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Screening method for the onset of bonding of molten polyamide resin layers to continuous fiber reinforced laminate sheets

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ABSTRACT

Thermoplastic polymer composites (TPC) with multiple fabric layers of continuous fiber reinforcement are laminate sheets designed to be thermally stamped and overmolded leading to low cycle times and thus high volume composite parts. Injection over-molding is one way to combine the high processability of thermoplastic melts with the less processable TPC sheets, for complex part making. To simulate the adhesion development during processes like over-molding, a non-isothermal screening method for bonding molten polyamide (PA) to a solid TPC surface has been developed and applied to evaluate differences in the threshold temperatures for good bond formation as a function of TPC matrix composition. Pure PA66 and aromatic high temperature nylons (PPA) in addition to miscible PPA blends comprising different ratios of PA66, were used as TPC matrices, and retain most of the very high melting point of 100% PPA. We have devised experiments to address two critical aspects: The first is to develop a screening test that probes very short timescales relevant to practical part making. The second is to investigate various miscible semi-crystalline blend ratios as matrices for the TPC where both blend species are crystalline. This allows us to explore a practical improvement of a lower required bonding temperature without substantially decreasing the high melting point of the PPA. DSC was also used to correlate the various blend melting transitions with the temperature required for the onset of bonding. The interfaces are shown to develop high strength partly because of substantial surface melting of certain blend components of the initially solid TPC, and this quickly allows interpenetration and inter-diffusion across the interface, which then crystallizes and strengthens during cooling.

1. Introduction

Polyamide resins matrices in Thermoplastic Polymer Composites (TPC) have excellent toughness, hydrolysis resistance, and processability. Some studies of TPC with various fabrics have focused on resin impregnation rates which is important for productivity [1–4]. For example, medium molecular weight polyamides can lead to fairly high impregnation rates of continuous glass fiber fabrics. Thermoplastics have a further advantage over thermosets where bonding of molten resin to the TPC surface is attained thermally without the use of extra adhesive layers. Complex parts can be made by pre-heating the TPC, and then injection over-molding the molten resin [4]. Bonding or interface healing is accomplished by surface melting and is simulated by non-isothermal healing studies, which is related to fusion bonding for semi-crystalline polymers [4–8]. Substantial effort has been devoted to understanding the physics of healing rates to a composite or related surface when the matrix is semi-crystalline. This is somewhat more complicated [9] than healing of amorphous/amorphous interfaces where bond formation is governed by interdiffusion rates that can be predicted by standard chain diffusion theories [9–11]. Still, various experimental methodologies have probed these phenomena in isothermal and non-isothermal tests at high temperatures near the polymer melting points [4–8].

For our non-isothermal healing experiments, the intimate contact at the interface is close to instantaneous because of the nature of the very fluid molten layer used to contact a pre-heated TPC semi-crystalline surface. Thus, there are minimal effects from pressure, whereas in isothermal annealing the rate of attaining intimate contact can be very important close to the melting point [4,6,7]. Basic mechanisms for our non-isothermal studies include surface melting controlled by residence times at a certain high

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temperature, which govern the degree of melt penetration or interdiffusion into the solid side of the interface [9], followed by solidification or recrystallization across the interface during cooling.

For practical part making such as injection over-molding, the process is defined by very short time-scales because temperatures vary rapidly during the interfacial healing step. These short time-scales require accurate determination of the interface temperature, and we devoted substantial effort into detecting small temperature variations over time-scales of less than a few seconds. This comes at the expense of quantitative adhesion evaluation due to very small sample sizes, but can still be quite convincing as we evaluate the onset of the formation of bonds that are as strong as the polymer matrix at the TPC surface.

As with other high thermal stability and high melting point (T_m) polymers [8,9], bond formation with PPA TPC is quite difficult even as the TPC surface is contacted with molten PPA [12] due to the high T_m of the initially solid and crystalline TPC surface. Thus, we have investigated PPA blends as TPC matrices, where the T_m and T_g of PPA are reduced slightly by the addition of a lower melting nylon. The thermal properties of these blends are also measured as they vary with thermal history, including the somewhat aggressive thermal conditions used to impregnate the TPC (375 °C) to explore transamidation reactions. With these miscible semi-crystalline blend matrices for the TPC where both blend species are crystalline, we wish to increase the processing window by having a lower required bonding or healing temperature, without losing the high melting point of the PPA fraction in the blend. Initially, it was not obvious whether the threshold temperature for bonding should correspond to the surface melting of the lower or higher T_m species present in the TPC blend matrix, and since the variations were fairly small, this was another reason to develop quantitative interface temperature measurements.

2. Experimental

2.1. Method for making TPC with and without PPA blends

Resin powder or film layers were used with multiple glass fabric layers as described below to make the stacks for TPC pressing.

Films of blends or pure PA components were made by melt blending the resins in a twin-screw extruder at about 330 °C, and casting the films by extruding through an adaptor and a film die at about 310 °C, with casting performed onto an oil heated drum between 100 °C and 150 °C.

Blends of powder were made by mixing cryo-ground PA66 and PPA (average particle size 50 μm). The PPA was a copolymer polyamide made of 1,6-hexamethylenediamine (HMD) and terephthalic acid combined with HMD and 2-methylpentamethylenediamine (MPMD) (HMD:MPMD = 50:50 by mole%). The weight average molecular weight of this resin is 25,000 g/mol.

Stacks of 14 cm × 14 cm layers were made of 600 g/m^2 glass fiber fabrics (2 × 2 twill, 1200 dtex; 18 μm diameter fiber with TP specific amino silane sizing) with alternating layers of polyamide TPs (which were dried before pressing). These had the desired ratio of polyamide resin to fiber, with about 15% loss of resin during pressing due to squeeze-out, giving final resin/glass ratios of about 32/68 wt/wt. Square aramid paper "gaskets" 0.01 cm thick (DuPont, Co.) with an outside dimension of 12.7 cm and an inside dimension of 11 cm were placed on both outer sides of the fibrous material/polyamide resin stack, then after drying the entire assembly was placed between 0.16 cm thick steel plates treated with a mold release spray, and inserted in a 20 cm × 20 cm manual hydraulic Carver press and heated to the desired temperature of 375 °C for PPA and PPA blends for two minutes. This actual laminate core temperature of 375 °C was attained with a platen set temperature of 390 °C and pressure of 2.5 MPa (25 bars). An adjacent "cold" press was used to immediately quench the initially molten composite structure in order to freeze the sample under pressure at 2.5 MPa, and retain very high consolidation. For HTN TPC the cold press was set to 140 °C (thus the actual temperature for the 2 min "quench" was 150 °C because of the thermal mass of the 0.16 cm thick treated steel plates and the TPC).

2.2. DSC characterization

A TA Instruments (New Castle, DE) DSC was used in these experiments with heating and cooling rates of 10 °C/min. A N_2 purge was used for all experiments, and sample masses were 3–5 mg.

2.3. Method for determining threshold temperature (TT) for bond formation

We define the TT as the minimum temperature at which a very strong bond or joint between unfilled molten resin and TPC is formed (Table 1). At any joint temperature lower than TT in our 5 s of contact time, a joint is made that is easily broken apart. At any joint temperature above TT, the bond cannot be broken without cohesive resin failure. Adhesion is evaluated by using a small steel wedge inserted at the interface between film and TPC to pry the layers apart. Our adhesion is deemed good when the interface cannot be broken without destroying the film or laminate surface, where cohesive failure generally leaves a broad crater where much of the laminate surface is removed. Unless it spontaneously debonds upon cooling, generally we find with "marginal" adhesion that bonding is spotty, but the interface mainly fractures adhesively and cleanly with fairly low forces. These are not considered well bonded, and although slightly qualitative, the characterization showing interfaces that only fail cohesively is quite reproducible when performing repeat testing.

To prepare the crystalline TPC surface for these measurements, the TPC surface was scrubbed by acetone soaked paper towels to remove any mold release agent that had been transferred from our treated steel plates used to make the TPC. It was then dried to remove water at 110 °C for 18 h, as were all molding resins.

For the preparation the "molding resin" in this small scale test, a layer of resin about 0.75 mm thick and 1 cm × 1 cm in area was quickly heated and melted. The exact temperature is determined by placing this film on a metal block that is preset to a defined temperature. The film is heated for less than 60 s to avoid surface oxidation and degradation of the polyamide since rather high temperatures are used. The film also rests on a thin release layer (Kapton™ polyimide film) so it does not attach to the metal block. The laminate is preheated between temperature controlled blocks for 60 s to exactly 150 °C for all samples in Table 2, and 200 °C for all samples in Table 3. The size of the small TPC samples used is 2 cm × 2 cm × 0.16 cm (2 cm squares with a thickness of 0.16 cm). Finally, for evaluation of the bonding, the laminate is quickly brought together with the molten film at 20 psi (0.14 MPa), and held at this pressure for exactly 5 s on top of the molten film. During this time the film still rests on the hot metal block (Fig. 1). A thermocouple imbedded at the very surface of the TPC is used to determine the "joint" temperatures after 5 s of contact at the interface with the melt. The micro-thermocouples used were type J (Teflon coated). At exactly 5 s, the film/TPC pair are removed from the hot block and quenched with a cold brass block (>−100 °C/s cooling rate) to instantly cool and solidify the interface. Thermocouple readings and other typical parameters are given in Table 1.

Table 1 also shows a typical set of experiments needed for the determination of a single TT value. The TPC surface temperatures