



# Modelling the interphase of 3D printed photo-cured polymers

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## ABSTRACT

3D printing, in particular the Polyjet technology, has been widely employed for the production of complex heterogeneous composites such as co-continuous architectures (the so-called Interpenetrating Phase Composites, IPCs). It is a manufacturing method in which discrete photopolymer droplets of different materials can be deposited on a build tray and cured by UV light lamp. Previous research already demonstrated how the characteristics of the interface between different photopolymers can vary if formed before or after UV curing process, with the formation of a narrow or broad interphase. In the present work, the dynamic-mechanical properties of multilayer bimaterial composites (made combining a glassy and a rubbery polymer) were investigated under tensile loading, which is relatively insensitive to the spatial arrangement of layers, as opposed to bending. The use of a simple parallel configuration allowed the development of an analytical model which incorporates the properties of the two photopolymers and their interphase, considering their effect on both elastic and dissipative behaviour of the composites; in particular, the interphase behaviour is quite close to that of the glassy polymer and even small quantities are sufficient to dramatically change the overall dissipative behaviour of the composite. It is demonstrated that reliable modelling of real co-continuous architectures as obtained by Polyjet printing (and similar techniques) should include the effect of the interphase.

## Credit author statement

Lorenzo De Noni: Methodology, Software, Validation, Formal analysis, Investigation, Writing – Original draft, Writing – Review & Editing, Visualization. Laura Zorzetto: Resources, Writing – Review & Editing, Visualization. Francesco Briatico-Vangosa: Conceptualization, Methodology, Formal analysis, Writing – Review & Editing. Marta Rink: Conceptualization, Formal analysis, Investigation, Writing – Review & Editing. Davide Ruffoni: Conceptualization, Validation, Resources, Writing – Review & Editing. Luca Andena: Conceptualization, Methodology, Formal analysis, Data curation, Writing – Original draft, Writing – Review & Editing, Visualization, Supervision. All authors have read and agreed to the published version of the manuscript.

## 1. Introduction

Three-dimensional (3D) printing is traditionally used to prototype

new design concepts and to build layer-by-layer the desired component. It is commonly employed for the production of complex structures and to develop heterogeneous composites with tight control on the local microstructure and material composition [1–3]. Hence, in contrast with the more common subtractive techniques, which involve removing sections of material by cutting or machining it away, 3D printing consists in the addition of material layers to obtain the end-product. There is a lot of ongoing research aimed at improving the final characteristics of 3D printed objects acting on material formulation or on the optimization of printing process and parameters [4].

Among the many available techniques, Polyjet-based manufacturing is attracting a lot of interest since it allows the production of complex architectures by employing more than one material at the same time, whose properties can be widely different: for instance, a hard, glassy polymer coupled with a soft, rubbery one, with elastic moduli at room temperature differing by about three orders of magnitude. This feature has been recently exploited by several authors to produce bio-inspired

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composite materials [1,5–12]. Briefly, Polyjet 3D printing is a layer-by-layer method where one or more photo-curable liquid polymers are jetted in the form of droplets through several printing nozzles onto a build tray [1]. If necessary, a removable support material can sustain the deposited material to build overhanging features; then, a “levelling roller” immediately removes the excess of material on each pass of the inkjet head and subsequently a curing process is performed with UV lamps to harden each layer, as shown in Fig. 1. Currently, such technique allows an in-plane resolution of about 40  $\mu\text{m}$ .

Polyjet printing enables to combine different materials and structures to manufacture a large variety of components: for example, blends, also referred to as “digital materials”, with intermediate mechanical behaviour with respect to that of constituent materials [13,14]. Even more complex architectures, such as interpenetrating phase composites (IPCs), can be easily built [15]. IPCs are defined as “two phases or more that are interconnected in three dimensions and construct a topologically continuous network throughout the microstructure” [16]. Triply periodic minimal surfaces (TPMS) are a class of IPCs becoming more and more popular as minimal interface structures may enhance multifunctional aspects of composites [17–20]. Many experimental and numerical studies have shown how IPCs can be finely tuned to obtain final mechanical properties within a broad range.

Most of these studies implicitly assume that an ideal, zero-thickness interface exists between different phases of multimaterial composites [21,22]. However, several previous works demonstrated that the characteristics of the interface are highly critical for the overall composite behaviour [23–28]. Considering Polyjet printing, interface properties can vary significantly, depending on whether droplets of the different liquid photo-polymers get in contact either before or after the UV curing process. The former case occurs when the two liquid materials are simultaneously deposited on the printing tray, the latter when a given layer is deposited onto an already partially cured one made of a different photo-polymer. During simultaneous deposition, interdiffusion between the two polymers can give rise to a broad, “blurred” interface [23–25, 28–30], whose spatial extent is far from being negligible (about 150  $\mu\text{m}$  according to Ref. [23]) In the other case, when the second polymer is jetted on an already (at least partially) cured one, the interface is significantly sharper (less than 20–25  $\mu\text{m}$ ) [23,30] and actually narrower than the typical in-plane resolution of Polyjet printers (i.e., about 40  $\mu\text{m}$ ). In both cases, the layer which forms at the interface between stiff and compliant materials has a finite thickness and will be referred in this work as interphase, to highlight the blending of the two polymers and the possible formation of an effective third material with intermediate properties. The actual mechanism(s) of interphase generation and

its relation to the two parent phases are not well-known at the present stage. A more detailed study of the microscopic structure of the interphase would provide a precious insight about these aspects, but it is well beyond the scope of the present work. The two different types of interphase are clearly visible in Fig. 2, although visual appearance does not allow the determination of the relevant thickness as precisely as with more objective techniques, such as nanoindentation (as performed in Ref. [23]).

Interphase characteristics can be controlled by changing the layer arrangement in multi-layered composites and by modifying the printing direction. This possibility was exploited in Ref. [23] by producing composites having different configurations of stiff and compliant layers, that were later tested using nanoindentation and dynamic-mechanical analysis (DMA) to determine interphase width and macroscopic mechanical response. The study also highlighted a pivotal impact of the interphase on the load transfer between stiff and compliant layers. However, the choice of the most typical (at least for rigid plastics) DMA configuration, i.e. bending, introduced an additional degree of complication because the results were influenced by the spatial arrangement of the layers: those situated farther from the bending neutral axis obviously gave a much higher relative contribution. For this reason, bending-based DMA testing did not allow a straightforward characterization of the dynamic moduli of the interphase.

To overcome this limitation, the main aim of the present work is to develop and validate a model that accounts for the presence of an interphase between the two main polymer constituents. A simpler DMA tensile testing configuration was selected, with the obvious advantage that in tension a uniform loading strain is applied, thus allowing for a direct identification of the unknown interphase properties using simple parallel/series combinations. Such a model is a tool required to better understand the contribution of the interphase to the overall composite behaviour, in particular with respect to its dissipative properties. Additionally, the previously neglected effects of curing conditions and stacking sequence have also been investigated.

## 2. Materials and methods

### 2.1. Sample preparation

The same two base materials (VeroWhitePlus, VW+ and Tango-BlackPlus, TB+) and 3D printer (Objet 260, Stratasys, US) described in Ref. [23] were employed in the present study. Sample fabrication was performed according to the same printing setup and following the same experimental procedures detailed in our previous work. Briefly, samples

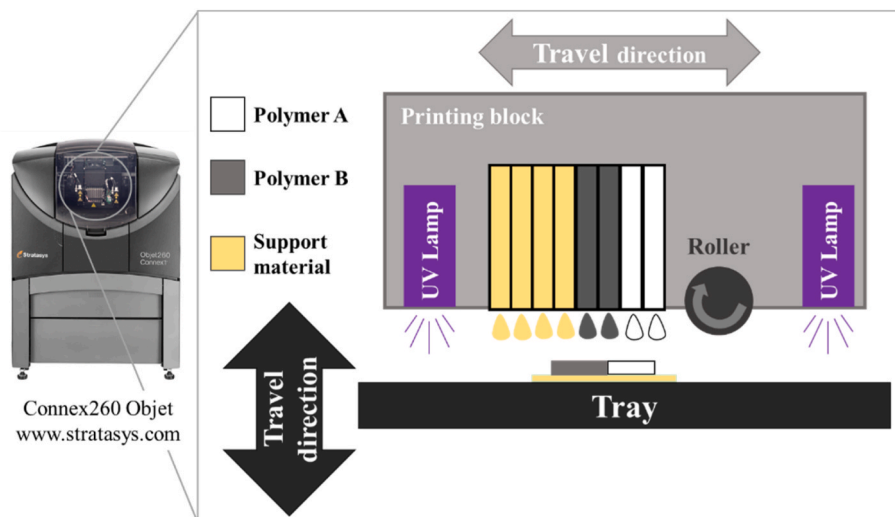


Fig. 1. Schematic overview of the 3D Polyjet technology with the main features of the printing process.

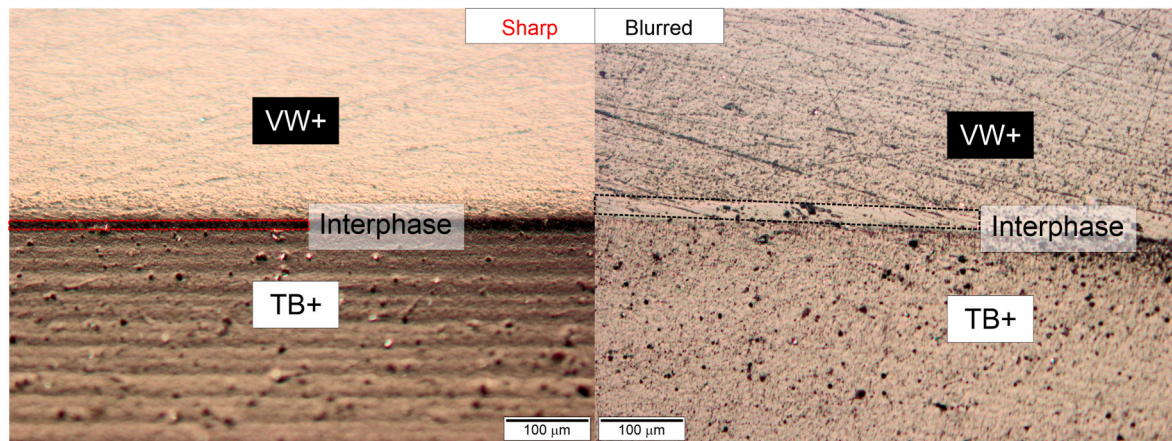


Fig. 2. Optical micrographs of the two types of interphase (sharp and blurred) investigated in Ref. [23] and in the present work.

were fabricated with the digital material option of the 3D printer allowing for a resolution of  $600 \times 300 \times 800$  dots per inch (DPI) along the x, y, and z direction, respectively. A glossy surface finish was used and support material was gently removed with a metal scraper. Up to 3 samples were manufactured simultaneously on the build tray, always at the same position. Sample manufacturing and storage were conducted in a laboratory with constant temperature and humidity. Since the (unknown) composition of the constituent materials is potentially subject to changes by the manufacturer at any time, base materials and composite samples were printed anew using single new batches of supplies from the producer.

Plate-like composite samples, all having 50-50 composition of VW+/TB+, were fabricated by stacking alternating layers of the two materials along their thickness (AT) or width (AW) as depicted in Fig. 3 (on the left and on the right, respectively). Samples were designed to evaluate the role of different interphase type (e.g. sharp or blurred) and arrangement on their macroscopic tensile properties: they were all 3D printed in such a way that during tensile testing a parallel configuration, with identical axial deformation on each layer and a total load equal to the sum over the layer sequence, is realized. However, as already mentioned in Ref. [23], each sample type can be produced using two different printing setups: horizontal (Fig. 2b-d) and vertical (Fig. 3a-2c). For a given configuration, each printing orientation is associated to the presence of a specific type of interphase (sharp or blurred) between the two jetted polymers.

Nominal sample dimensions were about 1 mm in thickness, 5.1–5.4 mm in width (depending on printing orientation) and 40 mm of gauge length. These values were chosen based on printer's resolution, number of layers and compatibility with DMA testing setup. The rigid VW + material was always placed at the outer layers, to provide a continuous, firm gripping surface. The whole set of specimens was designed to be symmetric with respect to their mid-plane in order to avoid in-plane bending coupling. Accordingly, multi-layered samples always have a

central TB + layer and two outer semi-layers having each half the thickness of the inner ones, so that the nominal volume of the two basic phases remains equal. Additionally, homogeneous samples made of the pure VW+ and TB + constituent materials were also prepared to obtain reference data. All samples were produced with two extra gripping regions, having each a length of 15 mm and always made of VW+, located at the opposite ends along the major axis (not shown in Fig. 3).

For composite samples, the number of layers was varied while keeping constant the relative volume fractions of VW+ and TB+. Fig. 4 summarizes the nominal thickness of the inner layers corresponding to each printed configuration (the two outer layers had always half the listed thickness). The interphase thickness was assumed equal to 20 and 150  $\mu\text{m}$ , based on nanoindentation results [23] for sharp and blurred scenarios, respectively. The volumetric fraction of the interphase was estimated accordingly for each configuration (AT or AW), number of layers and printing orientation (horizontal or vertical); relevant values are reported in Fig. 5. Printing of AT vertical samples with more than 4 layers proved unsuccessful, since the final geometry obtained was not sufficiently accurate in this case.

Finally, the effect of the relative content of the two constituents (VW+ and TB+) was investigated by producing modified 2-layers AT samples (horizontally printed) whose central TB + layer had increasing thickness corresponding to the following nominal (i.e. without considering the interphase) volume fractions of this constituent: 50% (standard, according to Fig. 4); 62.5%; 75%; 87.5%; 92%; 95%. All samples were produced in triplicates after calibrating the UV lamp to guarantee consistency of the curing process.

## 2.2. Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was carried out in tensile configuration with a RSA III Rheometrics System Analyzer (TA Instruments, US); for details on DMA background, the reader is referred to

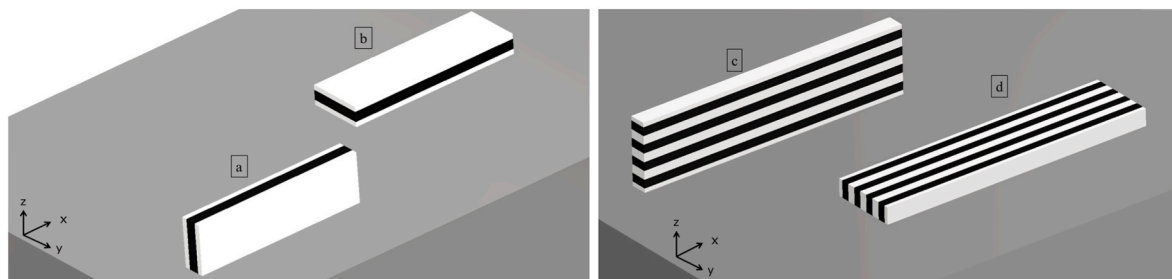


Fig. 3. Sketch of sample configurations: layers are stacked symmetrically on the left along the thickness (AT with 2 layers) and on the right along the width (AW with 8 layers). Each sample configuration can be printed according to vertical (a, c) or horizontal (b, d) orientation.



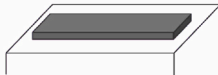
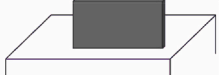
	along thickness (AT)			along width (AW)					
									
Type of interphase (sharp/blurred)	Sharp			Blurred			Sharp		
# of layers	AT2	AT4	AT8	AW8	AW16	AW32	AW8	AW16	AW32
individual layer thickness [mm]	500	250	125	680	340	170	640	320	160
	horizontal 						vertical 		

Fig. 4. Summary of the sample configurations investigated in the present study; for each one the type of interphase, number of layers and relevant layer thickness are reported.

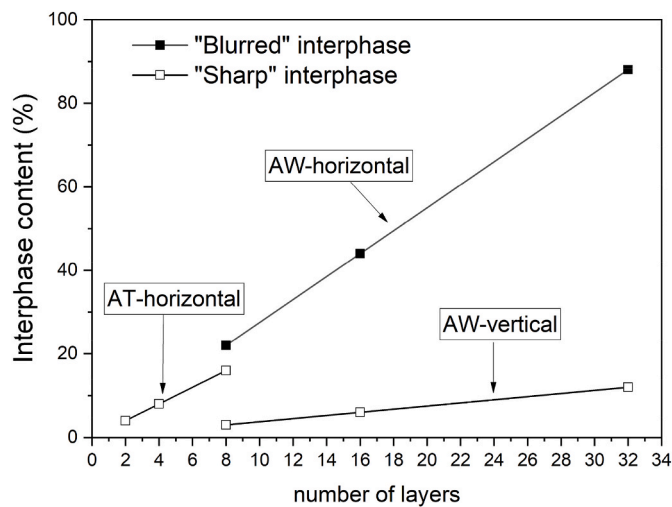


Fig. 5. Volumetric content of the interphase as a function of the sample configuration and printing direction: solid symbols refer to “blurred” interphase, whereas hollow symbols to “sharp” interphase.

Appendix. A temperature ramp was applied to measure the response in terms of storage modulus,  $E'$ , and of the major thermal transitions as detected by identifying the main peaks in the loss factor vs. temperature curves. The same heating rate (5 °C/min) used in Ref. [23] was applied, but the temperature range was extended in both directions to allow for completion of the glass transitions therein reported. Samples were first cooled from room temperature to −50 °C, stabilized for at least 5 min, and subsequently heated up to 80 °C. An oscillatory displacement resulting in 0.1% strain was applied along the main sample axis to keep the material within the linear viscoelastic regime; the selected frequency was 1 Hz, in agreement with our previous analysis [23]. Dynamic pre-tensioning of the sample was employed, adjusting the static force to 20% of the measured dynamic one to prevent complete unloading during the applied strain cycle. Force and phase angle data were collected every 12 s (i.e. every 1 °C). For each configuration, three samples were tested and results were averaged.

### 3. Preliminary tests

It is well known that many process parameters may affect the final properties of polymeric components, and this is true also for 3D-printed parts. In this section results of preliminary testing concerning curing

conditions and layer stacking are reported before moving on to the main objective of the investigation, to confirm the validity of the chosen approach.

#### 3.1. Effect of curing conditions

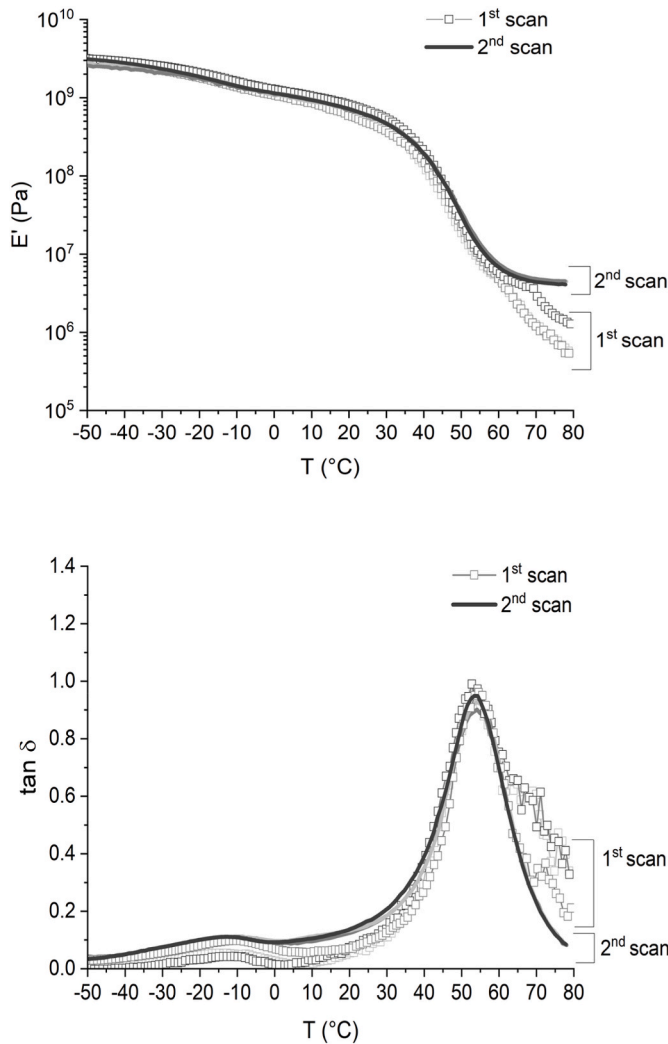
While exploring a broader temperature range with respect to our previous research [23], we observed some discrepancies in the data at high temperature obtained on supposedly identical samples. We attributed this unexpected variability to a non-uniform degree of crosslinking of the VW + phase in the newly printed samples. If the amount of UV radiation is not sufficient to ensure complete crosslinking, some variations may arise depending on the sample positioning on the printing tray. To confirm this hypothesis, we performed consecutive DMA scans interspersed by cooling cycles, always up to 80 °C as described in the previous section. A typical result of the comparison between the first two scans on the same VW + sample is displayed in Fig. 6.

The behaviour in the region above 60 °C is markedly different for the two scans. On the first one,  $E'$  data shows a continuously decreasing trend even above the reported glass transition of 54 °C for VW+ [23]. On the second run, a typical rubbery plateau is observed instead. Subsequent scans performed on the same samples produce data identical to the second one, and a very good repeatability of the data can be observed. This behaviour is common for all samples whose mechanical response depends on the presence of the VW + phase. The proposed interpretation is that standard curing conditions enforced by the Objet 260 printer do not ensure complete crosslinking of the VW + component, which is instead achieved by heating the sample up to 80 °C thereafter. Accordingly, a preliminary DMA scan was applied to all samples to make sure they were in the same state before actual testing. Results reported from now on belong to the 2nd scan performed on each sample.

#### 3.2. Effect of layer stacking sequence

To verify the independence of obtained results from the arrangement of the two constituent materials, the mechanical behaviour of samples having VW + or TB+ in the two outer semi-layers was compared. Results shown in Fig. 7 demonstrate how switching the two materials produces no effect even when only 2 layers (or, better, a single layer and two semi-layers) are present. This is by far the situation in which a possible influence of the spatial arrangement of the two materials with respect to the mid-section would be more easily identified and, accordingly, this scenario was not further considered.





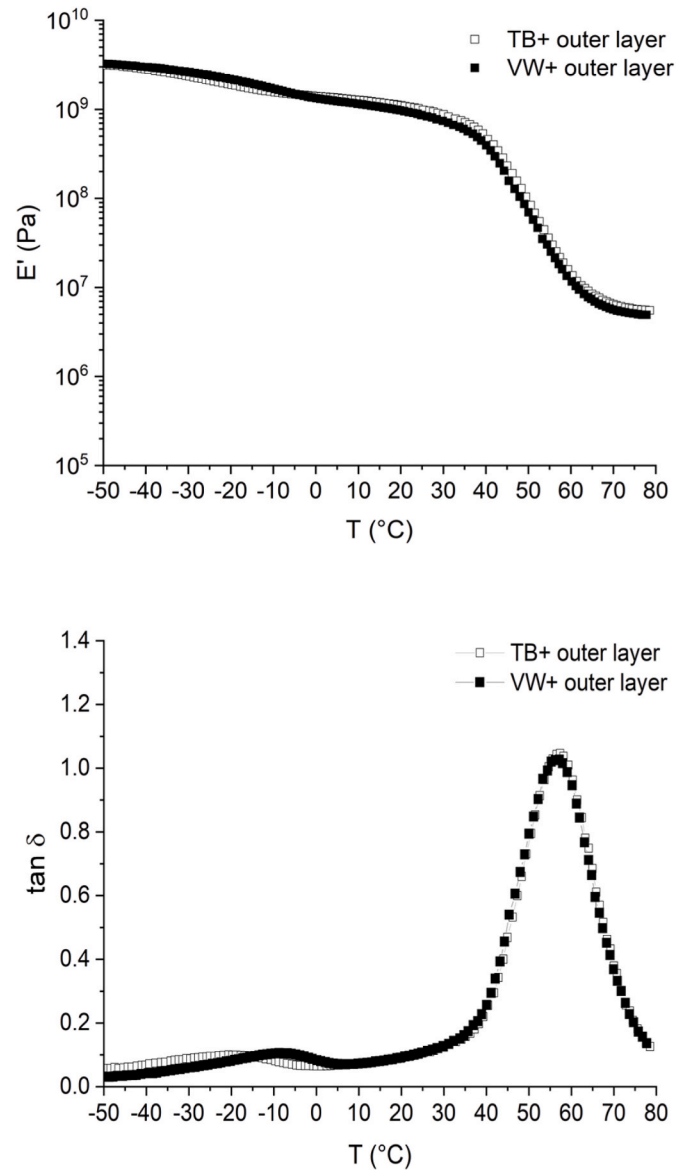
**Fig. 6.** Storage modulus (top) and loss factor (bottom) curves for horizontally printed AT samples with 2 layers: first scan (open square); second scan (continuous lines). The graphs also show an example of data repeatability (three samples) under same test conditions.

#### 4. Results and discussion

Moving now to the main findings, Fig. 8 shows results obtained on the two pure materials, VW+ and TB+. VW+ has a glass transition temperature of approximately 59 °C, across which the measured storage modulus decreases from the glassy plateau approximately at 3.5 GPa to the high-temperature rubbery plateau at about 10 MPa. In contrast, neat TB+ displays a glass transition temperature approximately at 6 °C across which the storage modulus is decreasing from 3 GPa to less than 1 MPa. It is worth noting that a single main peak can be detected in the loss factor curve of TB+. Other works based on DMA in tensile or compressive configurations also reported a single peak for similar rubbery constituents but at slightly lower temperature (−5 °C for TangoBlack [31] and −1 °C for Tango [32]).

##### 4.1. Composite samples: sharp and blurred interphase

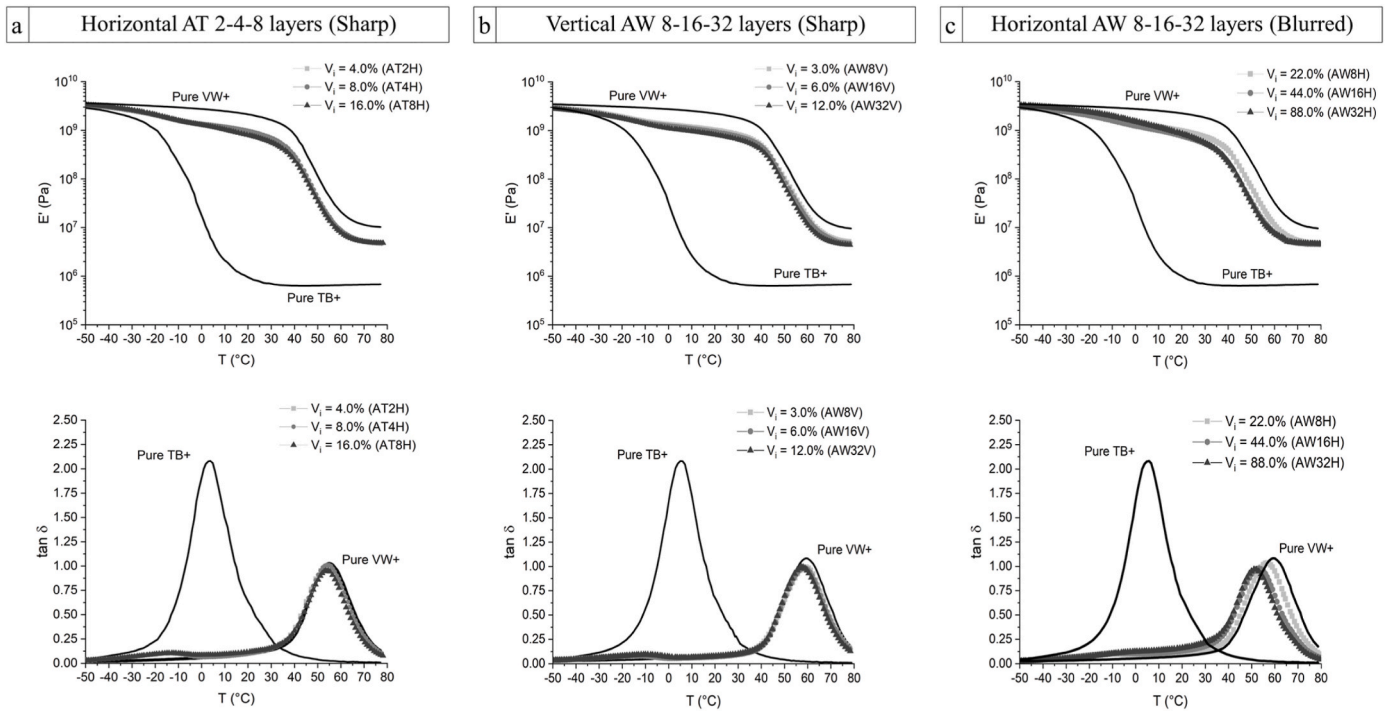
DMA data obtained on horizontally printed AT samples are reported in Fig. 8a. As expected, intermediate storage modulus values between those of pure VW+ and TB+ were obtained, in agreement with the nominal 50-50 ratio employed for all composites. In this case a sharp interphase is formed between adjacent layers; despite its larger surface (about 350 mm<sup>2</sup>, as opposed to about 70 mm<sup>2</sup> for AW configuration),



**Fig. 7.** Storage modulus (top) and loss factor (bottom) of a standard “horizontally”-printed 2-layer AT sample (VW + outside, TB + inside) and its counterpart with switched constituents.

estimated values of the total interphase volume do not exceed 16% of the overall sample volume. Accordingly, no significant effect of this variable (strictly associated to the number of layers) was observed. The same is true for loss factor data, in which curves for 2, 4 and 8 layers are almost identical. They are very similar to the reference VW+ curve, with a main loss peak shifted by only a few degrees towards lower temperatures, a fact that can be easily explained assuming a predominantly glassy (i.e., akin to that of VW+) behaviour of the interphase but allowing for a limited miscibility of the rubbery TB+ phase; this result is in accordance with previous findings [23]. A closer inspection of the loss factor curves for the AT composites reveals an additional peak, located at about −11 °C, in place of the main TB+ one at 6 °C which is almost completely suppressed in the composites. Its nature will be discussed later, once the results for the composite materials with higher TB+ content will be presented.

DMA scans of vertically printed AW samples are reported in Fig. 8b. Also in this case formation of a sharp interphase is expected. While its area is smaller, compared to AT configuration, the increased number of layers brings about a total interphase volume of 12%, which is



**Fig. 8.** Storage modulus (top) and loss factor (bottom) of pure VW+, pure TB+ (continuous lines) and composite samples, labelled according to the corresponding nominal values of interphase volume fraction shown in Fig. 5. The nomenclature used in the legend indicates: samples configuration (along width - AW or along thickness - AT), number of layers (2-32) and printing orientation (horizontal - H or vertical - V).

comparable to that of horizontally printed AT samples, as visible from Fig. 5. Accordingly, DMA results are similar for the two cases: again, no evident effect of the (relatively limited) interphase volume fraction is apparent in the data with the curves corresponding to 8, 16 and 32 layers being practically superimposed.

To explore the behaviour of composites having a very high volume fraction of interphase, horizontally printed AW samples were investigated. Again, the number of layers was set at 8, 16 and 32. In particular the 32-layer configuration was designed to be constituted almost completely by interphase: the layer thickness in this case (170  $\mu\text{m}$ ) practically coincides with the estimated dimension for the blurred interphase ( $\sim 150 \mu\text{m}$ ) [23]. This coincidence was exploited in the model presented later in this paper, by assuming the behaviour of this particular material to be representative of the blurred interphase. Relevant results are shown in Fig. 8c. At variance with those obtained at lower interphase content, an effect of its volumetric fraction is visible: the storage modulus in the transition region is appreciably lower for the high-volume interphase samples (16 and 32 layers, whose  $V_i$  is 44% and 88%, respectively). In a similar way, the main loss factor peak for 16- and 32-layers horizontally printed AW samples is further shifted towards a lower temperature (about 50  $^{\circ}\text{C}$ ) with respect to the rest of the data. These results support the assumption that the material of the 32-layer samples is entirely made up of blurred interphase, whose behaviour is very close to that of VW+ alone; the slight reduction observed in the glass transition temperature is justified by the high content (50%) of TB+ in this monophasic blend, which yet remains glassy at room temperature. A qualitatively similar behaviour was observed in our previous work when considering samples with a layer thickness comparable to interphase dimension [23].

#### 4.2. Parallel analog model

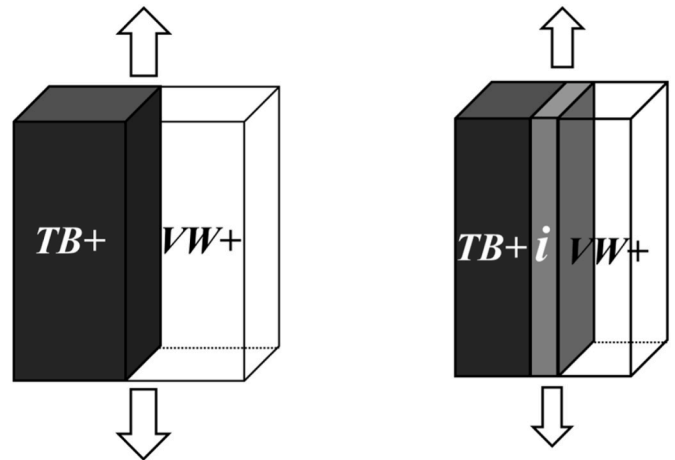
To improve understanding of the data, measured properties were compared by considering the constituents of the specimen in a parallel configuration, with and without the explicit presence of a third inter-

phase in addition to the two main VW+ and TB+ phases (see Fig. 9). Assuming DMA results obtained on pure VW+ and TB+ (continuous curves in Fig. 8) as reference values for the two constituents, the corresponding composite apparent elastic modulus and loss factor were computed for each temperature as the weighted average of the in-phase and out-of-phase components  $E'$  and  $E''$ :

$$E' = \sum_n v_n E'_n \quad (1)$$

$$E'' = \sum_n v_n E''_n \quad (2)$$

$$\tan \delta = \frac{E''}{E'} = \frac{\sum_n v_n \tan \delta_n E'_n}{\sum_n v_n E'_n} \quad (3)$$



**Fig. 9.** Analog models based on the rule of mixture for parallel configuration composites: without (left) and with (right) the explicit presence of the interphase.

In which  $v_n$ ,  $E'_n$  and  $E''_n$  are the volume fraction, storage and loss modulus and  $\tan\delta_n = \frac{E''_n}{E'_n}$  is the loss factor of the  $n_{th}$  phase. A detailed derivation of Equations (1)–(3) is provided in the Appendix.

As previously mentioned, the effective properties of the interphase were taken from the results of the 32-layer horizontally printed AW material, which had interphase content highly predominant over pure TB+ and VW+ phases.

Predictions of the model were compared with relevant experimental data. Fig. 10 shows model results for 8- and 16- layers horizontally printed AW samples, whose estimated volume fraction of (blurred) interphase is equal to 22% and 44%, respectively. Considering first a simpler model, corresponding to a sequence of pure alternating layers (of VW+ or TB+) with an ideal, zero-thickness interface, predicted values of the storage modulus are much higher than experimental ones in the main glass transition region, especially for the sample with  $V_i = 44\%$ . In turn, the model explicitly considering the presence of the interphase volume fraction provides a much better agreement with the experimental data. This observation is quantitatively supported by root mean square error (RMS) evaluation of  $\log E'$  vs.  $T$  data performed in both cases, which is reduced by 40% for the model with the interphase (Fig. 11). The comparison of predicted vs. experimental loss factor curves gives similar results, with the interphase model being more accurate especially at high interphase volume fraction. In particular at room temperature the more refined model is always closer to the experiments than its simpler version.

It is worth observing that the real situation is obviously more complicated than the idealized distinction between the two constituent materials and a “pure” interphase, because interdiffusion among the different phases will result in a graded material. The description of a

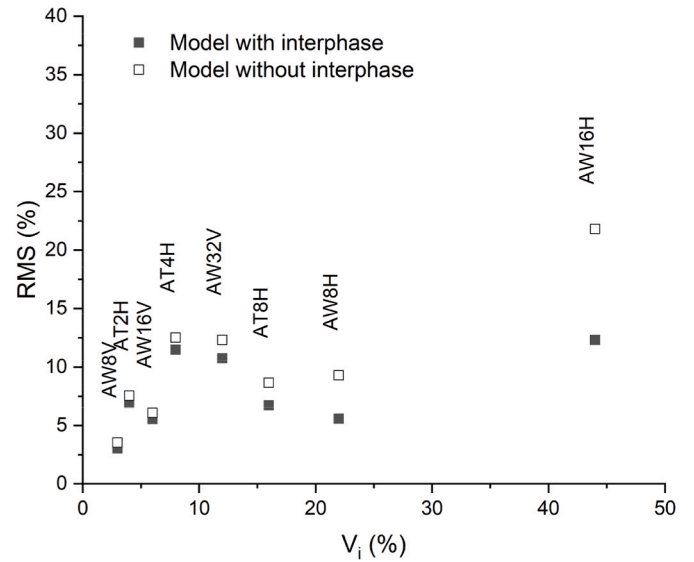


Fig. 11. RMS comparison between model prediction and experimental  $\log E'$  data for all tested samples, considering and neglecting the interphase.

graded region would require a certain number of additional parameters whose identification poses quite a challenge [28]. Nevertheless, the proposed simplified approach succeeds in giving accurate predictions, at the same time demonstrating how the presence of a blurred interphase between the two pure phases should be considered in view of a correct evaluation of the final composite properties. It is not limited to a

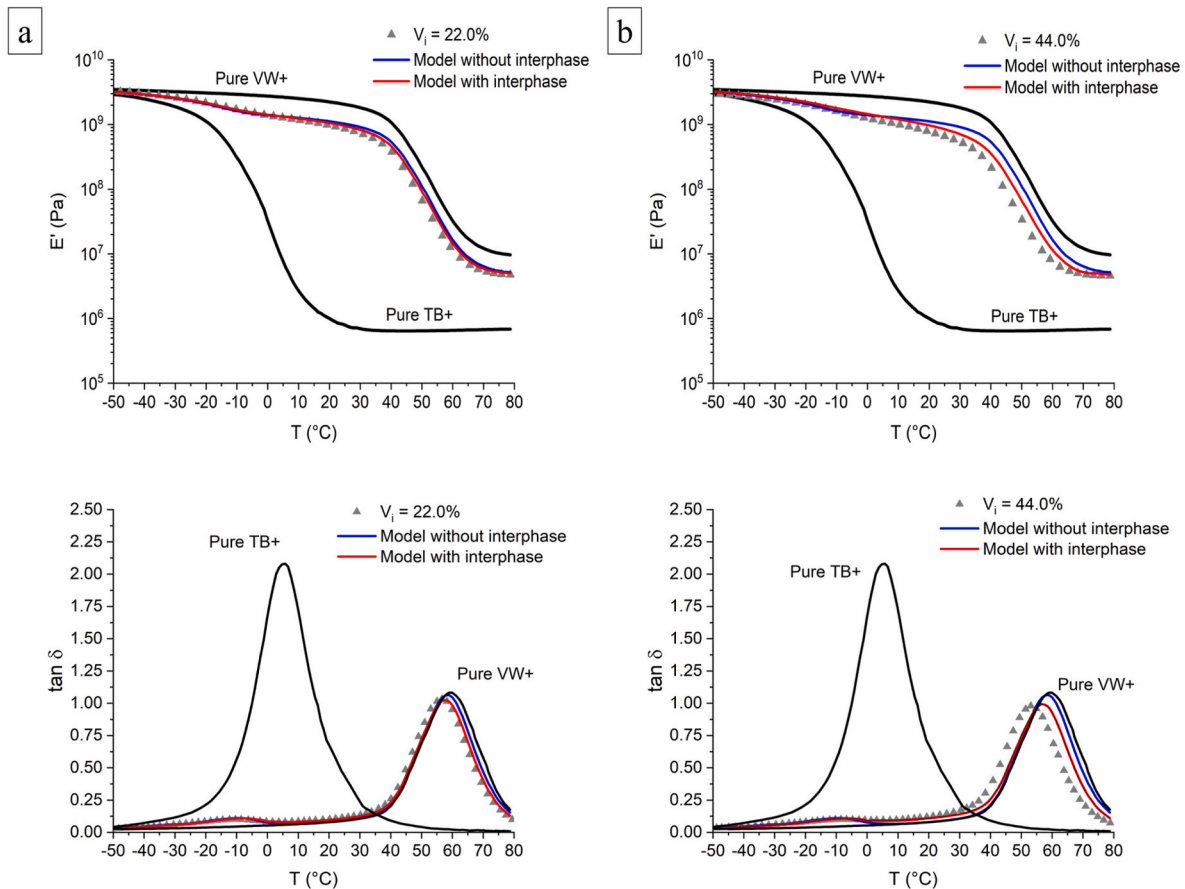


Fig. 10. Comparison between experimental data and model predictions for modulus (top) and loss factor (bottom), with and without interphase, for a) 8- and b) 16- layers horizontally printed AW samples. Samples are labelled according to the theoretical interphase volume fraction.

particular choice of materials or to a specific geometrical configuration, since it could be easily extended to any similar composite material produced via photo-polymerization provided properties of the constituents and the relevant interphase are firstly obtained. With a more detailed knowledge of the relationship between the printing orientation and the interphase thickness (currently limited to the extreme conditions corresponding to a “sharp” and “blurred” situation), the approach could be transferred to a more sophisticated (e.g. numerical) model able to predict the behaviour of composite structures of any geometry.

Considering the extensive usage of multimaterial Polyjet printing and the increasing interest in optimizing and predicting the behaviour of the printed composites with the support of numerical models [15,29,33,34] our results demonstrate that neglecting the presence of a significant fraction of interphase will inevitably affect the accuracy of these predictions. This is clearly true for the (visco)elastic properties at very small strains considered so far. However, it is likely to become even more important when considering more localized phenomena such as yielding and fracture processes [28,30,35], for which the coupling between materials (i.e. the two constituents and their interphase) possessing different yielding/damage mechanisms will certainly give rise to a complex interplay between material composition, spatial arrangement and processing parameters. These considerations are not limited to Polyjet 3D printers, but are equally relevant for any other 3D printing technique involving multi-material photopolymerization.

#### 4.3. Effect of sample composition

The final set of results considered in the present work concerns the effect of the material composition. Dynamic mechanical behaviour of samples having an unbalanced composition (in terms of the two constituents) ranging up to 95% TB+ was investigated; TB+ content lower than 50% was not considered since the 50:50 samples already demonstrated a behaviour close to the one of the pure glassy polymer. Data shown in Fig. 12a display a quite obvious trend, with the storage modulus of composites with increasing fraction of TB+ steadily approaching the values of the reference pure material. However, the shape of the curves is different and it is interesting to look at loss factor data (Fig. 12b) to analyse the two distinct loss peaks so far reported for many composite materials (Fig. 8). As soon as the TB+ volume fraction increases above 50%, their characteristic low-temperature loss peak at about  $-11^{\circ}\text{C}$  appears. Such low temperature transition was clearly observed in the multilayer samples as well as in the pure TB+ when tested in three-point-bending [23]. The peak amplitude progressively

increases and it shifts towards higher temperatures with increasing TB+ content, although even at a value as high as 95%, the amplitude is still nearly an order of magnitude less than the corresponding pure TB+ value: even a very small fraction of VW+ aligned with the loading direction can be very effective in suppressing viscoelastic dissipation of the composites. Considering the “glassy” high temperature peak at about  $59^{\circ}\text{C}$ , it remains substantially unaffected by an increasing content of TB+ until the highest value considered (95%) is reached. At this stage, the nominal amount of pure VW+ phase left is only 5%, as the remaining volume is almost completely taken up by the interphase. When this occurs, the peak shifts towards lower temperatures. Fig. 12 shows also the prediction of the parallel model presented earlier. Although the interphase volumetric fraction is rather small in this case (about 4%), the generally more accurate version accounting for its presence was used. The model well captures the reported trends generated by the increase in TB+ content, although the accuracy of its prediction decreases especially for the highest value of 95%. With such high a volume of rubbery phase, discrepancy may be expected because of a generalized loss of constraint (away from the rigid glassy or inter-phases) in the experiment.

It is worth noticing that the model predicts the slight reduction of the low-temperature loss peaks in the composite compared to that of pure TB+. This result is a direct consequence of considering a parallel model to obtain both storage and loss moduli of the composite and agrees with findings obtained by Dickie [36], who analysed composite structures having a rigid continuous matrix and soft dispersed particles by developing an equivalent mechanical model based on the Kerner equation. Depending on the ratio between the storage moduli of the two phases, the author showed that indeed a shift of the loss peak of the dispersed soft phase towards lower temperatures is expected, which becomes larger with decreasing soft phase volume content. Although the multilayer composites characterized here are not traditional matrix-inclusion systems, their dynamic mechanical behaviour show some analogy with the composites therein described. Accordingly, the observed loss peak should be considered as emerging from the complex dynamic interaction between the two phases and thus being representative not only of the glass transition of pure TB+, but also of the energy dissipation occurring following its incorporation in the composite, whose elastic behaviour is still dominated by the (at this temperature) glassy VW+ phase.

#### 5. Conclusions

This study explored the role of the interphase in 3D printed

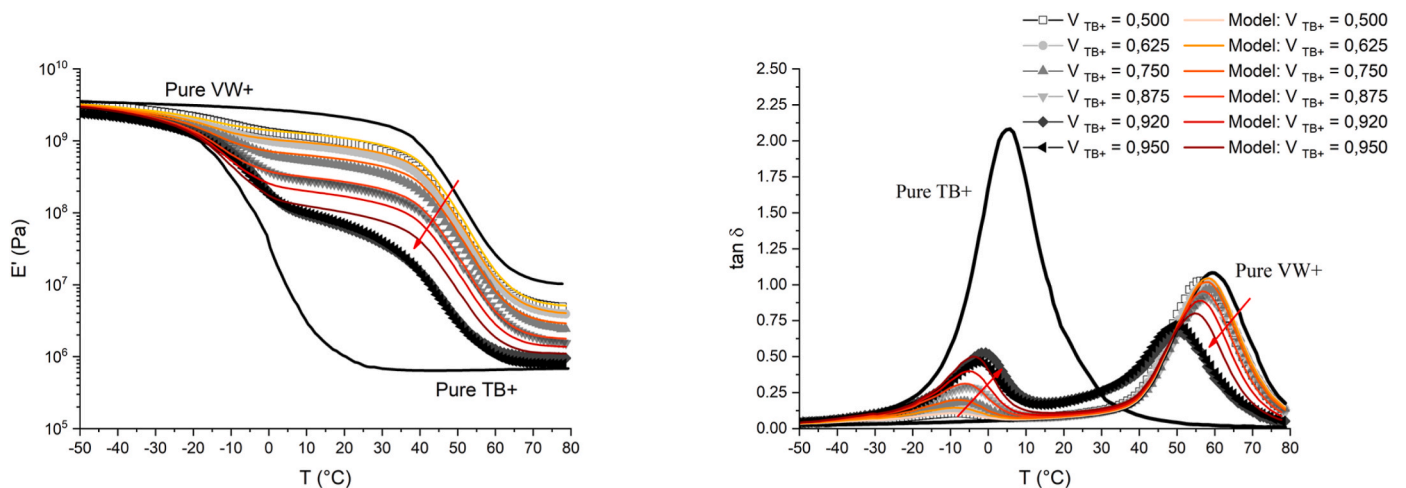


Fig. 12. Storage modulus vs temperature (a) and loss factor vs temperature (b) curves of samples with increasing volumetric fraction of TB+ (from 50% up to 95%) compared to pure TB+ and VW+ behaviour (black continuous lines). The coloured lines represent the behaviour according to the model taking into account the presence of the interphase; arrows represent the variation of the model prediction with the increasing volume fraction of TB+.



composites (fabricated via Polyjet technology) through tensile (dynamic) mechanical analysis performed on composite samples, prepared by stacking an equal number of layers made of two different polymers (one rubbery and the other glassy at room temperature) in various spatial configurations. The selected loading condition is favourable because a uniform stress state is enforced on every single layer, thus allowing the application of a very simple parallel model whose output was later compared with experimental results.

Firstly, we showed that the intrinsic variability in the mechanical behaviour of nominally identical 3D printed samples can be imputed to incomplete curing and such variability can be reduced by a proper thermal treatment.

It was found that for relatively low volume contents of interphase (below 20%) its presence could be neglected, since the samples substantially behave like the ideal bi-material composite they are meant to represent, with no or very little effect of the number and spatial arrangement of the different material layers. Conversely, when the volume fraction of the interphase is further increased because of the high number of layers and/or of the specific printing orientation, a clear effect can be observed. In fact, the interphase represents in this case a third constituent material whose behaviour is demonstrated to be quite similar to that of the base glassy polymer.

This was justified by a further study in which the composition of the samples was altered to include progressively larger fractions of the rubbery material. Results clearly showed that even modest volume fractions of the rigid glassy polymer (less than 10%) are sufficient to obtain an overall behaviour which substantially deviates from that of the pure rubbery constituent.

The model predictions compared well with all the previous findings. Interphase properties were determined by analysing many-layered

samples which were almost completely made up of this third constituent. Two variants were considered, with and without the explicit presence of the interphase. While the two agree well for low interphase content, the superiority of the model which also includes it was clearly demonstrated in the case of higher values.

The results provided by the present investigation are of great importance for the purpose of modelling the behaviour of complex co-continuous architectures (such as Interpenetrating Phase Composites) which are often seen as a way to create bio-inspired materials with tuneable properties. Due to the typically very large interface area generated in these structures, a strong influence of interphase properties is expected and the models used for their optimization need to take it into account. These findings, which are already significant when considering the small-strain (visco)elastic behaviour of co-continuous composites, may become critical if larger deformations are involved: the associated phenomena (namely yielding and fracture) are often very localized and may be dominated by the characteristics of the interphase.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix

In dynamic-mechanical tests, a sinusoidal strain history is applied to the material:

$$\varepsilon(t) = \varepsilon_0 \sin(\omega t) \quad (4)$$

with  $\varepsilon_0$  being the applied strain amplitude and  $\omega$  the corresponding angular frequency.

If the material exhibits a viscoelastic behaviour, its response is a sinusoidal stress  $\sigma$  which is out of phase by a phase angle  $\delta$ .

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta) \quad (5)$$

The material response can be decomposed into its in-phase and quadrature components:

$$\sigma(t) = \sigma_0 \cos(\delta) \sin(\omega t) + \sigma_0 \sin(\delta) \cos(\omega t) = \sigma_0' \sin(\omega t) + \sigma_0'' \cos(\omega t) \quad (6)$$

The first term represents the typical response of an ideal elastic (conservative) solid, while the second one of an ideal viscous (dissipative) fluid. From the decomposition, two properties can be defined:

i) storage modulus, the conservative component of the dynamic modulus

$$E' = \frac{\sigma_0'}{\varepsilon_0} = \frac{\sigma_0 \cos(\delta)}{\varepsilon_0} \quad (7)$$

ii) loss modulus, the dissipative component of the dynamic modulus

$$E'' = \frac{\sigma_0''}{\varepsilon_0} = \frac{\sigma_0 \sin(\delta)}{\varepsilon_0} \quad (8)$$

Furthermore, the loss factor is defined as the ratio between loss and storage moduli.

$$\tan(\delta) = \frac{E''}{E'} \quad (9)$$

$E'$ ,  $E''$  and  $\tan(\delta)$  are material properties which depend on both  $\omega$  and the temperature,  $T$ .

Now considering a bimaterial parallel model as the one shown on the left in Fig. 9, its behaviour in terms of global stress and strain ( $\sigma$  and  $\varepsilon$ , respectively) is described by the following equations:

$$\sigma = v_{TB+} \sigma_{TB+} + v_{VW+} \sigma_{VW+} \quad (10)$$

$$\varepsilon = \varepsilon_{TB+} = \varepsilon_{VW+} \quad (11)$$

In which  $v_{TB+}$  and  $v_{VW+}$  represent the volume fractions of the two phases.

By assuming that each of the two materials obeys Equations (7) and (8), with relevant properties identified by the proper subscript, the following relationship can be obtained:

$$\sigma = (v_{TB+}E'_{TB+} + v_{VW+}E'_{VW+})\varepsilon_0 \sin(\omega t) + (v_{TB+}E''_{TB+} + v_{VW+}E''_{VW+})\varepsilon_0 \cos(\omega t) \quad (12)$$

This leads to the identification of the following equivalent properties for the bimaterial composite:

$$E' = v_{TB+}E'_{TB+} + v_{VW+}E'_{VW+} \quad (13)$$

$$E'' = v_{TB+}E''_{TB+} + v_{VW+}E''_{VW+} \quad (14)$$

$$\tan(\delta) = \frac{E''}{E'} = \frac{v_{TB+}E''_{TB+} + v_{VW+}E''_{VW+}}{v_{TB+}E'_{TB+} + v_{VW+}E'_{VW+}} \quad (15)$$

The generalization to the case of  $n$  phases (e.g.  $n = 3$  with the interphase) is straightforward and leads to Equations (1)–(3).

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