

WARPAGE OF FIBER-REINFORCED THERMOSET POLYMERS CO-BONDED TO THERMOPLASTICS

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ABSTRACT

Co-bonding process often results in residual stresses leading to shape distortions. Understanding the formation of residual stresses and identifying the influence of the interaction between the co-bonded parts is required to optimize the manufacturing process of the hybrid composites. In this study, the warpage in fiber-reinforced thermosets co-bonded to thermoplastics is quantified and correlated to the interphase thickness between the co-bonded polymers. Two different thermoplastic plates, which result in distinct interphase thicknesses, are used for the co-bonding experiments. Strains are monitored with strain gauges placed on the already manufactured thermoplastic plates. The final warpage is measured using a coordinate measurement machine. Extensive process-induced deformations are observed for the hybrid composites. A larger interphase thickness correlated with a lower degree of warpage.

1. INTRODUCTION

Co-bonding is a manufacturing process in which a prefabricated insert is bonded with the base fiber reinforced thermoset polymer (FRTP) through the curing reaction of the thermoset resin, as illustrated in Figure 1. Co-bonded hybrid composites are preferred due to various reasons: they may offer superior mechanical performance over their single composite counterparts or facilitate cost-effective manufacturing by allowing the use of prefabricated parts that are cheaper to manufacture [1]. A recent application of the co-bonded hybrid composites is the Leading Edge Protection (LEP) of wind turbine blades, where an impact-resistant, tough thermoplastic is co-bonded to the base laminate of the wind turbine blade made of FRTP [2].

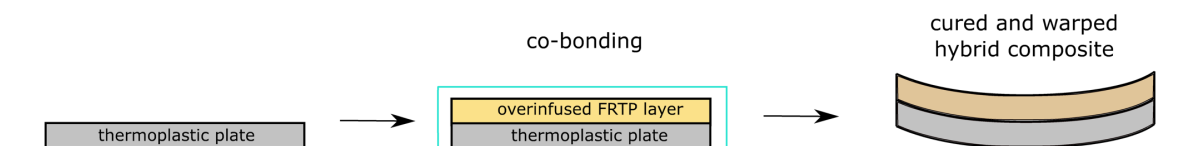


Figure 1: Schematic representation of the co-bonding process. Adapted from [3].

The co-bonding process often results in residual stresses leading to shape distortions (warpage). Understanding the underlying mechanisms of residual stress formation and the resulting warpage is required to optimize the manufacturing process and to develop process models, which will eventually facilitate widespread use of the hybrid composites.

Studies show that in addition to the factors such as the cure shrinkage, mismatch in the coefficient of thermal expansion of the two parts, and material anisotropy, the interaction between the parts (either between the tool and the cured composite or the co-bonded materials) also plays a significant role in the resulting warpage [3–5]. During the co-bonding process, polymer interdiffusion takes place between the co-bonded parts, which results in the formation of an interphase which has different properties than the bonded parts. The size of the interphase (interphase thickness) highly depends on the thermodynamic affinity between the bonded polymer materials, physical state of the thermoplastic, i.e. whether it is above or below its glass transition (T_g), and the viscosity and the gelation time of the thermoset resin [6–8]. For instance, a lower viscosity and a higher gelation time of the resin both promote a higher interphase thickness [6, 7]. This is because a lower viscosity results in an enhanced mobility of the polymer molecules and a higher gelation time provides more time for the molecules to diffuse. A survey of the literature shows that the warpage of the FRTPs co-bonded to thermoplastics and the effect of interphase on the resulting warpage was not investigated before.

In this study, the aim is to quantify, for the first time, the warpage in glass fiber-reinforced polyester co-bonded to thermoplastics and investigate its correlation to the level of interdiffusion between the two polymers. Already manufactured thermoplastic (TP) plates are co-molded with glass fabric infused by resin/initiator mixture. Warpage and the effect of interphase are investigated through two different manufacturing cases involving different TP plates, namely polycarbonate (PC) and polyvinyl chloride (PVC), which have remarkably different affinities to polyester resin. The evolution of process-induced residual strains during the co-bonding process is monitored by means of strain gauges placed on the already manufactured TP plates. After manufacturing the hybrid composites, warpage is measured via a coordinate measuring machine. Process-induced warpage is finally correlated to the interphase morphology (thickness) between the co-bonded materials.

2. EXPERIMENTATION

2.1 Materials

Unsaturated polyester resin (UPR) was used as the matrix of the FRTP, which was preferred for wind turbine blades thanks to its processability and cost-effectiveness. The resin was cured with a liquid peroxide initiator, where the ratio of the weight of the initiator to that of UPR is 1.5%. Fiber reinforcement of the FRTP was a glass fabric with a total areal weight of 750 g/m² composed of unidirectional (UD) roving (660 g/m²) and random filaments and stitching (90 g/m²). As TP materials, PC and PVC plates with a thickness of 2 mm were used. These materials were chosen since they have distinct thermodynamic affinities to UPR [6].

2.2 Characterization of the interphase, resin, and thermoplastics

To correlate the level of warpage with the interphase thickness, interphase between the TP polymers and neat UPR was investigated. Small pieces of TP plates with dimensions of 18 mm x 15 mm were embedded in UPR in cylindrical cups of 25 mm diameter. The embedded samples were polished using a Struers Tegramin 30 polisher. The interphase morphology was observed and the thickness was measured via a Keyence VHX-7000 digital optical microscope.

To investigate the relationship between the process-induced strains and the degree of cure, cure kinetics of the resin was characterized using Mettler-Toledo Differential Scanning Calorimetry (DSC) via an isothermal run of a resin-initiator mixture of about 20 mg.

Modulus of elasticity of the rectangular samples cut from TP plates was measured using a Zwick Retroline 1445 universal tensile tester. The modulus was found to be 2.17 ± 0.01 GPa for PC and 3.06 ± 0.06 GPa for PVC. This data was used later to evaluate the resulting warpage.

2.3 Laminate manufacturing

To manufacture the hybrid composites, first, two layers of dry glass fiber reinforcement were placed over a thermoplastic plate (200 mm x 250 mm) which had biaxial strain gauges at the mid-point of both surfaces to measure the process-induced strains. A thermocouple was placed between the TP plate and the fabric, close to the edge of the plate, to measure the temperature during processing. For the fiber-reinforced polyester to be balanced, the two layers of fabric were placed such that the random fibers from different layers face each other. UD fibers of the fabric were oriented along the short side of the plate. In order to allow the laminate to warp during processing, a vacuum bag was used on both sides of the stack. A schematic illustration of the stack is provided in Figure 2.

After the stack was prepared, the resin was mixed with the initiator for 3 minutes and degassed for about 15 minutes until the entrapped air was removed from the mixture. Later, the stack was impregnated with the resin-initiator mixture in a vacuum-assisted resin transfer molding process and left for curing at room temperature for 24 hours. After the curing was complete, the hybrid composite was trimmed to dimensions of about 190 mm x 240 mm, and, thereupon the warpage was measured using Crysta-PlusM 544 Mitutoyo Coordinate Measuring Machine (CMM).

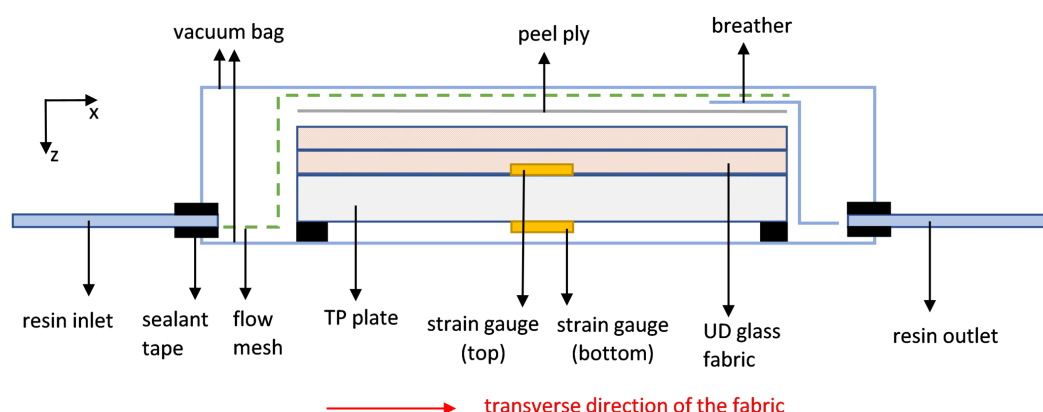


Figure 2: Schematic representation of the stack and vacuum-assisted resin transfer molding (VARTM) setup.

3. RESULTS

3.1 Interphase morphology

Optical micrographs of the interphase between the thermoplastics and UPR are shown in Figure 3. The average of the interphase thickness measured from the two surfaces of the TPs was $54 \mu\text{m}$ for PVC-UPR and $446 \mu\text{m}$ for PC-UPR. This substantial difference in the interphase thickness for the two different TPs stems from their different level of affinities to UPR, which is supported by Hansen Solubility analysis in [6].

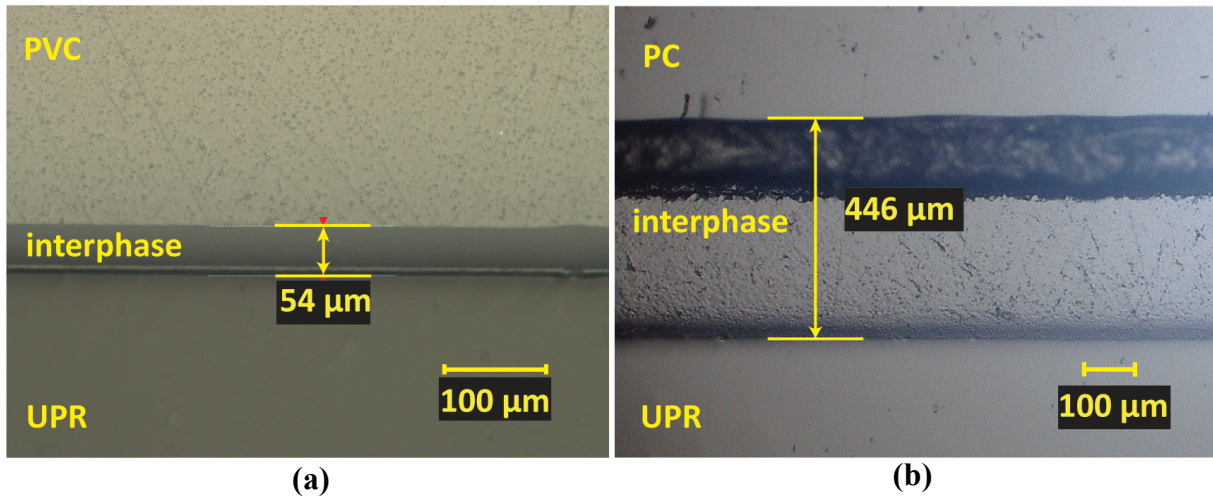


Figure 3: Optical micrographs of (a) PVC and (b) PC embedded in UPR.

3.2 Cure kinetics

Heat flow vs. time curve from an isothermal run at 25°C is provided in Figure 4a. Using the curve, upon constructing a baseline, the heat of cure was calculated to be 236 J/g. The heat of cure is used to calculate the normalized degree of cure, where the normalized degree of cure is defined as the ratio of heat of cure at a specific time to the total heat of cure. The evolution of the degree of cure with time is shown in Figure 4b. Volumetric shrinkage of the resin starts at the gelation point, where the degree of cure is around 0.15 for the polyester resin [3], and increases linearly to its maximum value when the degree of cure reaches 1 [9]. Resin shrinkage strain is related to the volumetric shrinkage via the relation $\Delta\varepsilon_r = \sqrt[3]{1 + \Delta V_{sh}} - 1$, where $\Delta\varepsilon_r$ is the change in shrinkage strain as a result of volumetric shrinkage of ΔV_{sh} . This relation results in an almost linear trend between the shrinkage strains and the degree of cure dependent volumetric shrinkage. Hence, the trend of the of shrinkage strains leading to warpage vs. time is expected to be similar to the trend of degree of cure shown in Figure 4b.

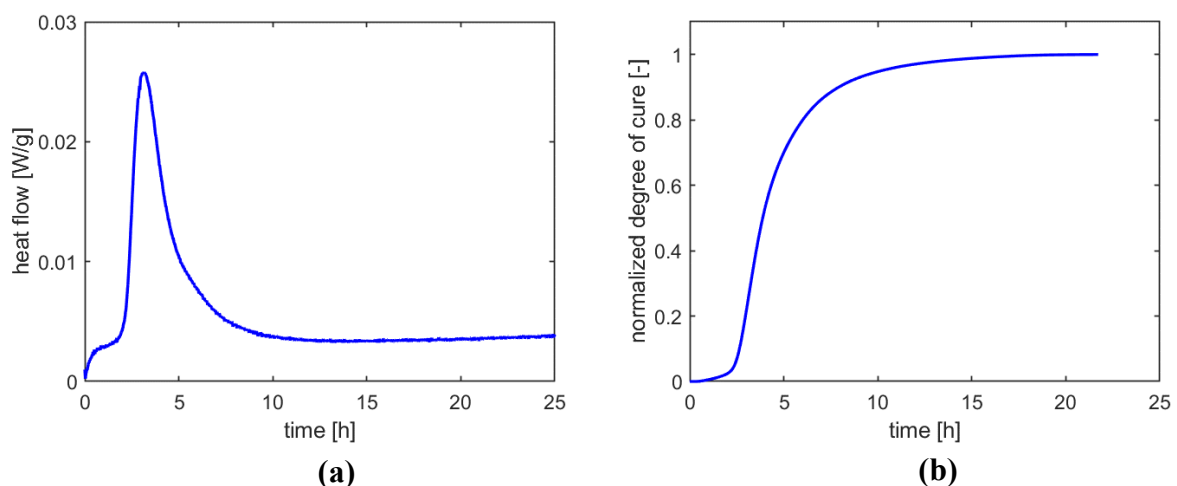


Figure 4: (a) DSC curve of UPR for an isothermal run at 25°C and (b) the evolution of the degree of cure.

3.3 Evolution of strain and temperature

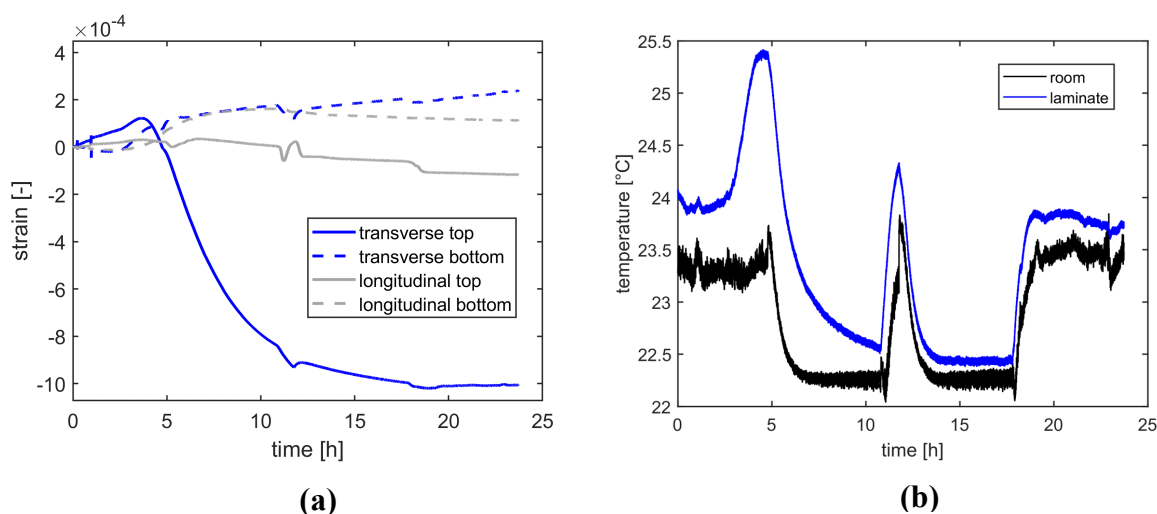


Figure 5: Evolution of (a) strains and (b) temperature with time during processing.

To illustrate the evolution of strains in hybrid composites during processing, the data obtained from the strain gauges are provided in Figure 5a for PVC-polyester/glass. It is seen that, transverse strains are observed to be larger than longitudinal strains, which can be explained by much larger shrinkage of the FRTP layer in the transverse direction. Since the strains in the longitudinal direction remain small, in the rest of this paper, we are going to focus mostly on the strains in the transverse direction. Temperature of the laminate and the room during processing is shown in Figure 5b. The temperature increase of the laminate due to curing was about 1.5°C , attained about 4.5 hours after the start of infusion. This time corresponded to the peak time of the isothermal DSC runs shown in Figure 4a. This temperature increase and other changes in the laminate temperature seen in Figure 5b are reflected on the strain readings shown in Figure 5a. Another correlation between the DSC data and strains can be found by comparing the largest strain reading, which is the transverse strain at the top, and the evolution of the degree of cure shown in Figure 4b. The comparison shows that the trend of strain vs. time and degree of cure vs. time are quite similar. This indicates that the strains in the hybrid composite result from the degree of cure dependent shrinkage of the resin in the FRTP layer.

Another remarkable finding on the process-induced strains was that the transverse strains at the **top** side were far larger as compared to those at the **bottom** side of the TP plate. A simple analytical explanation for this observation can be proposed by considering the load transfer from the shrinking FRTP layer on the TP plate, as illustrated in Figure 6, where only one-half of the TP plate is shown considering that the deformations take place symmetrically to z-axis at its mid-length. As the FRTP shrinks, it exerts a force on the TP plate. When moved to the centroid of the TP plate, this force results in a moment. The resulting normal force and the bending moment eventually create stresses in the TP plate. Since the stresses resulting both from the normal force and the bending moment are compressive at the top of the TP plate, larger strains are observed there. Conversely, stresses at the bottom have opposite signs, resulting in a lower tensile strain compared to the compressive strain at the top surface of the TP plate.

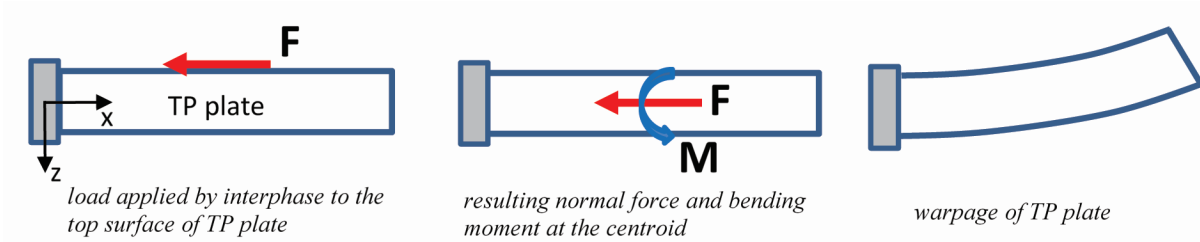


Figure 6: Simplified analytical explanation for the strain trend experimentally observed (F:force, M:moment).

3.4 Warpage

Having discussed the evolution of process-induced strains, in this section, the final warpage of the two hybrid composites measured by the CMM is presented. Figure 7a shows a 3-D plot of the coordinates of the warped laminates. Similar to lower strain readings in the longitudinal direction, the warpage in the longitudinal direction was found to be also quite low as compared to that in the transverse direction for both hybrid composites. To illustrate the warpage in the transverse direction more clearly, coordinates of the deformed hybrid composite are plotted in the xz -plane at their mid-width ($y=95$ mm). A remarkable finding is that the PC-polyester/glass exhibited a lower level of warpage, although the TP plate in PC-polyester/glass had a lower modulus. Without considering the presence of the interphase and assuming perfect bonding between the FRTP and the TP plate, one would expect PC-polyester/glass to exhibit more warpage due to its lower overall modulus. However, our observation shows that the presence of a larger interphase, as in the case of PC-polyester/glass, tends to decrease the warpage. This implies that the load transferred to the TP plate via the interphase decreases as the interphase thickness increases. It should be borne in mind that the bonding that takes place via the co-bonding process is very distinct from the perfect bonding since the mechanical properties of the interphase such as the interphase modulus evolve as the curing takes place. This means that the overall modulus of the interphase during processing is very low compared to its final value, which would allow significant relative displacement between the over-infused part and the TP plate [3] and eventually affect the load transfer.

The load transfer from the shrinking FRTP layer to the TP plate should take place via the interphase, which has a certain thickness and stiffness. Therefore, both of these aspects are expected to influence the load transfer. For instance, a larger interphase or interface stiffness is shown to result in a larger load transfer [3]. In our case, the stiffness of the interphase is not known yet. However, assuming that the interphase stiffness would be proportional to the stiffness of the TP plates, more load transfer that takes place in PVC-polyester/glass would agree with the expected larger interphase stiffness.

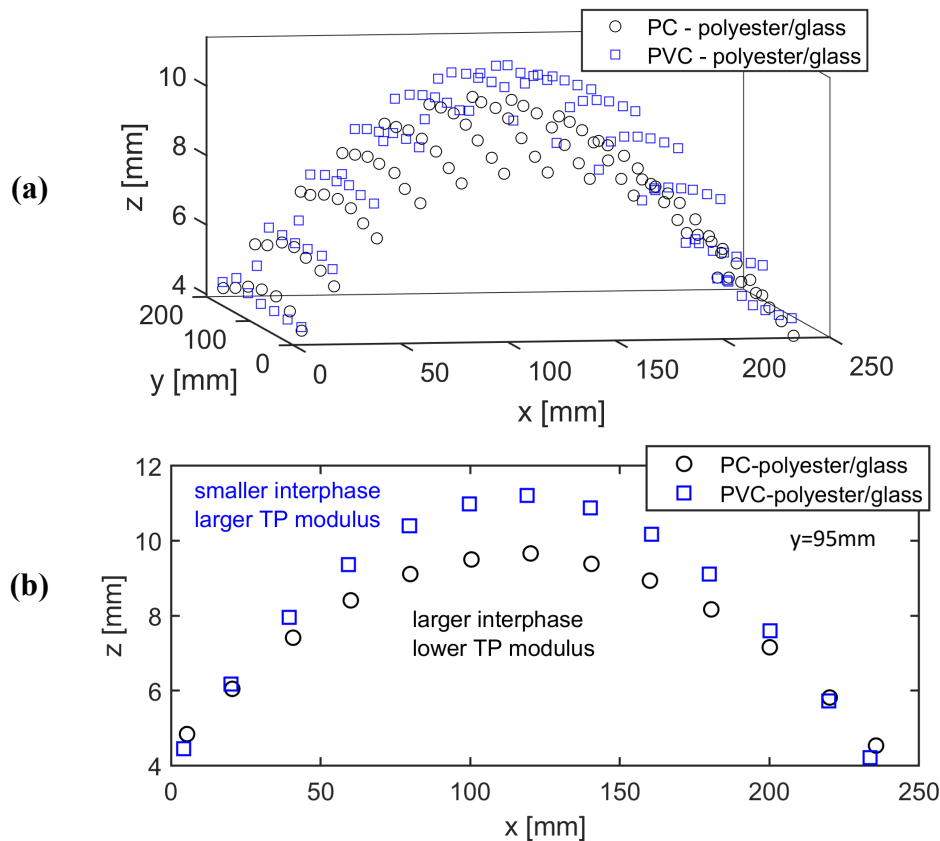


Figure 7: Coordinates of the warped hybrid composites in (a) 3-D and (b) 2-D plots.

4. CONCLUSIONS

In this work, process-induced residual strains and the final warpage were measured for the co-bonded PVC-polyester/glass and PC-polyester/glass hybrid composites. The link between the interphase thickness and the resulting warpage was investigated. The process-induced strains were measured in situ using a vacuum-assisted resin transfer molding setup that does not constrain the warpage of the hybrid composite as the curing takes place. Significant process-induced deformations were observed for both hybrid composites studied. The evolution of strains agreed well with the evolution of the degree of cure, underlining the effect of shrinkage strains on the resulting deformations. PC-polyester/glass, with a significantly larger interphase thickness compared to PVC-polyester/glass, exhibited lower warpage although PC has a modulus lower than that of PVC. This showed that a higher level of thermodynamic affinity between the co-bonded materials, and hence a larger interphase thickness, leads to a decrease in the load transfer to the co-bonded thermoplastic plate; eventually decreasing the process-induced shape deformations. Since a higher level of affinity is expected to result in higher bond strength as well, it can be claimed that the bond strength will not be sacrificed while designing hybrid composites with as small process-induced deformations as possible.

As future work, the modulus of the interphase will be measured to ascertain its contribution to the final warpage. Moreover, an experimental framework will be developed by which the effect of interphase thickness on warpage can be investigated using the same TP plates, allowing us to have the same TP moduli and similar interphase stiffnesses.

5. ACKNOWLEDGMENTS

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