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Time–temperature equivalence in the tack and dynamic stiffness of polymer prepreg and its application to automated composites manufacturing [☆]



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ABSTRACT

A recently developed peel test designed to simulate the automated tape lay-up (ATL) process was used to measure tack and dynamic stiffness of newly developed ATL prepreps. Resin was extracted from the prepreg process before impregnation of the fibres. Isothermal small amplitude frequency sweeps were carried out in shear rheology to determine time–temperature superposition parameters in the form of Williams–Landel–Ferry equation. Gel permeation chromatography and differential scanning calorimetry demonstrated that the resin was not significantly changed during the preprepping process. The WLF parameters were used to transpose isothermal tack and dynamic stiffness results with excellent agreement found. This relationship offers manufacturers using composite prepreg a method to maximise and maintain tack levels at different feed rates by appropriate changes in temperature. This is of significant importance in improving the reliability of automated composite lay-up processes such as AFP and ATL, whose feed rate must vary to accommodate lay-up operations.

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1. Introduction

Prepreg is a semi-flexible sheet consisting of fibres impregnated with a pre-catalysed polymer resin matrix used in the production of high performance composite parts. It is typically produced by passing fibres through a series of rollers where they are pressed between resin films or through a resin bath to form a continuous sheet. The resin is generally heated during impregnation to reduce its viscosity and allow good wetting of the fibres. It is then immediately cooled to hold the fibres in place and prevent unwanted curing of the resin [1,2].

In the production of composite components, the flexible prepreg is laid into a rigid mould which determines the finished geometry. The prepreg matrix is cured by a thermally activated chemical condensation reaction resulting in polymerisation and cross-linking. The rate of the cure reaction is temperature dependent, and temperatures over 80 °C are typically required to achieve complete cure over a period of a few hours. The cure reaction is finite and exothermic, and differential scanning calorimetry is the preferred method to determine the degree of cure through mea-

surement of the enthalpy of reaction. If any prior cure has occurred, then the remaining enthalpy of reaction is reduced [3]. Gel permeation chromatography (GPC) can also be used to indirectly infer the degree of cure from determination of the change in molecular weight. However, its use is limited to the early stages of cure since the resin must remain soluble in order to perform the test [4].

The process of laying the prepreg into the mould is known as laminating. For the majority of prepreg users, this process is carried out manually by a semi-skilled workforce. Lamination involves cutting plies into the required shape, removing the backing paper and placing them into a mould. Pressure is manually applied to ensure the ply conforms to the mould surface. The prepreg then remains in place due to the pressure sensitive adhesive properties, known as tack, of the uncured polymer matrix. Prepreg tack levels are formulated by the manufacturer such that the material remains in place throughout the lamination process and can be repositioned with ease if necessary. The tack level must be both low enough to allow the removal of the backing paper, and high enough to hold the lay-up together [5]. Tack is also affected by the prepreg storage history. The same cure reaction which allows a solid component to be formed in a matter of hours at elevated temperatures also occurs slowly, over a matter of weeks or months, at room temperature. When the resin is stored at room temperature, the tack of the prepreg gradually reduces, the stiffness increases, and lamination becomes increasingly difficult. For

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this reason, shelf life is also referred to as tack life. Prepreg is therefore stored at or below $-18\text{ }^{\circ}\text{C}$, where the curing reaction is slowed to a minimum and tack life is extended. Although the handling properties are reduced after long storage periods, the cured mechanical properties of the laminate are not always affected [1]. For hand lamination, such issues are mostly trivial as a skilled laminator is able to compensate for changes in tack and stiffness. Nevertheless, considerable time is spent manually positioning the plies during hand lamination, and part quality can suffer from human error. Therefore, due to its labour intensity, hand layup is considered a significant source of variability and cost, and there is no doubt that the lamination process can benefit significantly from automation [6].

Automated robotic lamination equipment is now commercially available in the form of automated tape lay-up (ATL) and automated fibre placement (AFP) machines. These machines carry out complex and intricate cutting and laying operations, accurately following mould contours. Such processes are reported to be efficient at producing repeat high performance components. However, they are not yet considered to be a mature technology and several difficulties have been reported with the lay-up process [7–9]. In particular, changes in prepreg adhesion due to a number of variables including mould releases, surface type, backing paper, resin distribution, prepreg variability, temperature and humidity are thought to be responsible. The result is that these automated processes require highly regulated environments and materials with constant monitoring and intervention by highly skilled operators, limiting their use to high value aerospace components.

In a typical automated lay-up process, the prepreg is guided off a spool and under a compaction tool head holding the tacky prepreg against the mould surface under a regulated compaction force. The process is illustrated in Fig. 1. High tack is considered favourable to hold the prepreg mould surface and subsequent plies. A stiffer prepreg aids release from the backing paper as it resists bending around the compaction tool. In ATL, the backing paper is then removed onto a take up spool in a continuous process. At this point tack to the backing paper is considered unfavourable as it prevents release and causes prepreg to lift from the mould surface. Therefore, prepreg tack levels are crucial to the automated lay-up process. Problems with tack levels in service are frequently alleviated by experimenting with lay-up temperature, but this requires significant time and material waste. During a production cycle, lay-up temperature is generally held constant [7,10] or, less commonly, is varied linearly according to feed rate [11]. Changes in feed rate are required for cutting and steering operations and to overcome machine start-up inertia. Tack is also believed to be improved at lower feed rates, therefore machines are often slowed when starting a new ply [12].

Several previous studies of prepreg tack have employed established test methods from the pressure sensitive adhesive (PSA) [13–15]. Several standardised PSA methods for the determination of tack exist [16,17], and may be categorised into either probe or peel methods, depending on the separation mechanism.

Probe methods consist of a disc of resin between two parallel circular surfaces. The surfaces are brought together under controlled force or to reach a predefined gap. Force and extension are recorded during separation at a controlled rate. The probe tests are generally favoured by the PSA industry [18] and have been adopted in various prepreg studies [13,19,20]. However, the testing of prepreg discs is susceptible to a failure mechanism within the bulk fibres. This is not representative of the ATL process, where the fibres are continuous. Therefore, it is challenging to relate results from probe tests to automated lamination of continuous prepreg.

Peel methods include the floating roller peel test, extensively used in the PSA industry for adhesive tapes [18,21] and for the characterisation of prepreg [15]. Peel methods are often considered inferior to the probe methods, for several reasons. Most importantly, they generally do not define or include the application stage of the adhesive tape to the rigid substrate. Secondly, they inevitably include bending of the tapes, and it is not always trivial to separate bending forces from adhesive forces [22]. Lastly, peel methods are generally constrained by slow application times and contact conditions, making them unsuitable for reproducing conditions in automated lay-up.

A new tack and stiffness measurement test method has recently been developed in our laboratory for characterisation of prepreg tack in a process which replicates automated lay-up [23]. The test ensures that the application process time and the contact time are both controlled, and that they are inversely proportional to feed rate. Preliminary results suggested that the tack levels can be related to the viscoelastic properties of the resin, provided impregnation levels, surface roughness and other process characteristics remain constant. Results have also highlighted the sensitivity of tack to several variables, in particular to temperature and feed rate. Previous research in our laboratory identified an inverse logarithmic relationship between feed rate and temperature [24]. This has led to the suggestion that a time–temperature superposition (TTS) relationship of the kind frequently encountered with polymeric materials may be applicable to tack levels.

Time temperature superposition (TTS) is a concept for describing polymer viscoelasticity over a wide temperature range and a broad range of either rates or times [25]. It has been in use for many years for producing mastercurves of polymer properties, and is helpful in predicting the results of long term creep experiments by conducting experiments at increased temperatures

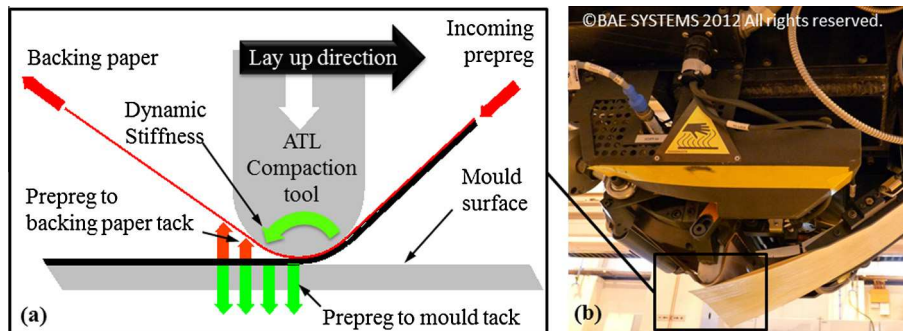


Fig. 1. A Cincinatti V4 ATL delivery head (b) and simplified operational diagram (a) shows tack and stiffness forces which are favourable in laminating prepreg to the mould (green) along with tape tension and backing paper tack forces which may cause undesirable peel (red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

[26]. In order to identify the correct shift in timescales that is associated with particular temperatures, models such as the Williams–Landel–Ferry (WLF) equation are frequently employed [27].

TTS has been readily observed and studied in conventional peel testing of PSA tape. Shift factors found from viscoelastic data obtained by small amplitude oscillatory shear (SAOS) rheometry have matched those found from peel testing, allowing a master peel curve to be produced [22]. This curve can be sub-divided into regions corresponding to different modes of failure. The point of interfacial, or contact, failure appears to be rate-dependent, despite an application process that does not scale proportionately with peel rate [28]. The peel sample is applied to the plate prior to conducting the test, suggesting that only a fully established interface may be tested. Interfacial failure then occurs quickly under high loads, revealing little information about the formation of tack. The nature of the application and instantaneous peel of our laboratory's newly developed test now allows for a greater range of measurements of tack in the interfacial failure domain, specifically focusing on conditions where the interface may not be fully established.

The objective of this study is to explore the applicability of TTS to the tack and dynamic stiffness of prepregs, with particular emphasis on conditions that are relevant to automated lay-up. It is also of considerable industrial relevance to explore whether parameters required for predicting changes in tack levels with rate and temperature can be obtained by more conventional and convenient rheometric techniques. SAOS rheology was performed on resin obtained prior to prepregging, and GPC was used to record changes in resin properties that may have occurred during prepregging. The paper concludes with a discussion of the theoretical basis for TTS in prepregs, and of the relevance of TTS to industrial applications.

2. Experimental method

2.1. Materials

Two non-commercial 400 g m⁻² E-glass low tack bisphenol A epoxy, 28 wt.% resin, ATL prepreg tapes were used in this study. The tapes were nominally identical but originated from separate batches, and as a result, had slightly different storage histories. A small amount of resin, without fibres, was taken before the prepregging process and was used in rheometry. This resin was stored with its corresponding prepreg to ensure consistent ageing. Batch one with prepreg reference PP1 and resin reference R1 were stored for approximately 4–10 days at 20 °C and 120 days at –18 °C. Batch two with prepreg reference PP2 and resin reference R2 were stored for approximately 3 days at 20 °C and 30 days at –18 °C.

2.2. Dsc

Differential scanning calorimetry (DSC) was conducted using a TA instruments Q10 DSC with open aluminium pans under a nitrogen atmosphere (50 ml min⁻¹) on resin samples R1 and R2. Approximately 8 mg of each resin was subjected to a temperature ramp at a rate of 5 °C min⁻¹ from room temperature through to 300 °C in order to determine the enthalpy of the cure reaction.

2.3. Gpc

Gel permeation chromatography (GPC) was carried out using a Polymer Labs PL-120. Using two 30 cm PLgel Mixed-C gel columns in series using THF as the eluent calibrated using polystyrene standards. All calibration and analyses were performed at 40 °C with a flow rate of 1 ml min⁻¹. R1 and R2 resin samples were dissolved in

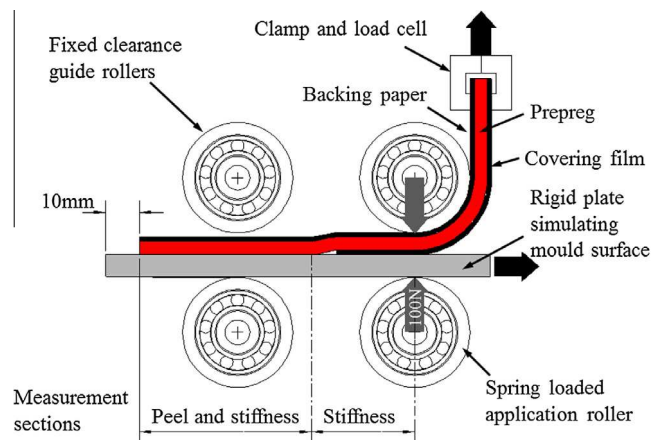


Fig. 2. The prepreg peel tack and dynamic stiffness measuring equipment. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

THF at a concentration of 7.5–10 mg ml⁻¹. PP1 and PP2 resins were extracted by dissolving a patch of prepreg in THF, at a resin concentration of 7.5–10 mg ml⁻¹. Three measurements were carried out on each sample.

2.4. Rheology

Small amplitude oscillatory shear (SAOS) rheology was carried out using a Bohlin C-Vor Rheometer with a temperature controlled ETC. oven with liquid nitrogen cooling. R1 and R2 resin samples were tested using a \varnothing 25 mm 2.5° cone and plate geometry. Isothermal frequency sweeps were carried out at 16 logarithmically increasing frequencies ranging from 0.6 to 188 rad s⁻¹, at temperatures from 10 °C to 40 °C, in 3° intervals.

2.5. Peel testing

Prepreg peel testing was conducted using a recently developed peel test with a controlled application stage which also allows measurement of dynamic stiffness. The test method has been described in detail previously [23], and only a brief account is given here. The peel specimen consists of a length of prepreg covered on both sides with a thin polythene film. A portion of the covering film is removed from the prepreg exposing the tacky surface prior to the beginning of the test. The peel test equipment consists of a set of four low friction bearing rollers fixed in position at the base of a standard mechanical test machine, and is shown in Fig. 2. The peel specimen is threaded through the rollers and clamped to the upper jaw and load cell. It rests face down against a free floating rigid stainless steel substrate with a standard annealed commercial surface finish of 0.18 μ m that acts as the simulated mould surface. The underside roller nearest the centreline of the machine is spring mounted, allowing a compaction force of 100 N to be applied onto the peel specimen. During the test, the rollers are closed and the prepreg material is pulled upwards while the rigid plate is ejected horizontally. The peel test equipment was mounted in a universal test machine fitted with a 1 kN load cell. A single test thus provides two measurements: in the first part, the prepreg is covered by the polythene film, and the vertical component of the force arising from the dynamic bending stiffness of the prepreg is measured. In the second part, the sum of the contributions to the vertical component of the force from both bending stiffness and peel adhesion are recorded.

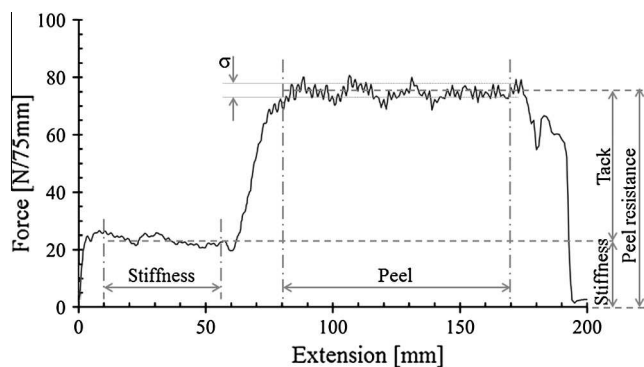


Fig. 3. A typical measurement of force during a peel test.

2.5.1. Analysis of peel test measurements

A measurement of the force recorded during a typical peel experiment is shown in Fig. 3. The measurement of tack force is found by subtracting the average force measured during the dynamic stiffness part of the test from the average force measured during the second part, comprising both stiffness and peel. The standard deviation σ is determined across the peel distance and is a measure of the uniformity of the peel process. Small corrections to the force are made to account for bearing and rolling friction, and for the additional stiffness of the covering film (in the stiffness part of the test only) [23]. Tack and dynamic stiffness forces are reported in Newtons per specimen width, consistent with peel resistance PSA measurement techniques [18].

Peel tests were carried out on specimens of PP1 and PP2 prepregs at temperatures ranging from 20–45 °C at 3–4 °C intervals with feed rate ranging from 1–1000 mm min⁻¹ at approximately 10 logarithmic intervals at each temperature. A new specimen was used for each test. Temperature was measured using a Fluke 62 mini infrared thermometer at the prepreg surface immediately following completion of the test. The temperatures recorded from the series of tests with the same oven setting were within ± 1 °C of each other. The prepreg specimens were 215 mm long and 75 mm wide. Within each specimen, 50 mm of measurement distance along the specimen length was used for dynamic stiffness and 80 mm for continuous peel.

3. Results

3.1. Dsc

The cure enthalpy was obtained by integration of the exothermic peak. Both resin samples displayed a similar cure profile, but a lower cure enthalpy was recorded in R1 compared to R2: 182 J g⁻¹ and 192.7 J g⁻¹ respectively. This reduction is consistent with the small degree of cure expected to have occurred during storage, but could also be attributed to manufacturing deviations between resin batches.

3.2. Gpc

A typical GPC trace is shown in Fig. 4. Four distinct consistent peaks were recorded. Of these, peak 4 is attributed to the solvent. Peaks 1–3 relate to the different chemical components of the epoxy resin, and can be attributed to epoxy prepolymer resin, hardener and Bisphenol A diglycidyl ether (DGEBA) respectively [29].

Measurements of number average and weight average molar mass (M_n and M_w) are reported in Table 1 for peaks 1–3. Three repeats were conducted for each resin, and results presented are average values and standard deviations. The differences in molar mass before and after prepregging are statistically insignificant.

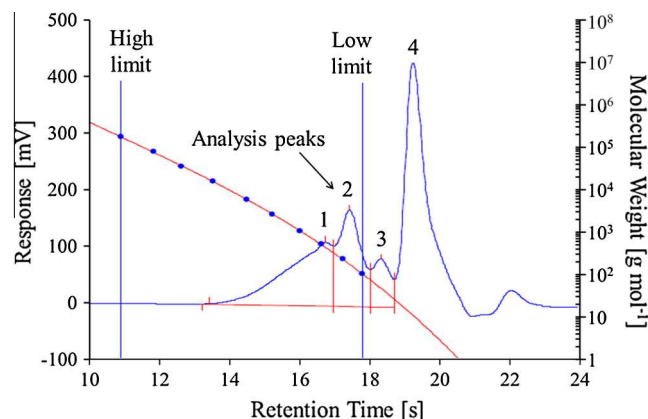


Fig. 4. GPC analysis of R1 resin sample showing four peaks, consistent for all samples, against a molecular weight calibration for polystyrene. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

Number average and weight average molar masses of resins R1 and R2, and of prepregs PP1 and PP2, obtained from GPC analysis.

Sample	Peak 1	Peak 2	Peak 3
M_n (g mol ⁻¹)			
R1	3792 ± 107.62	863 ± 20.6	285.7 ± 8.62
PP1	3816 ± 53.48	865 ± 11.5	286 ± 4.58
R2	3431 ± 46	834 ± 10.54	284 ± 4.36
PP2	3439 ± 11.02	842 ± 1.15	285 ± 0
M_w (g mol ⁻¹)			
R1	6613 ± 225.06	962 ± 22.94	304 ± 8.19
PP1	6532 ± 125.3	967 ± 11.68	304.7 ± 5.03
R2	5582 ± 94.64	926 ± 11.02	301.7 ± 3.79
PP2	5502 ± 64.08	934 ± 1	304 ± 0

This suggests that no detectable cure occurs during the prepregging process. Therefore, rheometry conducted on the resin samples can be considered representative of the rheology of the resin within the prepregs. A noticeable increase in both M_n and M_w is observed in R1 resin compared with R2. This is consistent with a small degree of polymerisation, or cure, occurring during the additional storage period.

3.3. Rheology

Storage and loss moduli obtained using parallel plate shear rheometry at a shear strain amplitude of 0.5% for frequencies ranging from 0.6 to 188 rad s⁻¹ on resin R1 are shown in Fig. 5. Similar, but not identical, results were obtained from measurements on resin R2 (not shown). The viscoelastic response is typical of a polymeric material near the transition to flow. Horizontal time–temperature shifting was performed in such a way as to determine an optimum pair of parameters C_1 and C_2 that, when applied to the WLF relationship, allow measured frequencies ω_i obtained at temperature T_i to be shifted to frequencies $A\omega_i$ at a reference temperature T_0 . The form of the WLF equation used here is

$$\log(A_T) = \frac{-C_1(T - T_0)}{C_2 + (T - T_0)} \quad (1)$$

The constants were determined using the optimiser Reptate [30] with no vertical shift applied. Resin R1 constants were determined as $C_1 = 12.8$ and $C_2 = 66.8$ with R2 determined as $C_1 = 13.7$

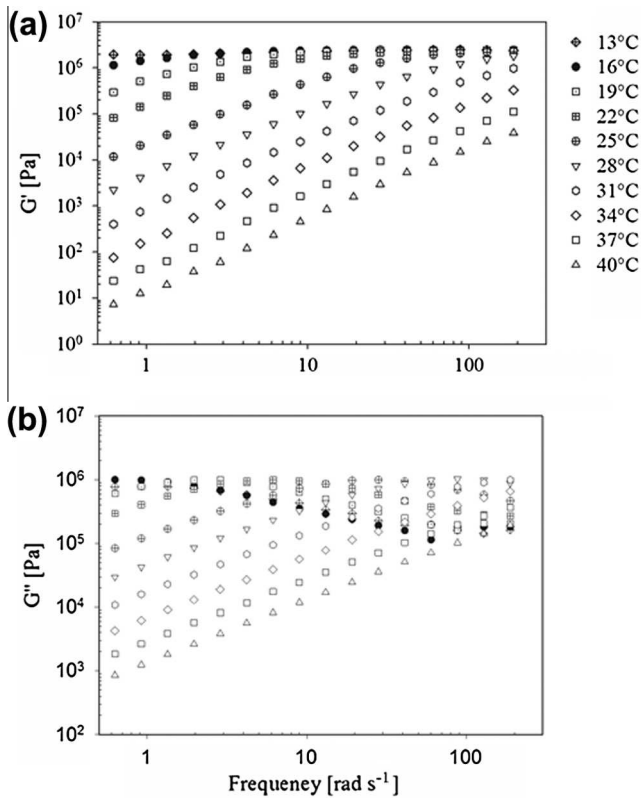


Fig. 5. Storage (a) and loss (b) moduli of R1 resin obtained from isothermal frequency sweeps at a strain amplitude of 0.5%.

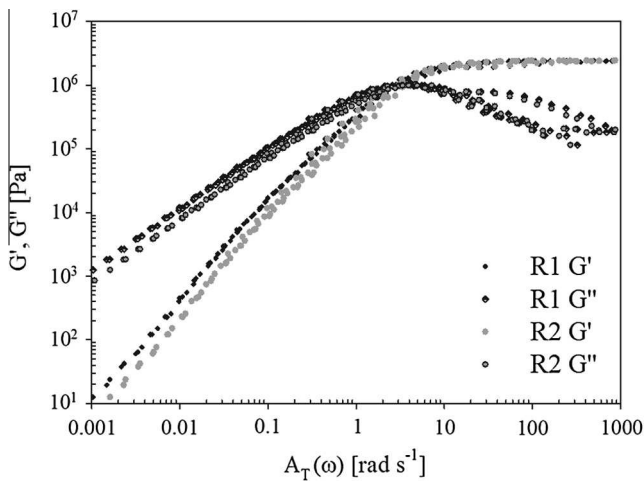


Fig. 6. Viscoelastic shear moduli as a function of reduced frequency, shifted using the WLF parameters.

and $C_2 = 79.4$ at a reference temperature $T_0 = 20$ °C. These parameters could then be employed to produce viscoelastic master curves, shown in Fig. 6.

3.4. Tack and dynamic stiffness

Measurements of dynamic stiffness and of tack for both PP1 and PP2 are shown in Figs. 7 and 9, where both exhibit a strong sensitivity to feed rate and temperature which is similar in both sam-

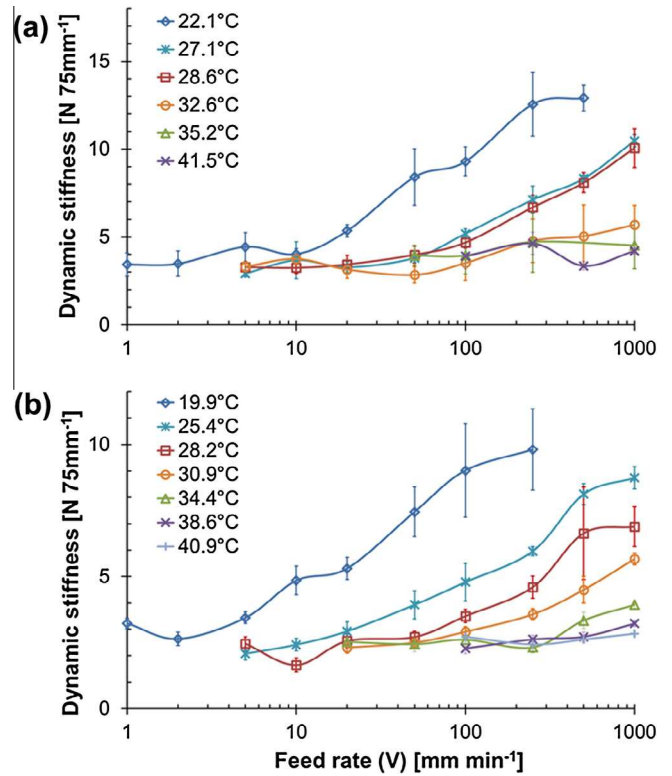


Fig. 7. The dynamic stiffness of PP1 (a) and PP2 (b) prepreg at isothermal temperatures over a feed rate range. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

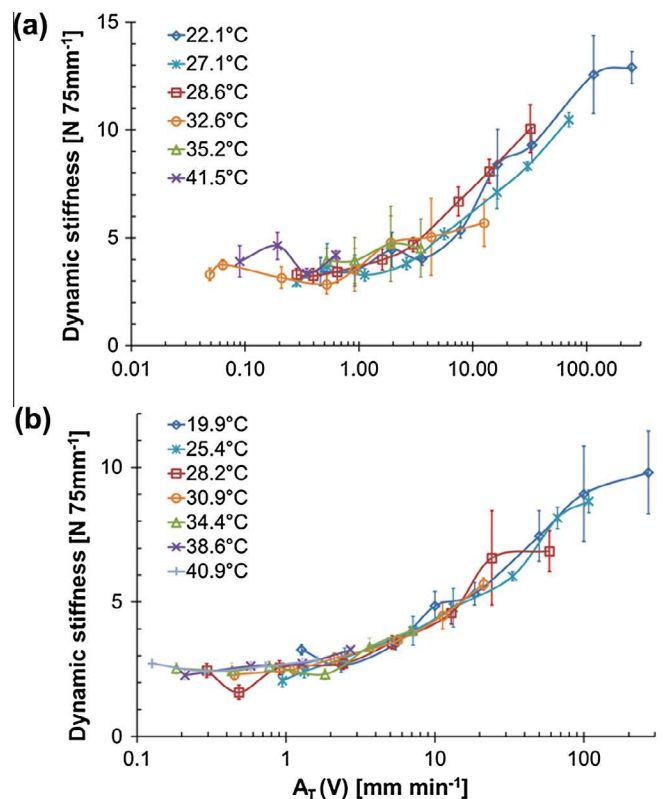


Fig. 8. The dynamic stiffness of PP1 (a) and PP2 (b) prepreg reduced using the WLF equation and parameters found by rheology ($T_0 = 20$ °C). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

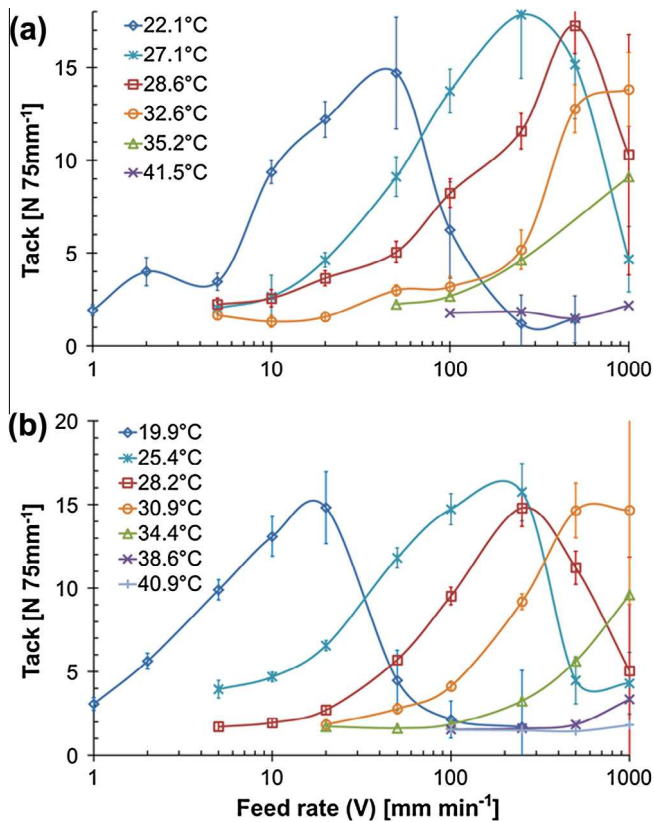


Fig. 9. The tack of PP1 (a) and PP2 (b) prepreg at isothermal temperatures over a feed rate range. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ples. The WLF equation was used with parameters found by rheology (Section 3.3), to shift tack and stiffness results in the time domain. Both prepregs exhibit excellent agreement with the TTS principle for both stiffness and tack shown in Figs. 8 and 10.

4. Discussion

4.1. Peel test configuration and failure modes

Two types of failure were observed during the peel test: interfacial failure and cohesive failure. Interfacial failure appears as a failure at the interface of prepreg and metallic substrate, and is a symptom of a poorly formed bond across the interface. This results in very limited resin residue on the plate, and low levels of tack. Interfacial failure typically occurs at high feed rates and low temperatures where the resin has insufficient flow to conform to the microscopically rough surface or insufficient internal energy to establish non-covalent molecular bonds needed to obtain tack. A typical example of interfacial failure is shown in Fig 11. Cohesive failure appears as a failure in the resin film, with fibrillation and significant resin deposition on the test surface. It generally results in low tack at very low feed rates or at high deposition temperatures, as the resin viscosity and resistance to shearing are reduced. The mode of failure appears to undergo a transition across the peak in tack in the reduced feed rate plots. Interfacial failure is evident on the left hand side of the peak, and cohesive failure on the right. The transition region is consistent with the point of highest tack, where the compromise between flow and internal resin strength is optimum.

Failure modes can also be distinguished by observing the resin deposition pattern on the rigid plate after a peel test, as shown in Fig 12 for a range of peel conditions carried out on prepreg PP1. A

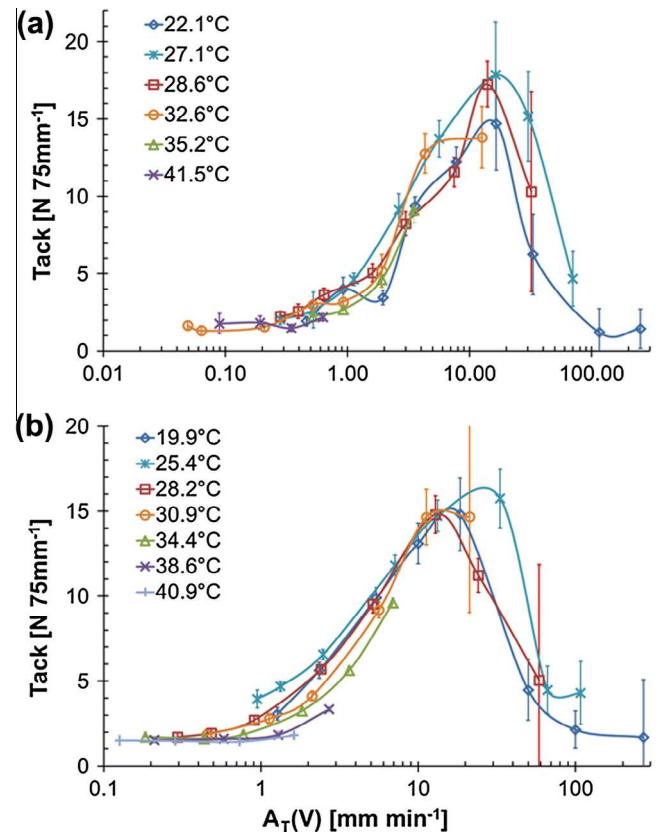


Fig. 10. The tack of PP1 (a) and PP2 (b) prepreg reduced using the WLF equation and parameters found by rheology ($T_0 = 20\text{ }^\circ\text{C}$). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

high deposition volume is synonymous with cohesive failure. There is a transition region during which the deposition becomes patchy. Eventually there is virtually no deposition, associated with interfacial failure.

These failure modes may be compared to the four failure modes observed in PSA peel tests typically known as Interfacial mode I (at the surface), Interfacial mode II (at the backing substrate), Cohesive and the transition region often termed the 'stick-slip condition' [18]. However, mode II failure was not readily observed in prepreg. This is most likely due to the presence of fibres which are constrained at the ends during the test. The fibres are well dispersed throughout the thickness, therefore, prepreg lacks a defined second interface such as that seen at the backing paper of PSA tapes. The stick slip region is also less prominent in prepreg peel testing results, The stick slip phenomenon is typically considered to be the result of the storage and instantaneous release of viscoelastic energy [18]. The spring loaded compaction roller or fibres within the prepreg may provide a damping effect reducing the occurrence and severity of this phenomenon.

In traditional PSA peel testing the TTS relationship has been observed mostly in the cohesive failure mode [22]. A transition in failure mode is dependent on temperature and rate in a manner consistent with TTS. However, because the material has been applied in a separate process, the contact time is typically much longer and does not scale proportionately with peel rate. Therefore, the interface is typically well established and a much higher viscoelastic stiffness is required to cause a shift in failure mode. Typically, for pre-applied PSAs this stiffness is not achieved until the resin reaches a rubbery or glassy state. Therefore, the failure mode has been referred to as 'glassy fracture' [28]. As failure switches to the interface, the resin, in its solid like state, is unable to deform

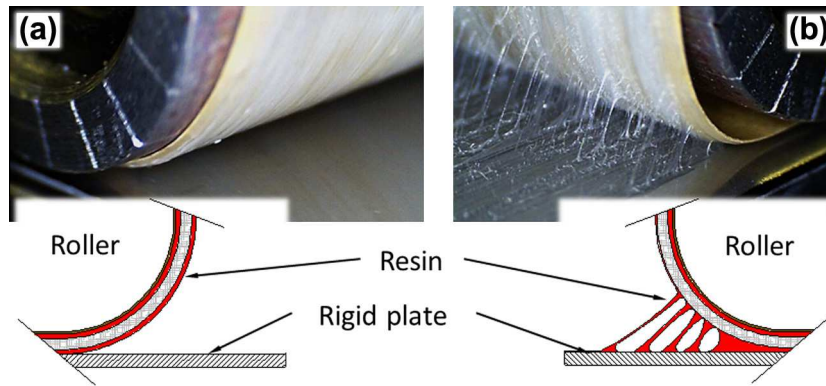


Fig. 11. Interfacial (a) and cohesive (b) failure modes identified by observation of peel behaviour and resin deposition pattern on the rigid plate. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

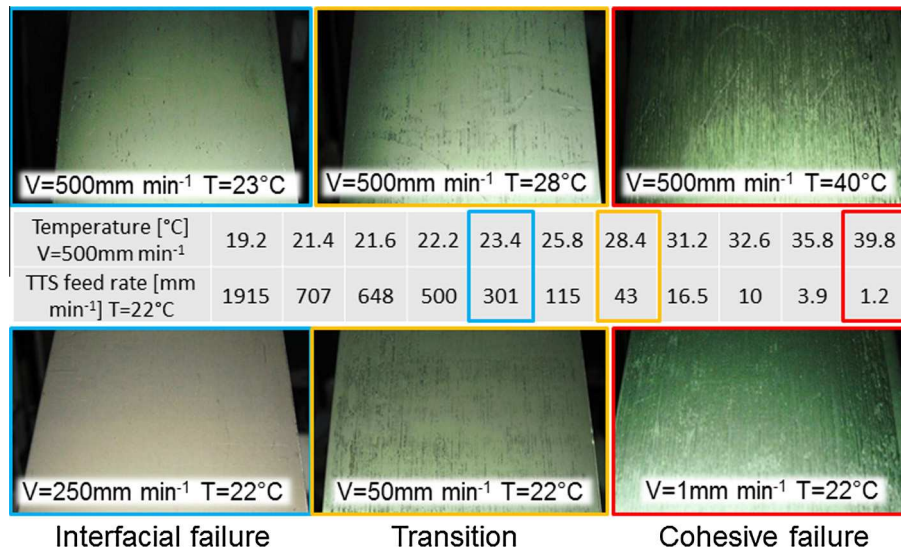


Fig. 12. Resin deposition patterns of PP1 peel tests. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

at the crack front and minimal energy is absorbed. The result is a fast fracture with a significant reduction in peel resistance [31]. This explains why, with traditional peel methods, it is difficult to obtain meaningful measurements in the transition region, and why no information can be obtained about the formation of the initial surface bond.

The newly devised peel test incorporates both the application of the prepreg and the peeling process. In this test application times are short and inversely proportional to peel rate. Thus, both interfacial and cohesive tack failure mechanisms are each related to the formation and failure of the interface. This helps to explain why not only interfacial tack levels but also cohesive tack levels both appear to obey the same TTS parameters as obtained in linear rheology. This is convincing evidence that the quality of surface interaction is determined by diffusion of polymer chains in the melt. In order to generate a good bond, polymer chains must reptate into the crevices present due to the roughness of the metal substrate. Therefore, if diffusion of the polymer chains is limited in time, then the surface contact area may also be reduced. Another explanation that has been suggested is that the timescales governing the processes of diffusion in the bulk and of surface interaction could be sufficiently similar. This accounts for the effects of changes in surface energy observed in recent dynamic molecular models, where accurate melt and surface behaviour are mostly influenced by Van der Waals force field parameters [32,33].

4.2. Application to automation

The new peel test was devised specifically to simulate the automated lay-up process, where tack and dynamic stiffness are two key parameters for consistent lay-up [23]. It is well established that tack is sensitive to temperature and rate fluctuations and most modern ATL and AFP machines include a means of maintaining a constant temperature [34]. It is less well known that tack is sensitive to changes in feed rate [12] and that changing temperature according to the feed rate can help to alleviate tack fluctuations. However, thus far only linear changes in feed rate with temperature have been applied [11]. The results of the peel experiments in this study suggest that tack and stiffness are sensitive to temperature and feed rate in the same way as the viscoelastic properties of the resin. Thus, constant tack and stiffness properties should be maintained throughout lay-up operations by observing TTS through a WLF relationship.

5. Conclusions

This study has investigated the cross-linking enthalpy, molar mass, linear viscoelastic rheology and tack handling properties of two prepreps and matching resin samples with differing storage histories. Differential scanning calorimetry (DSC) has revealed that

a small degree of cure has occurred during storage. Gel permeation chromatography (GPC) supports DSC results by indicating an increase in molar mass of the aged prepreg and resin sample. GPC results also confirm that no significant changes in molar mass have occurred in the resin during prepregging, and that rheology experiments carried out on resins extracted before the prepregging process are representative of the handling properties of the uncured prepreg.

Isothermal small amplitude oscillatory shear rheometry on the extracted resin component revealed frequency and temperature sensitive viscoelastic properties that follow time–temperature superposition. The difference in viscoelastic properties between the two resin samples is consistent with the small increase in molar mass for the aged resin.

A recently developed peel method which simulates the automated tape laying (ATL) process was used to determine the dynamic stiffness and the peel force at a range of feed rates and temperatures. Results have revealed sensitivity to both temperature and feed rate. By transposing the measured data using a WLF equation and constants determined from rheology, TTS was demonstrated for both prepreg tack and dynamic stiffness. Tack and dynamic stiffness are the major handling properties which dictate the reliability of automated lay-up. The application of TTS to control temperature and feed-rate to maximise and maintain tack levels is expected to allow increased reliability in automated processing.

References

- [1] Akay M. Effects of prepreg aging and post-cure hygrothermal conditioning on the mechanical-behavior of carbon-fiber epoxy laminates. *Compos Sci Technol* 1990;38(4):359–70.
- [2] Ahn KJ, Seferis JC. Prepreg process analysis. *Polym Compos* 1993;14(4):349–60.
- [3] Rosu D et al. Cure kinetics of epoxy resins studied by non-isothermal DSC data. *Thermochim Acta* 2002;383(1–2):119–27.
- [4] Boey FYC, Yap BH, Chia L. Microwave curing of epoxy-amine system – effect of curing agent on rate enhancement. *Polym Testing* 1999;18(2):93–109.
- [5] Goode K. Automated Ply Lamination, *ASM Handbook*, vol. 21, Composites, ASM International; 1987.
- [6] Newell GC, Buckingham RO, Khodabandehloo K. The automated manufacture of prepreg broadgoods components – a review of literature. *Compos Part A – Appl Sci Manuf* 1996;27(3):211–7.
- [7] Grimshaw, MN. Automated Tape Laying, *ASM Handbook*, vol. 21, Composites, ASM, International; 2001. p. 480–5.
- [8] Repecka L. Prepreg characteristics and their effects on automated tape laying machines, *SAMPE 88, New Generation Materials and Processes: Milan*; 1988. p. 55–64.
- [9] Shirinzadeh B et al. Fabrication process of open surfaces by robotic fibre placement. *Robot Comput-Integr Manuf* 2004;20(1):17–28.
- [10] Olsen HB, Craig JJ. Automated Composite Tape Lay-up Using Robotic Devices, vols. 1–3. In: *Proceedings: IEEE international conference on robotics and automation*; 1993. p. C291–7.
- [11] Schulz MD, Grimshaw MN, Beard J. Tape temperature control system for automated tape-laying of low tack prepreps. In: *33rd International SAMPE symposium*. SAMPE, California, 1988.
- [12] Gutowski TG, Bonhomme L. The mechanics of prepreg conformance. *J Compos Mater* 1988;22(3):204–23.
- [13] Seferis JC, Meissonnier J. Development of a tack and drape test for prepreps based on viscoelastic principles. *Sampe Quarter-Soc Adv Mater Process Eng* 1989;20(3):55–64.
- [14] Dubois O, Cam JBL, Beakou A. Experimental analysis of prepreg tack. *Exp Mech* 2009 [Online].
- [15] Banks R et al. Development of a new structural prepreg: characterisation of handling, drape and tack properties. *Compos Struct* 2004;66(1–4):169–74.
- [16] Anon. Tack measurement for pressure sensitive adhesives – Determination of rooling ball tack. London: BSI; 1999.
- [17] Anon. Tack measurement for pressure sensitive adhesives – Determination of loop tack. London: BSI; 1999.
- [18] Benedek I, Feldstein MM. *Fundamentals of pressure sensitivity*. London: CRC Press; 2009.
- [19] Ahn KJ et al. Analysis and characterization of prepreg tack. *Polym Compos* 1992;13(3):197–206.
- [20] Putnam JW, Hayes BS, Seferis JC. Prepreg process-structure-property analysis and scale-up for manufacturing and performance. *J Adv Mater* 1996;27(4):47–57.
- [21] Anon. Determination of peel resistance of high-strength adhesive bonds – Floating roller method. London: BSI; 1995.
- [22] Derail C et al. Relationship between viscoelastic and peeling properties of model adhesives. Part 1. Cohesive fracture. *J Adhes* 1997;61(1–4):123–57.
- [23] Crossley RJ, Schubel PJ, Warrior NA. The experimental determination of prepreg tack and dynamic stiffness. *Compos A Appl Sci Manuf* 2011;43(3):423–34.
- [24] Crossley RJ, Schubel PJ, Warrior NA. Experimental determination and control of prepreg tack for automated manufacture. *Plast Rubber Compos* 2011;40(6–7):363–8.
- [25] Dealy JM, Plazek D. Time–temperature superposition – a users guide. *Rheology Bulletin* 2009;78(2):16–32.
- [26] Rudin A. *The elements of polymer science and engineering*. 2nd ed. London: Academic Press; 1999.
- [27] Ferry JD. *Viscoelastic properties of polymers*. 3rd ed. New York: John Wiley & Sons; 1980.
- [28] Derail C et al. Relationship between viscoelastic and peeling properties of model adhesives. Part 2. The interfacial fracture domains. *J Adhes* 1999;68(3–4):203–28.
- [29] Saunders KJ. *Organic polymer chemistry*. Chapman & Hall; 1994.
- [30] Ramirez J, Likhtmen A. Reptate: Rheology of entangled polymers toolkit for analysis of theory and experiment; 2009. Available from: <www.reptate.com>.
- [31] Gibert FX et al. Effect of the rheological properties of industrial hot-melt and pressure-sensitive adhesives on the peel behavior. *J Adhes Sci Technol* 1999;13(9):1029–44.
- [32] Wu CF, Xu WJ. Atomistic molecular modelling of crosslinked epoxy resin. *Polymer* 2006;47(16):6004–9.
- [33] Johnston K, Harmandaris V. Properties of benzene confined between two Au(111) surfaces using a combined density functional theory and classical molecular dynamics approach. *J Phys Chem C* 2011;115(30):14707–17.
- [34] Grimshaw MN, Grant CG, Diaz JML. Advanced technology tape laying for affordable manufacturing of large composite structures. *Polym Compos* 2007;13(3):197–206.