order to investigate the mechanical properties and to evaluate the effects of the ageing on both pristine and modified adhesives, substrates made of homopolymer polypropylene (PP) with 10% of talc were adopted. This type of substrates have been chosen because this compound is widely used in the automotive sector for internal and external applications. For the mechanical tests, 5 replications have been made in order to give to the study statistical basis.

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## 3. Experimental results

### 3.1 Mechanical characterisation

Fig. 1 shows the typical trend of a SLJ test for two different adhesive formulations without the effects of the ageing. The two curves are the average of the five measured curves for each of the two adhesive types. The curve called “Pristine HMA” refers to the pristine adhesive, the other curve is related to the adhesive modified adding 5% in weight of magnetite nano-particles. In this figure, it is possible to notice an increase of the maximum shear strength of the modified adhesive. Furthermore the initial trend is almost the same but the total area under the modified adhesive curve, which is the amount of deformation energy, is wider.

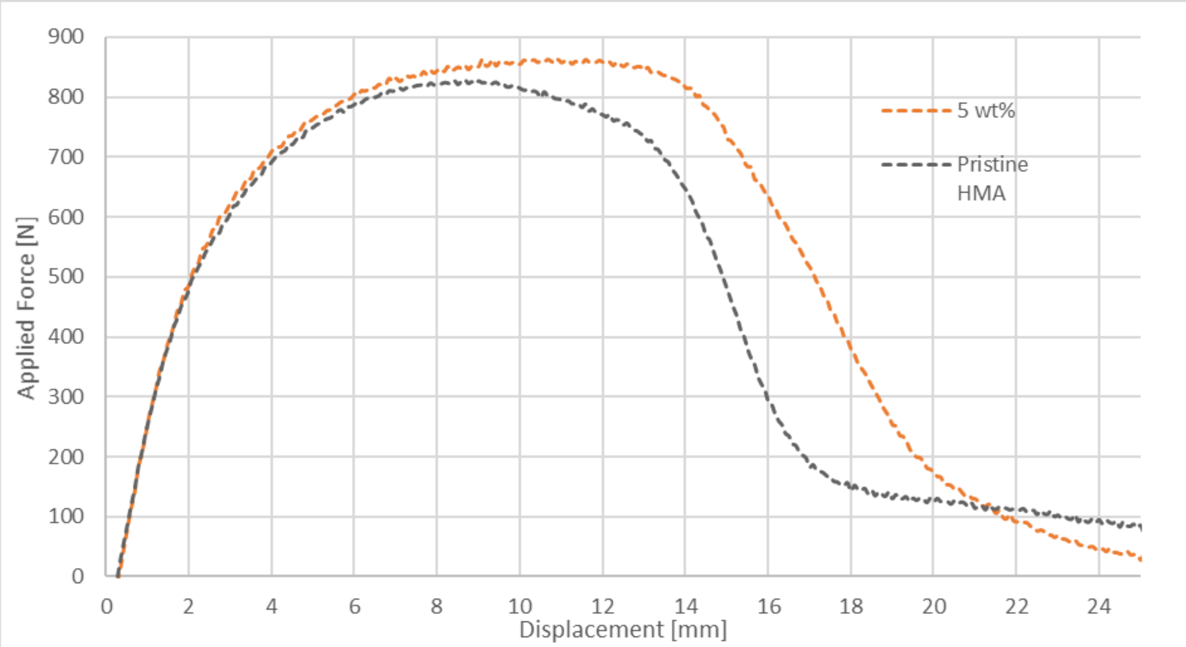


Figure 1: Applied force/displacement curve for SLJ prepared with unmodified and modified adhesive

This behaviour has been already explained by Verna et Al. [5]. The above evidences suggest that the interfacial interactions between the nanoparticles and the adhesive matrix allow the transfer of stress to the reinforcing particles which results in an increase in material strength. Figure 2 shows the pictures of the joint separation surfaces after the SLJ test. It can be seen that the disbonded profile is quite similar.

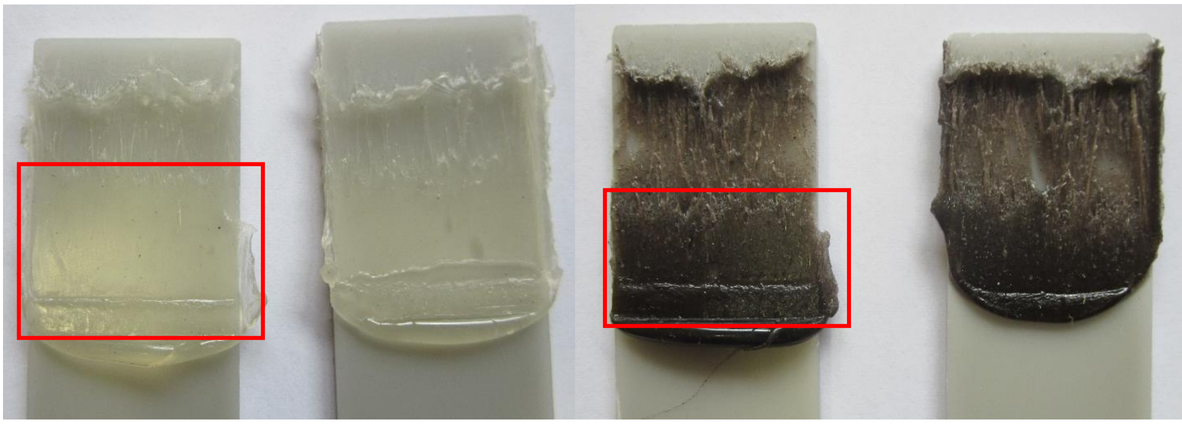

Figure 2: Disbonded SLJ specimens with pristine and modified adhesives.

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This figure highlights also the kind of fracture that is of the cohesive type for around the 80% of the total failure surface. As evidenced in figure 2, the failure of the modified HMA (pictures on the right) is slightly more of the cohesive type than the pristine one (pictures on the left). The red rectangles in the figure put in evidence the equivalent adhesive fracture. This behaviour is confirmed in all the five replications.
Figure 3 highlights the differences in the trends and values in the force-displacement diagrams among the SLJ specimens after the different A, B and C accelerated ageing cycles in comparison with the pristine HMA. It is evident from the results that the accelerated ageing cycle A is the most aggressive for the adhesive: it leads to a decrement of the joint ultimate strength of about 50%. Comparing the average curves of the SLJ specimens without ageing and with ageing B and C, it is clear that the differences are not too large in the first part of the diagram and the ultimate strengths of the joints are very similar. The only little evident variation can be found in the right tails of the curves, in fact the curves are shorter (i.e. the resulting behaviour is a little bit less ductile) in comparison with the pristine HMA without ageing curve.

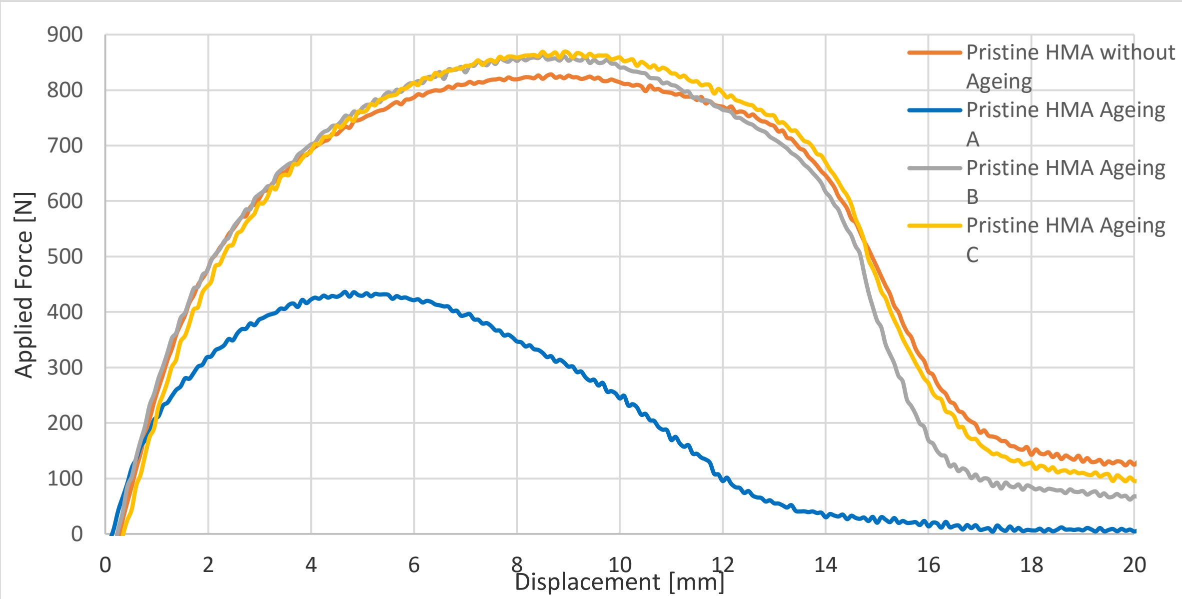


Figure 3: Applied force/displacement curve of the SLJ test for the accelerated ageing cycles, pristine adhesive.

The same can be said for the 5% modified HMA, as illustrated in figure 4. The cycle A is again more aggressive compared to the B and C cycles. In this case it leads to a decrement of the joint ultimate strength of more than 50%. The trend of the curve of the SLJ specimens without ageing, with the ageing A and C are very similar in the left parts but some differences are visible in the right parts. In this occasion, the ageing B results in an increase of the mechanical characteristics with respect to the ageing C. The improvement consists of the increase of the ultimate strength and in the huger right tail, as shown by the grey curve. Ageing C reflects the same trend of the pristine adhesive, ultimate strengths are similar ageing but the tail is shorter.

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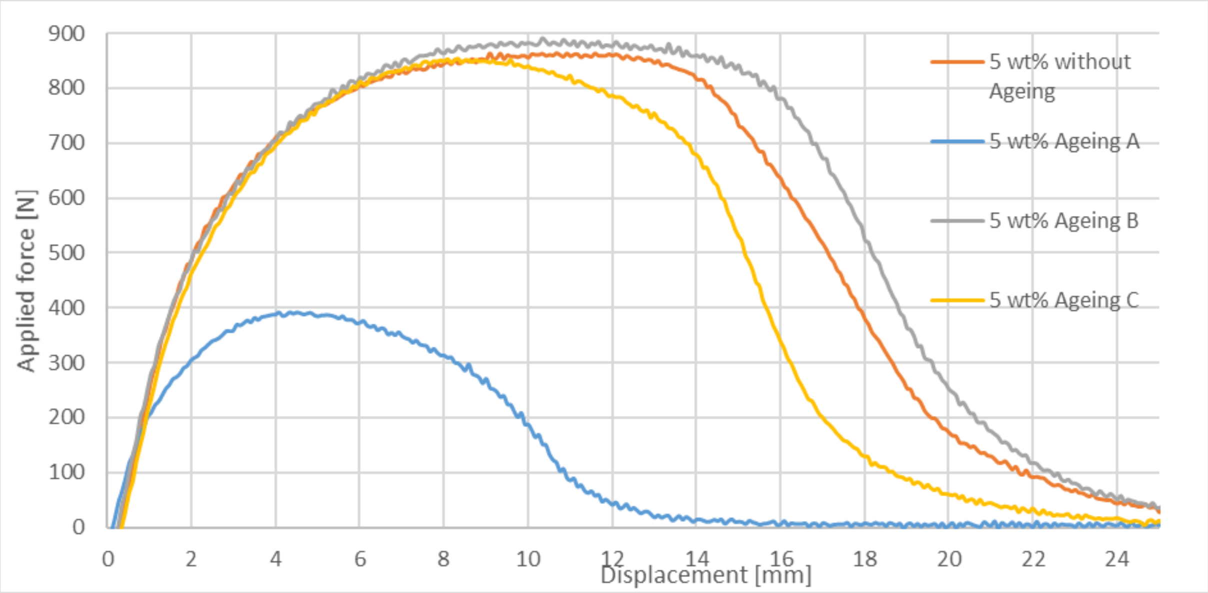


Figure 4: Applied force/displacement curve of the SLJ test for the accelerated ageing cycles, modified adhesive.

Figure 5 shows the trends of the shear tests for the naturally aged SLJ specimens compared with the SLJ specimens without ageing. This comparison has been done on a different diagram because the tests have been performed on substrates of polypropylene of a different supplier. This figure illustrates the comparison between the mechanical behaviour of the SLJ specimens after 6 months of normal ageing and 5 days after the preparation of the SLJ. After 6 months of normal ageing, the maximum shear strengths have decreased of about 50 N for the modified adhesive whereas the pristine adhesive increases of 5 N. Another important point to note is the initial stiffness and the left tails that are almost unchanged after ageing cycle N.

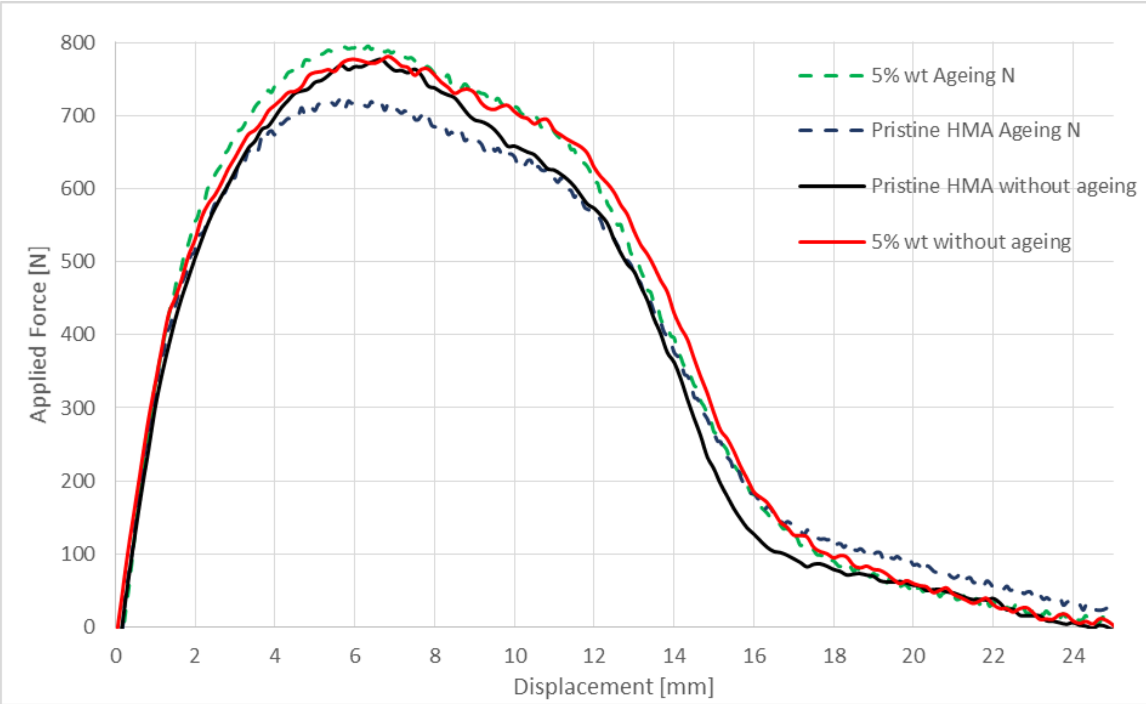


Figure 5: Applied force/displacement curve of the SLJ test for the normal ageing cycles, modified and pristine adhesive.

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### 3.2 Fouier Transform Infrared Spectroscopy (FTIR) and thermogravimetric analysis

The chemical properties of the adhesive have been analysed with the FT-IR and TGA. For this analysis, the results obtained on the fractured SLJ specimens gave ambiguous answers because we were not able to select always the same position on the specimen, because of the position of the detector and because of the different fracture of the adhesive. For these reasons some HMA samples were spread above a sheet of Teflon and then aged. In this way the adhesive was directly exposed to the ageing chamber condition and it was possible to position the FTIR detector above the adhesive. Of course this ageing condition is worse than the HMA inside the SLJ, but it was the only way to analyse the real ageing effect on the adhesive. In this way, the effect of the ageing on the HMA is amplified, but it is giving repeatable results and thus is helpful to understand the effect on the mechanical behaviour.
Figure 6 shows ATR-FTIR spectra, the differences in the spectral absorbance of the pristine HMA withoutageing and with all the considered ageing cycles. The area of major interests are is in the wavelength range between 1800-1500 $cm^{-1}$ and 1300-1100 $cm^{-1}$. In the first cited range it is possible to find the peaks due to C=O bond of ketones, carboxylic acids, esters, common oxidation products of polyolefines [6]. The zoom in the figure illustrates that the oxidation (peaks at 1710 $cm^{-1}$, 1740 $cm^{-1}$ and 1780 $cm^{-1}$) is higher for the ageing cycle A whereas is almost the same for the not aged sample and the others cycles. In the range 1300-1100 $cm^{-1}$ peaks are relative to C-O bond [6], again connected to oxidation products and also in this range, the peaks are higher for the cycle A whereas the HMA specimens without ageing and with the others ageing cycles have a similar absorbance

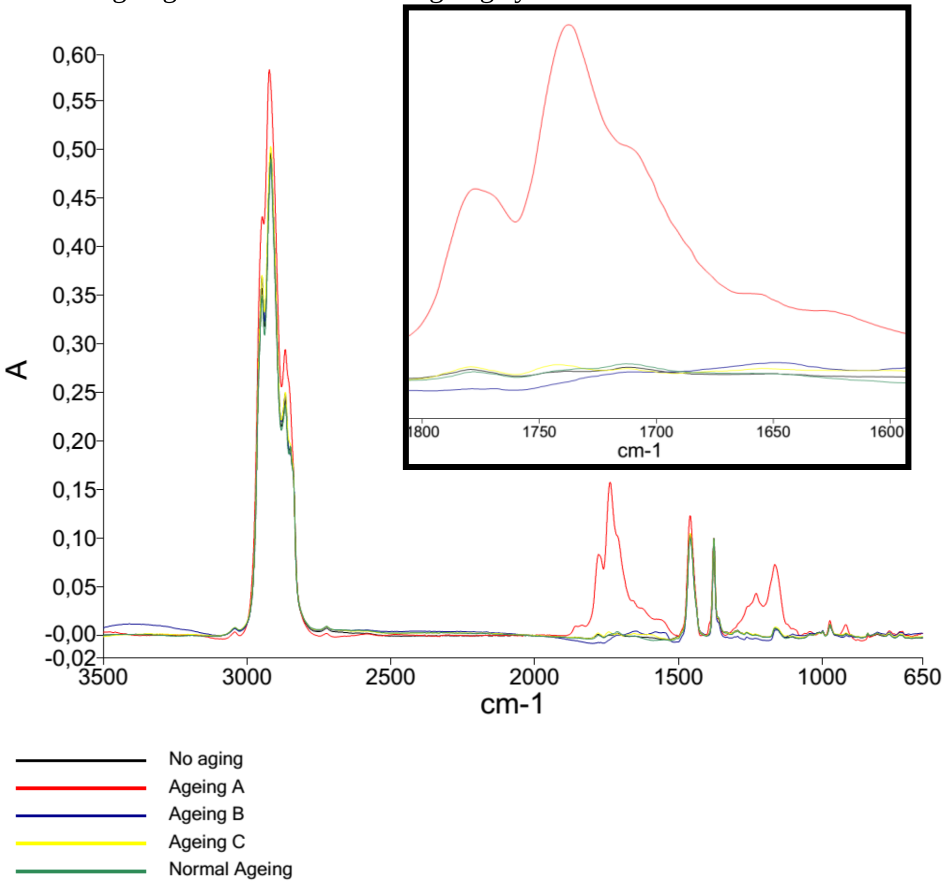


Figure 6: ATR-FT-IR spectra of the pristine HMA.

Figure 7 shows the differences in the spectral absorbance of the modified HMA without ageing and with all the ageing cycles analysed. In this diagram it is possible to note that the oxidation level is not too high like it was for the pristine adhesive. The oxidation level is still higher for the cycle A (peaks

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at 1740 cm$^{-1}$ and 1780 cm$^{-1}$) and the curve of the cycle A is higher also in the range 1300-1100 cm$^{-1}$. The presence of the magnetite seems to decrease the tendency of the HMA to oxidise.

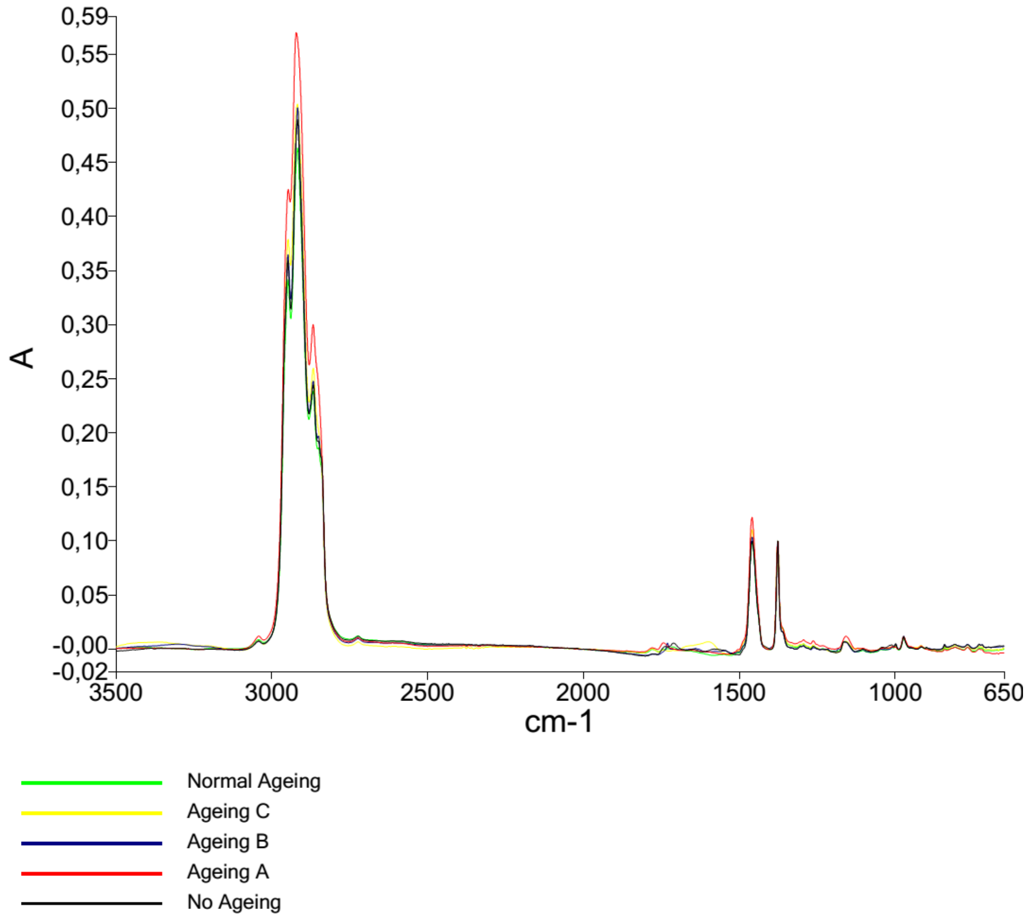


Figure 7: ATR-FT-IR spectra of the modified HMA.

For this study TGA analysis has been used to understand whether there were some differences in the degradation level between the ageing cycles. This analysis was not able to show significant evidences, for this reason its results have not been reported in this paper.

## 3. Discussion and conclusions

Prior works have documented the increase of the mechanical properties of HMA using magnetite nanoparticles and the effect of ageing; papers [4] and [5] for example, report respectively the mechanical behaviour of the HMA and the effects of the ageing. However these works have not tried to establish a correlation between accelerated and normal ageing for the considered HMA. This work was intended to understand if this correlation is possible, further we evaluated the residual mechanical and chemical proprieties of HMA after the ageing cycles.
Two types of HMA adhesives have been considered, one is the pristine and one has been modified by adding 5% in weight of magnetite nano-particles. Three ageing cycles, typically used in the automotive industry, have been adopted.
For what concerns the mechanical properties, we found that the ageing cycles B and C are not aggressive like cycle A. The cycle B seems to be the less aggressive for the SLJ specimens, in fact, both the modified and the pristine HMA present a slight modification in the force-displacement curve with respect to the not-aged HMA. The same can be said for the cycle C. Cycle A causes the worst

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effect on the mechanical properties, in fact, in this case, there is a drop of the maximum load of 47% in the case of the pristine adhesive and 55% in the case of modified HMA. On the contrary, with the natural ageing there is a considerable increase in the maximum load. This increment is not comparably larger with respect to those obtained by means of the ageing cycles C and B.
For what concerns the physical and chemical properties, we found that the TGA was not able to find significant differences for the different cycles. The FT-IR results highlight modification of HMAs chemical structure. The FT-IR revealed that the cycle A resulted the most aggressive, especially for the pristine adhesive. The different spectra showed that there are some similarity among cycles B, C and natural ageing. This result can be due to the properties of the HMA to resist at the humidity.
Finally, the study showed that the use of magnetite nanoparticles in the HMA increases the mechanical properties of the adhesive. The nanoparticles have also a positive effect on the physical and chemical characteristic after ageing. This means that the development of a technology with nanoparticles able to disbond components during ageing and at the end of vehicle life, represents a potential way to reuse and recycle vehicle components.

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