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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

Table 1
For 100% PPA TPC, a typical set of experiments for determination of a single TT value is shown where TT is measured to be 308 °C from the data in this table. The 100% PPA TPC surface temperatures are the "joint temperatures" which are simply varied from sample to sample here by changing the melt temperature (i.e., the initial molten film temperature). For these data, TPC were pre-heated to 150 °C/60 s as was the case for Table 2.

Molten polymer	Metal block temp., °C	Initial molten film temp., °C	Time (sec)	"Joint" temperature at 5 s, °C	Result
PPA	325	300	5	275	Detached
PPA	335	310	5	283	Marginal
PPA	345	315	5	287	Marginal
PPA	350	320	5	292	Marginal
PPA	355	325	5	295	Marginal
PPA	365	335	5	303	Marginal
PPA	370	340	5	308	Good
PPA	378	345	5	312	Good

Table 2
Measured values of TT for the indicated TPC compositions pre-heated to 150 °C/60 s, and contacted with different temperature PPA molten films and quenched after 5 s (see text).

TPC composition	Threshold temperature, joint, °C	Initial molten film, temperature, °C	Metal block temperature, °C
100% PPA	308	340	370
PPA/66 (90/10) blend	292	320	350
PPA/66 (80/20) blend	287	315	345
PPA/66 (60/40) blend	287	315	345
100% PA66	287	315	345

Table 3
Measured values of TT for the indicated TPC compositions pre-heated to 200 °C/60 s, and contacted with different temperature PA66 molten films and quenched after 5 s (see text).

TPC composition	Threshold temperature, joint, °C	Initial molten film temperature, °C	Metal block temperature °C
100% PPA	290	315	330
100% PPA, new sample	290	315	330
PPA/66 powder (90/10) blend	265	290	300
PPA/66 powder (80/20) blend	265	290	300
PPA/66 powder (70/30) blend	265	290	300
PPA/66 powder (60/40) blend	265	290	300
100% PA66	265	290	300

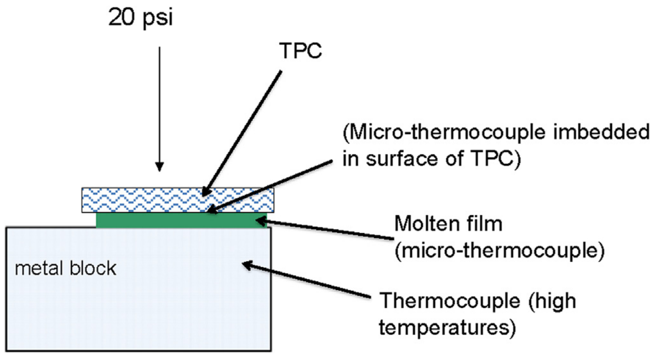

Fig. 1. Configuration of molten film and TPC, and various thermocouples.

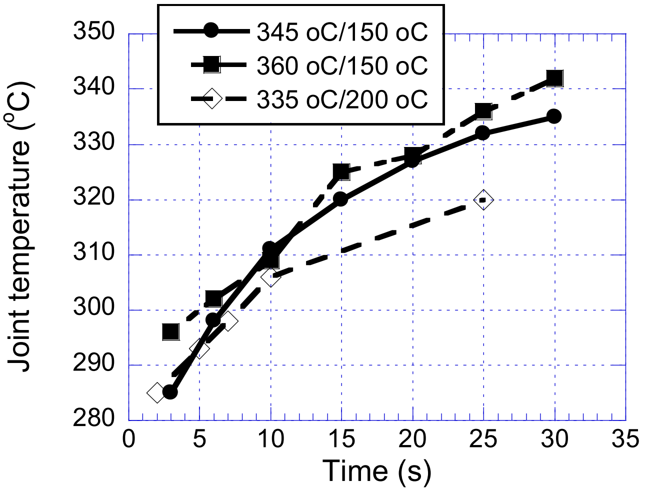

Fig. 2. Examples of thermocouple readings at TPC surface ("joint temperature") versus time for two different representative conditions of TPC pre-heating temperatures (either 150 °C or 200 °C) and initial molten film temperatures (higher values of temperature in legend).

are the "joint temperatures" which are simply varied from sample to sample in the table by changing the melt temperature. The adhesion is seen to be marginal until this threshold "TT", at which point it becomes very strong if joint temperatures rise to 308 °C or higher. Obviously there are many other times and thermal profiles that can lead to the same phenomena. We have chosen fairly short times because of the practical implication of rapid bond formation in actual part making where a cooler TPC is joined with a hot injection molded resin layer, and bonds must form quickly because the interface is cooled fairly rapidly by the mold.

Regarding details of our heating profiles and calibration at 5 s, typical examples of the temperature variation with time are shown in Fig. 2. The zero point is the instant when the TPC is contacted with the molten film. Note that we are mainly concerned with the values at 5 s, but the entire profiles are basically controlled by the initial temperature gradients between the warm TPC and the hot melt as expected.

3. Results

3.1. Rapid bonding experiments to measure TT as a function of blend composition

As discussed above, for each entry in Tables 2 and 3, a series of separate samples were needed to measure a single "threshold temperature". For example, the metal block or "molten film" temperature is stepped by about 5 or 10° for each new sample that was pressed together. Starting with various TPC pre-heated to 150 °C and bonded to molten films of 100% PPA, the TT values indicated in Table 2 are seen to drop as a low melting PA66 component is added to the indicated TPC matrices consisting of PPA/PA66 blends at different ratios. Even at only 80/20 PPA/PA66, the TT values are essentially the same as that for a TPC made with 100% PA66.

Table 3 shows similar series of blend TPC compositions, but in this case they are pre-heated to 200 °C and bonded to pure PA66 molten films. The drop in TT for the blends relative to the 100% PPA TPC occurs immediately. For example, at a 90/10 PPA/PA66 ratio it is seen that TT drops to 265 °C which is 25 °C lower than the TT value for TPC made with pure PPA.

It is also seen that the value of TT for molten PA66 bonded to 100% PPA TPC is 290 °C (Table 3), while the value of TT for molten PPA bonded to a 100% PPA TPC is 308 °C (Table 2). Explanations could include higher mobility or higher transamidation rates [13] of PA66 relative to PPA.

3.2. Correlation of TT values with blend melting points from thermal analysis

We expect the values of TT will correlate with some aspect of the melting of various species at the TPC surface. Thus, we ran a series of DSC experiments, and these showed that there were sometimes double endothermic melting corresponding to crystals of the two different polymers. Fig. 3 shows DSC data for a blend in addition to the pure PA66 or PPA polymers. It is seen that the PPA/PA66 72/28 blend has a fairly high T_g of 100 °C which is in between the T_g of 60 °C for PA66, and 135 °C for PPA, as expected for these melt miscible PAs. It is also seen that the crystallization of PA66 is suppressed in this blend in the first DSC heating (the starting state in Fig. 3 was an initially quenched amorphous blend which explains the cold crystallization exotherm at 132 °C). This is partly due to the fact that it is miscible and is highly diluted with PPA. Dilution with high T_g resin in miscible blends is known to reduce the crystallization rates of lower T_g blend components because of lowered mobility imparted by this high T_g component [14,15]. In this case PPA makes it difficult for the PA66 to crystallize especially since PA66 is the minor fraction. There may also be a slight amount of transamidation at the 330 °C blending temperature which would also reduce the crystallization rate.

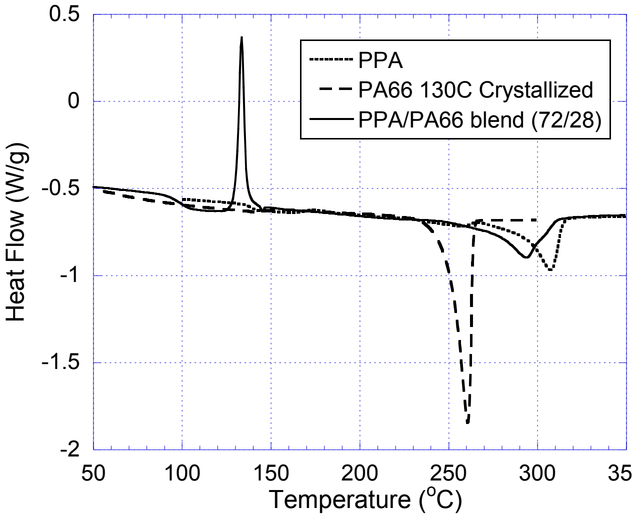

Fig. 3. 10 °C/min DSC heating curves for the indicated polymers including a PPA/PA66 72/28 blend which has high T_g of 100 °C, and it is also seen that PA66 crystallization suppressed in this blend (initially quenched amorphous blend shown here). Note that end of melting for PPA is about 320 °C for this heating rate.

DSC heating curves, including that for a 50/50 blend exhibiting a double melting region, again show that both species are able to crystallize upon heating an initially quenched amorphous film (Fig. 4). A T_m of 250 °C is found for the PA66 species, and a T_m of 290 °C is seen for the PPA species. The glass transitions are plotted in Fig. 5 showing other clear evidence that these are miscible as we know from many related tests. The melting peaks are lower and somewhat weaker than they would be for pure respective species given this 50/50 ratio because of some of the dilution effects discussed above.

Figs. 6–8 show DSC curves for a powder blend that was made using the same composition used for the TPC. To prepare the samples for DSC, we heated initially unmelted blended powder samples (~20 mg) between Kapton™ release films for either 10 s or 45 s at high temperatures (350 °C) with minimal external shear. At these temperatures, viscosity is very low and interdiffusion to erase initial particles that had melted should be fairly rapid. We used a 10 s annealing time to try to completely restrict mixing of the powder and transamidation, and 45 s to try to induce some mixing by giving it enough time for interdiffusion. Fig. 6 shows DSC first heating curves on these 70/30 PPA/PA66 powder blends after annealing for 10 or 45 s at 350 °C, and quenching to an initially amorphous state. For the 10 s annealing, complete intermixing had not yet occurred because a double T_g is seen corresponding to both PA66 and PPA phases. A single T_g is seen for the blend annealed at 45 s showing that time for interdiffusion at this temperature was sufficient. One can see PA66 and PPA melting in these blends even after some transamidation in the 45 s case. After heating to a maximum temperature of 330 °C in the first DSC scan, the cooling curves at −10 °C/min were recorded (Fig. 7). Presumably, this high temperature annealing in the DSC cell was enough to fully

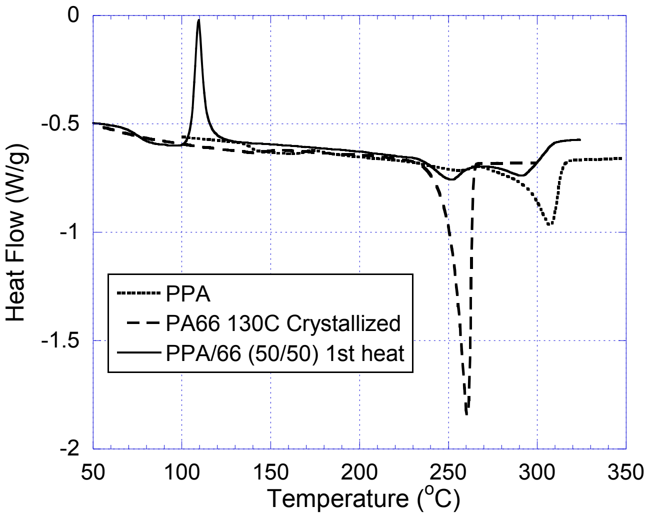

Fig. 4. DSC heating for indicated polymers including a 50/50 PA66/PPA blend.

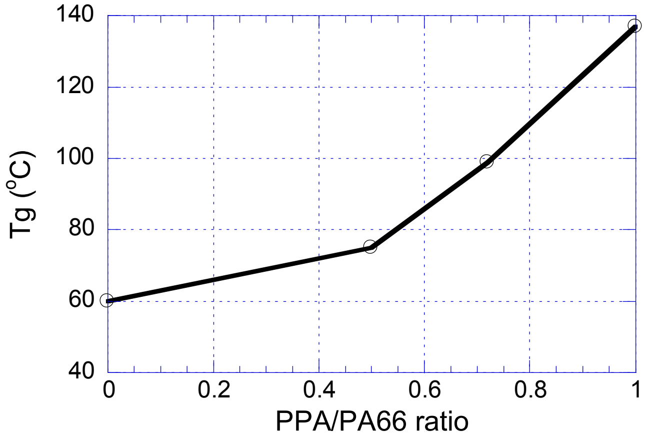

Fig. 5. Plot of dry T_g versus weight fraction of PPA for pure components and PA66 blends mixed at 340 °C for about 5 s.

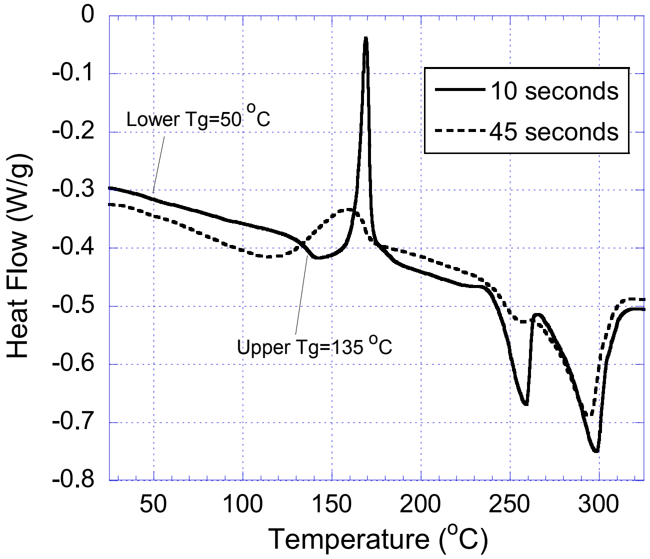

Fig. 6. Heating curves on 30/70 PA66/PPA powder blends after annealing for 10 or 45 s at 350 °C, and quenching to an initially amorphous state. For the 10 s annealing, intermixing has not yet occurred because a double T_g is seen for both PA66 and PPA phases. A single T_g at about 80 °C is seen for the blend annealed for 45 C.

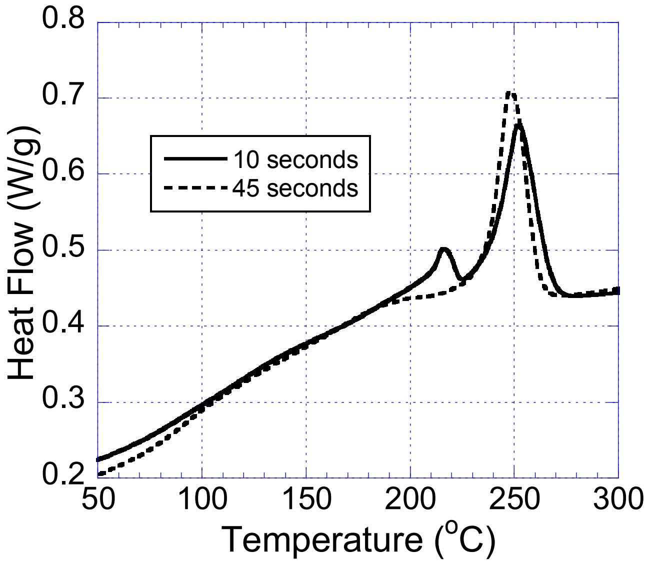

Fig. 7. Cooling curves of the samples from Fig. 6 after heating to 335 °C showing some PA66 crystallization in these blends even after some minor transamidation.

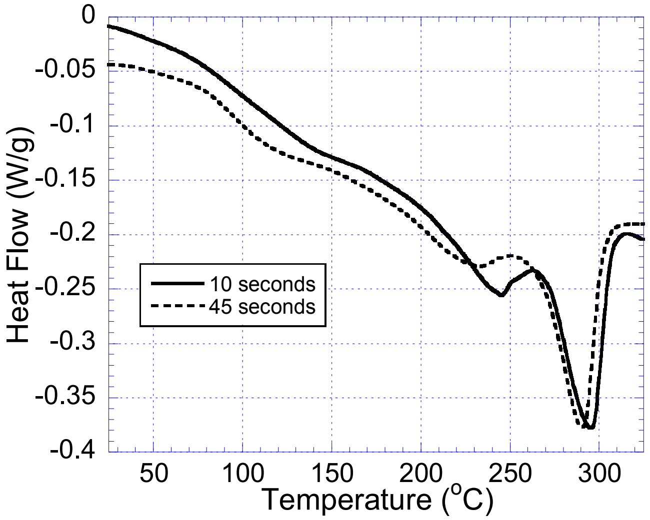

Fig. 8. Subsequent (2nd) heating curves of the samples in Fig. 7 showing some PA66 melting in these blends even after some transamidation.

interdiffuse the blend leading to a single melt phase, and it is seen that the curves are similar with the PA66 component having a smaller exotherm at 220 °C for the 45 s annealed blend possibly due to dilution effects or a slight degree of transamidation. A similar trend is seen in the DSC cooling (Fig. 7) and second heating scans (Fig. 8) where transamidation may have shifted the peaks slightly, as is evidenced by the lower melting peak for the 45 s annealed sample that is weaker and at a lower temperature.

4. Discussion

In these miscible blends where both species are able to crystallize, it is common that upon cooling from the melt that the high T_m component crystallizes first which removes a certain fraction of this polymer from the miscible amorphous phase, and then this amorphous phase develops an enhanced concentration of the lower melting component both within and outside of spherulites of the higher T_m species [15]. As it is cooled further, the lower melting component crystallizes but generally in restricted spaces due to the pre-existing stacks of lamellae and spherulites of the higher T_m polymer. The restricted spaces in addition to nucleation by existing lamellae, generally lead to much smaller crystalline aggregates of the lower melting species, and sometimes restrict the growth of lamellar stacks enough that the melting point of this lower melting species can be lower than that observed in the pure polymer [15]. Co-crystallization polyamides does not generally occur [16], and DSC data below for PA66 and PPA blends show separate melting peaks confirming that co-crystallization is not occurring.

In the initial stages of our study, it was not certain whether the end of melting was important, or whether the peak melting points [5–7] would govern the onset of bond formation represented by TT. As shown in Figs. 3 and 4, peak T_m values from DSC endotherms are about 307 °C for pure PPA, and around 290 °C for PA66/PPA blends. At 10 °C/min, it is seen that the end of melting is around 320 °C for many of these PPA and blend resins, yet it is clear from Table 2 that the bonding is accomplished at temperatures closer to the peak T_m in the case of pure PPA resin film bonded to a 100% PPA TPC. Of course the peak in the endotherm is somewhat dependent on DSC scan rate, and complicated by recrystallization because of the slow DSC scan rates [17], but in general at the temperature indicated by the peak (T_m), the sample is at least half melted. The data confirm that substantial but not complete melting is needed for bonding in these determinations of TT.

In the case of the blend TPC (Table 2), the values of TT drop by 21 °C relative to those for pure PPA TPC to 287 °C, fairly consistent with a peak melting point change from 308 °C for PPA, to 290 °C for the 72/28 and 50/50 PPA/PA66 blends in Figs. 3 and 4, respectively. Thus, in this case the PPA melting, as represented by the higher endotherm peaks in blend DSC curves such as in Fig. 4, the onset of surface melting facilitates interpenetration of the PPA melt into the TPC surface. This is similar to the case of the temperature required for bonding to the surface of semi-crystalline polypropylene and PA12 [4–6].

The fact that full bond strengths can be reached in less than a couple of seconds is not unusual. Experimentally, Lamethe, et al. [8] have shown full bonding in a quarter of a second, and analysis of interdiffusion rates based on reptation theory have shown interpenetration of a fully melted interface should occur in less than a millisecond because of the moderate molecular weights and very low viscosities of these polymers when molten at these very high temperatures [9]. In all these cases, interpenetrated chains can later be bridged by crystals across the original interface upon cooling, naturally leading to extremely strong interfaces as we have observed.

For the data in Table 3 with the same TPC, but bonded to PA66 molten films, the trend is slightly different, and the TPC made with blends have lower TT values that are very close to the end of melting of the PA66 fraction. The same is true for the 100% PA66 TPC where TT is 265 °C (Table 3), and the end of melting for PA66 is about 265 °C (Fig. 3). Although our time scales are shorter, this relative value of TT is similar to those from Plummer [8] where for polypropylene a temperature 12 °C above the DSC peak T_m is required for good bonding. For our blend TPC, this is explained by the melting of the PA66 fraction at the surface, even if the temperature is not nearly high enough to melt most of the HTN at the TPC blend surface. These blends rich in HTN (Table 3) have as a minority phase PA66, but this is mixed with amorphous HTN in these low crystallinity miscible blends, yet inter-diffusion in this mixed amorphous fraction at the surface at TT = 265 °C is enough to lead to interface strengths at least as high as the resin cohesive strength. The DSC trace for the blend in Fig. 3 also shows that melting of a small fraction of defective the PPA crystals begins at temperatures above about 250 °C, so by 265 °C this would be an additional amorphous fraction at the TPC blend surface. Thus, bond strengths form at a remarkably low temperature (Table 3), and are explained by interpenetration across the interface by diffusion even at low PA66 fractions at the surface.

5. Conclusions

High T_m matrices in long glass fiber fabric reinforced TPC lead to difficulties in thermal bonding. Non-isothermal healing to TPC surfaces during processes that simulate injection over-molding were studied with the method described here with good time and temperature resolution. This was applied to evaluate differences in the threshold temperatures (TT) required for good bond formation for either PA66 or PPA molten "over-molding" resins contacting different composition TPC resin matrices. Our test probes very short timescales on the order of seconds, making the data relevant to practical part making. Our threshold temperature required for healing in 5 s refers to strong bonds that cannot be broken without cohesive resin failure. Interdiffusion for these fairly low molecular weight polyamides at these very high temperatures is known to be rapid, suggesting that melting or partial melting of lamellae in the TPC and near the surface can occur quite fast.

Pure PA66 and aromatic high temperature nylons (PPA) in addition to miscible PPA/PA66 blends comprising different ratios of PA66 were used as TPC matrices. These miscible semi-crystalline blend matrices for the TPC were studied at blend fractions where both PA66 and PPA species can both crystallize. DSC confirmed the variation of T_g as expected for miscible blends, and also provided the dual melting endotherms with the higher one corresponding to the PPA melting region. A practical improvement would be a lower required bonding temperature [4] without substantially decreasing the thermal properties of the PPA blends.

Comparison of the TT values with the measured DSC melting endotherms for the TPC matrix shows that interfaces develop high strength because of substantial surface melting of the initially solid TPC. For example, peak T_m values from the highest DSC endotherm peaks are about 307 °C for pure PPA, and 290 °C for PA66/PPA blends, and Table 2 shows that the TT values are 308 and 287 °C, respectively when bonded to 100% PPA melts. The data confirm that substantial but not complete melting is needed for bonding in these determinations of TT. Thus, in this case the PPA melting as represented by the higher endotherm peak in blend DSC curves such as in Fig. 4, seems to dominate the temperature at which there is enough surface melting to allow interpenetration of the PPA melt into the TPC surface, similar to the case of polypropylene and PA12(nylon 12) [4–6]. For the data in Table 3 with the same TPC, but bonded to PA66 molten films, the TPC made with blends have lower TT values (265 °C) which is just above the end of melting of the PA66 fraction. Evidently these species are mobile enough that even with low molten PA66 amorphous fractions, effectively enhanced by being mixed with some amorphous HTN fraction at the TPC surface, interpenetration across the interface by diffusion can occur to an extent that gives very high bond strengths. This is aided by the start of melting of PPA at 265 °C seen in the DSC, and happens even though there certainly is PPA crystallinity at these TPC blend surfaces.

References

[1] X. Wang, C. Mayer, M. Neitzel, Some issues on impregnation in manufacturing of thermoplastic composites by using a double belt press, Polym. Compos. 18 (6) (1997) 701–710.
[2] C. Mayer, X. Wang, M. Neitzel, Macro- and micro- impregnation phenomena in continuous manufacturing of fabric reinforced thermoplastic composites, Compos. Part A 29A (1998) 783–793.
[3] S.T. Jespersen, M.D. Wakeman, V. Michaud, D. Cramer, J.-A.E. Månson, Film stacking impregnation model for novel net shape thermoplastic composite preforming process, Compos Sci. Technol. 68 (2008) 1822–1830.
[4] P.-E. Bourban, N. Bernet, J.-E. Zanetto, J.-A.E. Månson, Material phenomena controlling rapid processing of thermoplastic composites, Compos. Part A 32 (2001) 1045–1057.
[5] J.-E. Zanetto, C.J.G. Plummer, P.-E. Bourban, J.-A.E. Månson, Fusion bonding of polyamide 12, Polym. Eng. Sci. 41 (5) (2001) 890–897.
[6] G.D. Smith, C.J.G. Plummer, P.-E. Bourban, J.-A.E. Månson, Non-isothermal fusion bonding of polypropylene, Polymer 42 (2001) 6247–6257.
[7] C.J.G. Plummer, P.-E. Bourban, J.-E. Zanetto, G.D. Smith, J.-A.E. Månson, Non-isothermal fusion bonding in semicrystalline thermoplastics, J. Appl. Polym. Sci. 87 (2003) 1267–1276.
[8] J.F. Lamèthe, P. Beauchêne, L. Léger, Polymer dynamics applied to PEEK matrix composite welding, Aerosp. Sci. Technol. 9 (2005) 233–240.
[9] W.J.B. Grouve, L.L. Warnet, B. Reitman, H.A. Visser, R. Akkerman, Optimization of the tape process parameters for carbon-PPS composites, Compos. Part A 50 (2013) 44–53.
[10] R.P. Wool, Polymer Interfaces, Carl Hanser Verlag, 1995.
[11] Y.M. Boiko, G. Guérin, V.A. Marikhin, R.E. Prud'homme, Healing of interfaces of amorphous and semi-crystalline poly(ethylene terephthalate) in the vicinity of the glass transition temperature, Polymer 42 (2001) 8695–8702.
[12] Elia A.E, Kirchner O.N, Mesaros D.V, Wakeman M.D, Yuan S. U.S. Patent Appl. US 2012/0108124 A1, May 3, 2012.

[13] Y.P. Khanna, N.S. Murthy, W.P. Kuhn, E.D. Day, Pseudo super-miscibility: blends of semi-crystalline nylon pairs exhibiting a single Tg and a single Tm, Polym. Eng. Sci. 39 (1999) 2222–2232.

[14] T.S. Ellis, Miscibility in blends of aliphatic polyamides and an aromatic polyamide, nylon 3Me6T, Polymer 29 (1988) 2015–2026.

[15] B.S. Hsiao, B.B. Sauer, Glass transition and crystallization phenomena in poly(aryl ether ketone) and poly(ether imide) blends, J. Polym. Sci. Polym. Phys. Ed. 31 (1993) 901–915.

[16] E.D. Harvey, F.J. Hybart, Rates of crystallization of copolyamides. II. Random copolymers of nylons 66 and 6, J. Appl. Polym. Sci. 14 (1970) 2133–2143.

[17] T.F.J. Pijpers, V.B. Mathot, B. Goderis, R.L. Scherrenberg, E.W. van der Vegte, High speed calorimetry for the study of the kinetics of (de)vitrification, crystallization, and melting of macromolecules, Macromolecules 35 (2002) 3601–3613.