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Insights on the use of PVB nanocomposites as energy directors in ultrasonic welding of epoxy composites

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Abstract. The selection of an adequate coupling film for welding thermoset composites (TSC) is primary for improving the degree of automation in the composite industry. Ultrasonic welding (UW) is a well-established technique for joining composites and has recently been utilized in the aerospace and automotive industries. To achieve an efficient joining, the use of a polymer-based material placed at the welding interface called an energy director (ED) is required. The choice of the coupling layer material is linked to several requirements, such as processing temperature, high adhesion to the TSC adherend and mechanical strength of the resulting welded joints. Most importantly, the viscoelastic dissipation of the ED influences the heating mechanism and the joint behaviour since the hysteresis loops generated during welding are dissipated into viscoelastic heat. In this work, the authors investigated the possibility of using Poly-vinyl-butyral (PVB) reinforced with graphite nanoplatelets (GNPs) as a coupling layer in UW of TSC adherents, showing that an improvement of lap shear strength (LSS) of 80% with respect to neat PVB.

Introduction

Joining of TSCs has been limited to mechanical fastening and adhesive bonding, or a combination of the two [1]. In the first case, the drilling of holes results in stress concentrations and weakening of the thin composite structure, also significantly reducing its lightweight potential [2]. In contrast, adhesive bonding, although not requiring holes, needs rigorous surface preparation, high curing temperatures and pressures and long curing times to preserve the long-term durability of bonded composite joints [3].

Thus, the development of novel joining techniques able to overcome these drawbacks is required. Welding is a highly efficient process for joining composites, being capable of producing joints in relatively short cycle times, characterized by equivalent or better performance than adhesively bonded or mechanically fastened joints. Specifically, ultrasonic welding (UW) is a well-established technique for joining composites and has recently been utilized in the aerospace and automotive industries [4,5]. However, it requires the melting or softening ability of the polymer with increasing temperature, being applicable only in joining fibre-reinforced thermoplastic composites (TPC). To weld TSC, the use of polymer-based films placed at the welding interface is required to promote frictional and viscoelastic heating [6]. These coupling films, called energy director (ED), must satisfy various requirements such as processing temperature, high adhesion to the TSC adherend and mechanical and environmental performance of the resulting welded joint [7].

In contrast to other welding processes, in the UW, heat is generated by the internal damping of an applied ultrasonic vibration. During ultrasonic welding, the parts are subjected to a longitudinal mechanical vibration with a high frequency (typically 10-40 kHz). The mechanical vibration causes a standing wave in the welding parts in the form of heat [8]. The mechanism of heat

generation is via viscoelastic dissipation due to the cyclic deformation of the plastic. In a purely elastic material, the driving force causes deformation rates in the part that is in phase with the force so there is no energy dissipation. The deformation rate in a purely viscous material is proportional to the applied force but has a phase difference of 90° dissipating the energy. Thus, in UW, the driving dynamic welding force depends on the material properties and shape of the product. When the ED heats, melts and flows to fill the interface joining the parts. With increasing temperature, the damping factor grows and the increasing vibrational energy is converted into heat by hysteresis losses [9].

The transformation of mechanical vibration into heat depends on a large number of mechanical and thermal properties of the material: the damping has to reach a certain level to cause high hysteresis losses, which are responsible for the elevation of the temperature. On the other hand, the material has to be stiff enough to successfully transmit the vibrational energy from the horn to the joint interface.

The polymer itself may not reach these mechanical requirements. Nanomaterials can effectively increase the mechanical performances of polymers both in terms of elastic modulus and damping, thanks to the energy dissipation that occurs at the interface with the matrix. Nanoparticles with a lamellar (2D) structure, such as graphene and its analogues (graphene oxide, GO, graphene nanoplatelets, GNP, etc.), can significantly improve the damping capabilities of nanocomposites [10] and also fracture toughness [11]. The nanoparticle shape factor and content can influence the mechanical behaviour of nanocomposites and in particular the damping factor (tanδ) [12].

In this work, the authors investigated the possibility of using Poly-vynil-butyral (PVB) reinforced with graphite nanoplatelets (GNPs) as a coupling layer in UW of TSC adherents. The effect of GNPs' weight content and flake dimensions on the temperature-dependent dynamic characteristics of nanocomposites and their influence on joint quality have been assessed. Specifically, nanocomposites with GNPs content varying from 0.5 wt% to 2.0 wt% and different aspect ratios have been fabricated using a lab mixer. Both the viscoelastic behaviour and morphology of the nanocomposites have been investigated. Finally, the interlaminar shear properties, through lap shear strength and short beam strength of UW joints have been investigated.

Materials and Methods

Poly-vinyl-butyral (PVB) (Mowital B60H) is a tough plastic resin commonly used for bonding. The presence of hydrophilic vinyl alcohol units and the hydrophobic vinyl butyral units confer both high adhesion to inorganic material and elasticity and toughness.

Two-dimensional graphite nanoplatelets (GNPs) are multilayer graphene obtained by the exfoliation of graphite. Nanoplatelets with different aspect ratios have been selected in this study and their geometry is listed in Table 1.

Table 1. Properties of selected nanoplatelets.

Nanoplatelet	SSA*	Lateral size	Thickness	Aspect ratio
MICRO850	14 m^2/g	4 μm	850 nm	4.70
AVA 1240	22 m^2/g	40 μm	12 nm	3333
G2NAN	30 m^2/g	30 μm	14 nm	2143

*SSA=specific surface area

Nanocomposites filled with selected GNPs were produced following a mixing and moulding process. Firstly, the polymer and the nanoplatelets are mixed using a Thermo Haake Rheomix for 10 min at a temperature of 150°C. Then, films of 200 μm thickness are fabricated using a hot platen press at 140°C and 200 bar for 20 min.

A number of 8 different coupons have been fabricated, varying the filler concentration and aspect ratio (Table 2). Also, an unfilled PVB film has been produced as reference.

Table 2. Fabricated nanocomposites.

Sample	***Filler***	***Nominal filler content*** [wt%]
Ref	Neat	-
1	AVA1240	2.0
2	G2Nan	0.5
3	G2Nan	1.0
4	G2Nan	1.5
5	G2Nan	2.0
6	MICRO850	0.5
7	MICRO850	1.5
8	MICRO850	2.0

Thermogravimetric analysis (TGA) (TA Instruments Q500) was conducted to evaluate the real filler/matrix composition of the films. Measurements were performed in an inert atmosphere, using nitrogen gas, with a temperature ramp of 10°C/min from room temperature to 700°C. The weight loss is evaluated at 500°C.

The thermal properties of the PVB/GNPs films were investigated by differential scanning calorimetry (DSC) using the DSC Discovery instrument. Each specimen was heated and cooled twice from 0 to 300°C at a rate of 10°C/min and the glass transition temperature (T_g) values were extracted from the DSC curves.

Dynamic mechanical analysis (DMA) was employed to measure the loss modulus and assess the viscous behaviour of the PVB/GNPs nanocomposites. A TA Instruments Q800 DMA equipped with a single cantilever clamp was used to perform a temperature sweep from 30 to 120°C at a heating rate of 3°C/min and a frequency of 1 Hz and considering an initial amplitude of 20 μm. Data are elaborated according to the ASTM D790 standard for the flexural behaviour of composites [13].

An optical microscope Olympus BX 51M, equipped with Linkam THM600 hot stage, was employed to assess the morphology of the material and the quality of the dispersion of the nanoparticles.

A carbon fabric/epoxy prepreg with a fibre volume content of 58% was used. 8 plies of CF/epoxy prepreg were stacked with a [(0/90)/ (45/-45)/(-45/45)/ (90/0)]s lamination sequences. The CF/epoxy stack were cured in autoclave at 120°C for 2 hours and 3 bar with vacuum bag, resulting in a laminate with a final thickness of 2 mm. Subsequently the CF/epoxy cured adherends were ultrasonic welded using the PVB/GNP film as coupling layer and ED.

Ultrasonic welding of individual coupons was performed using a Rinco Dynamic 3000 ultrasonic welder. The following process parameters were used: 500 N welding force, 36 μm peak-to-peak amplitude, 1000 ms welding time and 500 Ws maximum welding energy.

The coupons were saw cut from the cured CF/epoxy laminates to the dimensions of 36 x 12 mm for the Interlaminar Shear Strength (ILSS) tests (Fig. 1Fig. **1**) and 25 x 100 mm for the Lap Shear Strength (LSS) tests (Fig. 1).

ILSS tests were performed according to ASTM D2344 standard to evaluate the interfacial strength of the ultrasonic welded joints; the bonding characteristics of the ultrasonic welded joint was evaluated by LSS tests, according to ASTM D5868 standard. The tests were carried out with a 50-kN load cell in a Instron 68TM-50 Mechanical tester.

The interlaminar shear strength (ILSS) was calculated by dividing the peak recorded reaction force, F_{max} by the area of the cross section (A_{ILSS}), equal to 40 x 12 mm^2, as shown in Eq. 1.

$$ILSS = \frac{3}{4} \cdot \frac{F_{max}}{A_{ILSS}} \quad (1)$$

The LSS of the joints was calculated as the maximum load divided by the total overlap area. The total overlap area (A_{LSS}) was about 25 x 25 mm^2, Eq. 2.

$$LSS = \frac{F_{max}}{A_{LSS}} \quad (2)$$

A minimum of three specimens were tested per type of PVB/GN coupling layer used in this study.

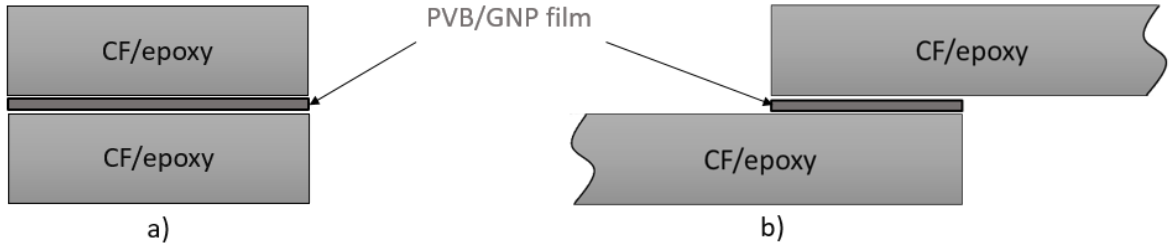

Fig. 1. Schematic representation of the CF/Epoxy/PVB joints in (a) ILSS and (b) LSS configurations.

Results and Discussion

The results of thermal analyses are reported in Table 3. The actual filler content is equal to the nominal value, as confirmed by TGA. Also, the glass transition temperature (T_g) of the polymer is not affected by the inclusions: it is equal to that of the unfilled polymer (73°C) for all samples.

Table 3. Results of thermal analyses conducted on PVB/GNPs nanocomposites.

Sample	***Actual filler content*** [wt%]	T_g [°C]
1	1.7	73
2	0.5	72
3	1.0	73
4	1.5	73
5	2.1	73
6	0.5	72
7	1.5	70
8	1.7	72

Micrographs show excellent dispersion in the case of MICRO850 and G2Nan in contrast to AVA1240. The morphology of the material changes considerably according to the selected GNPs. In the case of AVA1240, the presence of agglomerates can be observed, with a non-uniform distribution of particles (Fig.2). The quality of the dispersion increases significantly in the case of G2Nan (Fig.3). In this case, the distribution of nanoparticles is uniform for all concentrations from

0.5 wt% to 2.0 wt%, with a slight level of agglomeration. Finally, the best dispersion was observed for MICRO850 for all contents, with a very good level of homogeneity and absence of clusters (Fig. 4).

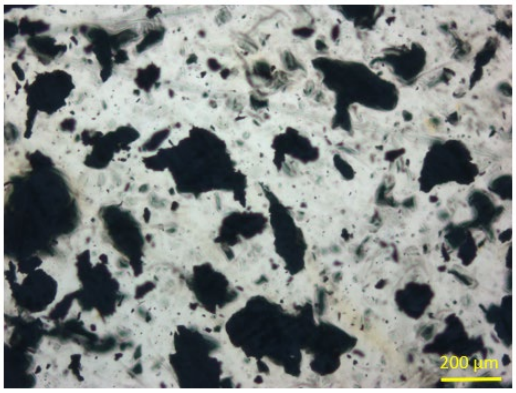

Fig. 2. Micrograph of PVB reinforced with AVA1240 at 2 wt%.

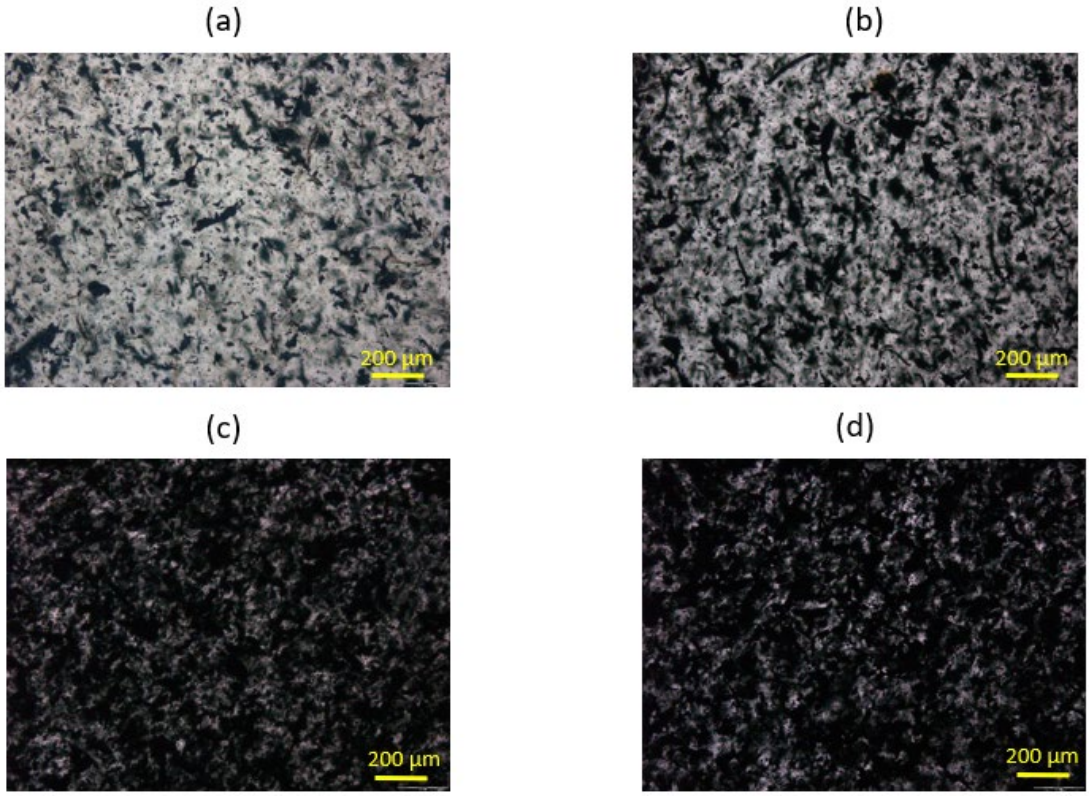

Fig. 3. Micrograph of PVB reinforced with G2Nan at 0.5 wt% (a), 1 wt% (b), 1.5 wt% (c) e 2 wt% (d).

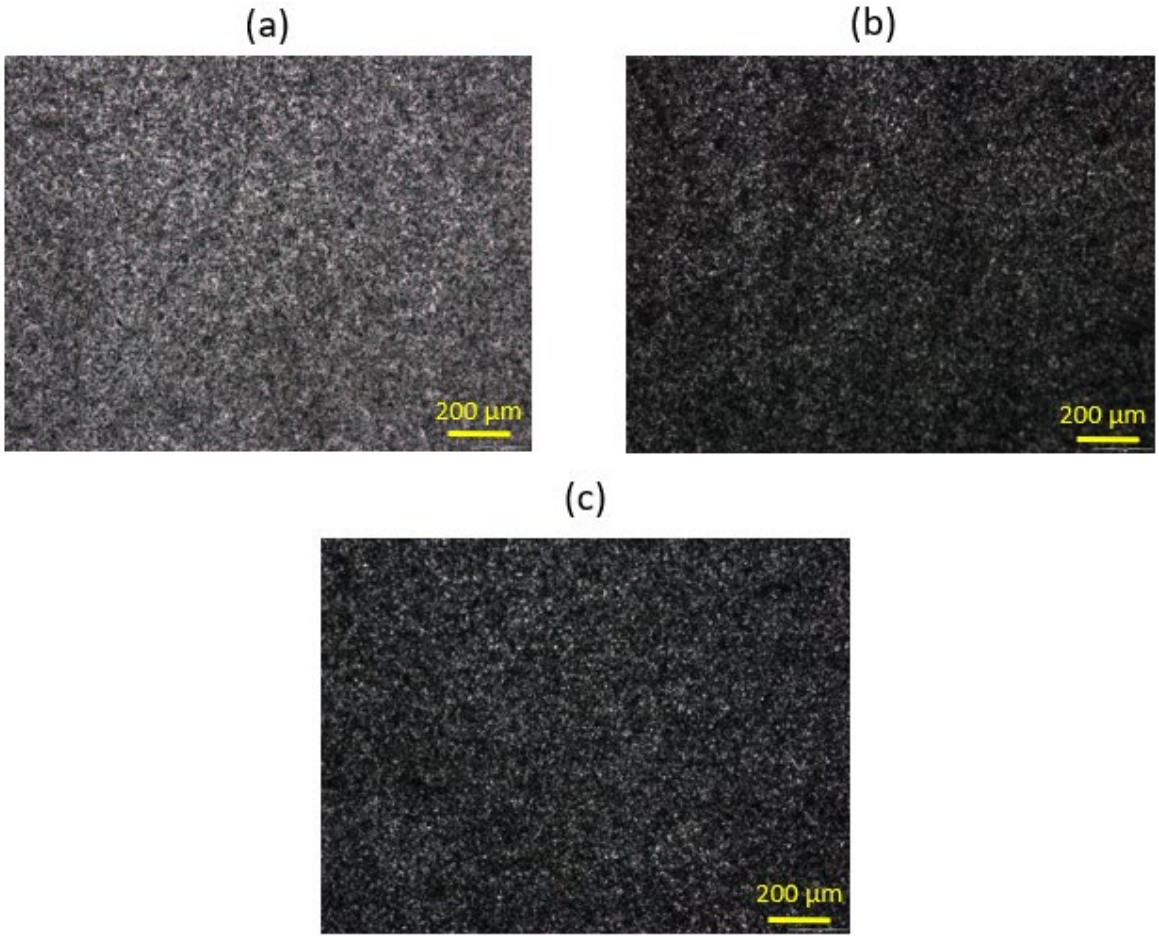

Fig. 4. Micrograph of PVB reinforced with MICRO850 at 0.5 wt%(a), 1.5 wt% (b), 2wt% (c).

The quality of GNPs dispersion is reflected in the mechanical performance of the nanocomposite. The results of the analyses carried out showed an improvement in the mechanical properties in the case of G2Nan and MICRO850 reinforced PVB compared to the unfilled polymer, and a deterioration in the case of AVA1240, both in terms of elastic modulus and damping.

In a viscoelastic material, the properties are intermediate between those of an ideal solid and those of an ideal liquid, as there is a phase lag between strain and deformation due to the time required to obtain molecular rearrangements. A measure of the elastic or pseudo-solid nature of the material is represented by the storage modulus (*E'*), while a measure of the viscous or pseudo-liquid nature of the material is represented by the loss modulus (*E''*). From a physical point of view, the storage modulus is related to the stiffness of the material and the loss modulus reflects the damping capacity of the material. The damping factor, tanδ represents the ratio between the viscoelastic and elastic response of a material and defines the dissipative capacity of the material. The results of the dynamic mechanical analyses conducted on the samples, in terms of storage and tanδ are reported in Fig. 5.

In the case of G2Nan, a maximum elastic modulus is observed for samples with a GNP content of 0.5 wt%, an increase of 9% compared to unfilled PVB. As the filler content increases, the possible presence of clusters leads to a decrease in the elastic modulus with respect to the neat PVB, albeit insignificant. The damping factor increases as the GNP content increases, with a maximum in correspondence of filler content of 1.5 wt%. This configuration provides a 33% increase in tanδ, without altering the elastic modulus of the material (2% reduction).

In the case of MICRO850, due to the small particle size, dispersion is uniform at all concentrations and the elastic modulus increases with increasing filler content. Again, a 30% increase in tanδ is observed for 1.5% GNP content.

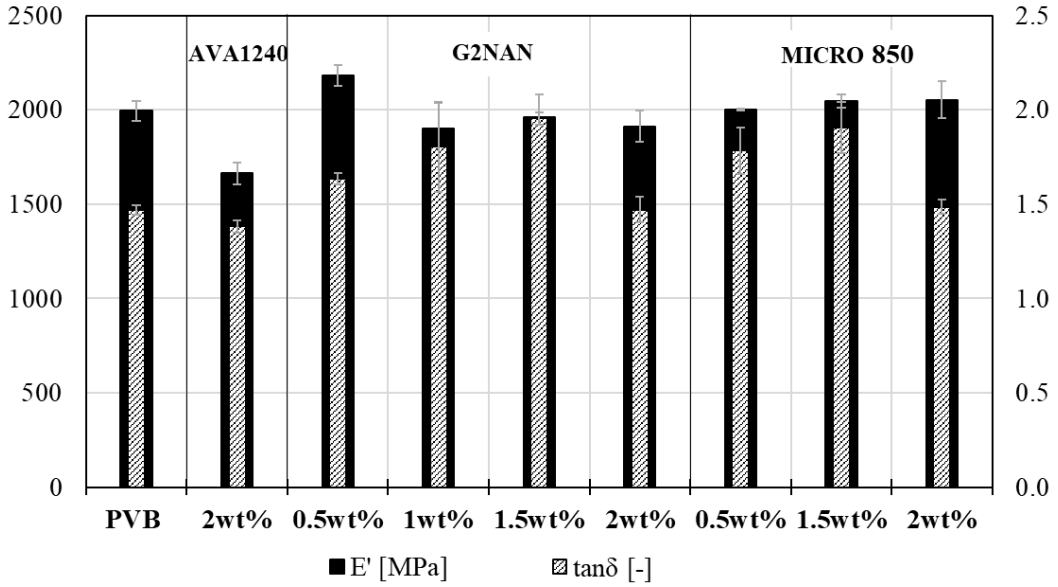

Fig. 5. Comparison between storage modulus at room temperature and damping ratio at peak of the tested nanocomposites.

In UW, the energy directors need to match damping and stiffness requirements to guarantee a certain level of hysteresis losses and to successfully transmit the vibrational energy from the horn to the joint interface respectively. Therefore, AVA1240 has not been considered for further investigation.

A strict correlation between the results of DMA and the short beam shear (SBS) is observed (Fig. 6). The mechanical properties of the coupling layer influence the strength of the joint. Welded joints with nanocomposites with high elastic modulus showed higher SBS with respect to the neat PVB, with a maximum of 40 MPa for PVB filled with 0.5 wt% of G2Nan. At low lamellar nanoparticles content, the fracture toughness of polymers improves, since the inclusions delay crack propagation [11].

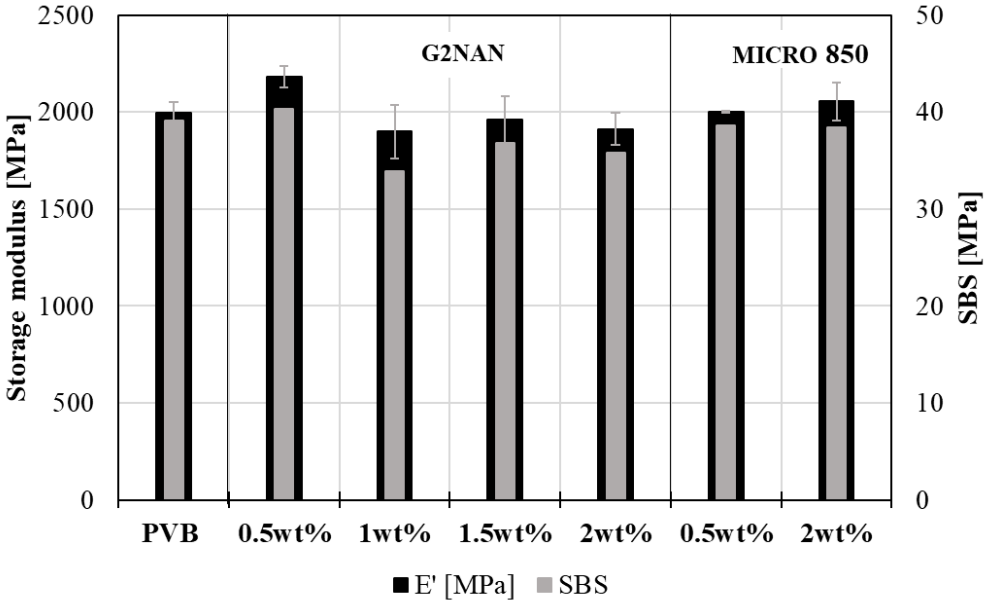

Fig. 6. Comparison between SBS and storage modulus

Lap shear strength has been assessed only for nanocomposites reinforced with G2Nan at different filler content. It is shown in Fig. 7 that this value is always higher than that of the neat PVB and it is maximum for the case of PVB filled with 0.5 wt% of G2Nan.

PVB filled with 0.5 wt% of G2Nan showed an improved quality of the joint with respect to the other samples. According to [14] the higher the material damping and the storage modulus (i.e. the higher the loss modulus) the higher the heat generation during welding and the lower the energy required for the welding process. It means that the ultrasonic weldability significantly depends on the loss modulus of the material [9]. Indeed, the LSS and E'' at 120°C (Fig. 7) show a similar trend.

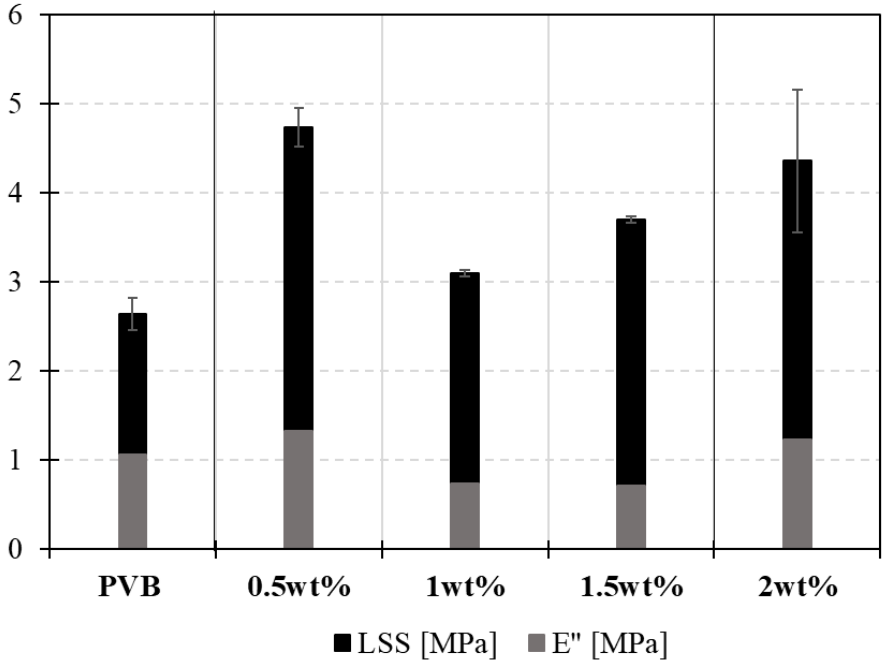

Fig. 7. Comparison between LSS and loss modulus.

Summary

The possibility of using PVB/GNP coupling films as energy directors in UW of TSC has been demonstrated. The influence of GNPs' weight content and flake aspect ratio on the mechanical properties of nanocomposites and joint quality has been assessed.

It was found that the use of lamellar nanoparticles can effectively improve the mechanical performances of polymers both in terms of damping and elastic modulus and consequently weldability. Unlike neat PVB, the inclusions act as reinforcement, supporting part of the load that is transferred from the matrix, both improving the elastic properties and the dissipative capabilities of the material. The high hysteresis losses ensure the elevation of the temperature during welding and the high stiffness ensure the transmission of the vibrational energy from the horn to the joint interface.

An improvement of 28% of loss modulus and 80% of LSS is shown for PVB reinforced with 0.5% of G2Nan, meaning that GNPs positively affect the damping capacity of PVB and therefore the joint strength.

In order to further optimize and increase weld strength future investigations will be addressed. Strategies will be aimed at modifying the thickness of coupling layers and adding the PVB reinforced films as an intermediate material co-cured with the TSC laminates.

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