

VISCOUS BEHAVIOR OF RESIN AND FLOW THROUGH THE FIBER NETWORK OF CARBON/PEKK BASED THERMOPLASTIC COMPOSITE

Hasan Salek ¹, Suong. V. Hoa ^{1,3} and Johanne Denault ²

¹ *Concordia Center for Composites, Concordia University,
1455 de Maisonneuve Blvd. West, Montreal, Quebec, H3G 1M8, Canada*

² *Industrial Materials Institute (IMI), 75 Boulevard de Mortagne, Boucherville, J4B 6Y4, Quebec*

³ *Corresponding author's Email: hoasuon@alcor.concordia.ca*

SUMMARY: Semi-crystalline thermoplastic polymer, such as Poly Ether Ketone Ketone (PEKK), based composites are gaining interest of many researchers due to their higher glass transition temperature (156°C), high strength and stiffness, high toughness, low moisture absorption and excellent environmental resistance. In this study, 5 harness satin weave of Carbon/PEKK semipreg is used to manufacture composite laminates using compression molding technique. During processing, the dry carbon fiber network is deformed and wetted by molten PEKK upon application of sufficient pressure, temperature and time. Different stages of fiber network deformation throughout the consolidation process are described. Influence of processing parameters on the quality of the final laminate is also discussed. Affects of temperature and time to initiate degradation during viscosity measurement of PEKK polymer are investigated. Some extent of crosslinking within the polymer is also observed during viscosity measurements.

KEYWORDS: carbon/PEKK, thermoplastic, viscosity, resin flow, fiber network

INTRODUCTION

Thermoplastics and their composites, in general, have an indefinite shelf life, low moisture absorption, excellent thermal stability, high toughness and damage tolerance, short and simple processing cycles and potential for significant reductions in manufacturing costs. In addition, they have the ability to be remelted and reprocessed and also damaged structures can be repaired by the application of heat and pressure. Thermoplastics also possess few drawbacks such as high viscosity and processing temperature, hence difficult to handle during manufacturing [1, 2, 3].

Researches have developed number of different manufacturing process models and permeability models for thermoplastic based composites. Dara and Loos [4] proposed processing model for Graphite/Polysulphone tape based composites where they investigated the autohesion and

intimate contact behavior of such a thermoplastic. The effects of the processing parameters such as pressure, temperature and time on the quality of such a composite have been discussed. Lee and Springer [5] presented a model on the manufacturing process of Graphite/PEEK composites. Their model was divided into three sub models such as impregnation, consolidation and crystallinity submodel. The experimental verifications of these models were based on prepreg tape material and compression molding technique. Mantell and Springer [6] developed manufacturing process models for Carbon/PEEK composites but for different manufacturing techniques such as autoclave, press, tape layup and filament winding. They considered both composite plates and cylinders to validate their model. Li and Loos [8] presented another model, based on their previous work [7], on interplay intimate contact. The model used prepreg geometric properties, constituent material properties and processing parameters as input. Two types of prepregs were used in this investigation: Graphite/Polysulphone and APC-2 AS4/PEEK. Simacek and Advani [9] presented a permeability model for plain weave material for RTM technique. They computed the model for in-plane permeability of a woven fabric and suggested an extension for multi-layered structure. Ranganathan, Phelan and Advani [10] proposed a generalized model for transverse permeability in unidirectional fibrous media for RTM process. Four basic flow deformation processes such as resin percolation, transverse (squeezing) flow, intraply shearing flow and interplay slip-cooperative flow are presented by various authors [11-12]. None of these works were focused on semipreg type fiber reinforced thermoplastics with a multiple-harness weave network and their permeability prediction. This study is a primary ground work on the way to establish an understanding of the flow process through the multiple-harness weave fiber network and finally to develop a permeability model.

One of the main challenges of thermoplastic based composite processing is the high viscosity and hence high temperature processing. Hence, a user carefully selects the manufacturing parameters (temperature, pressure and time) depending on the material type. All these manufacturing parameters need a meticulous selection to obtain the optimum properties of the final product. This part of the work focuses on understanding the PEKK polymer behavior and the affect of variable processing parameters on the polymer flow through the fiber network.

MATERIAL INFORMATION

The material used for this work is neat Poly Ether Ketone Ketone (PEKK) polymer film and 5 harness satin weave Carbon/PEKK semipreg.

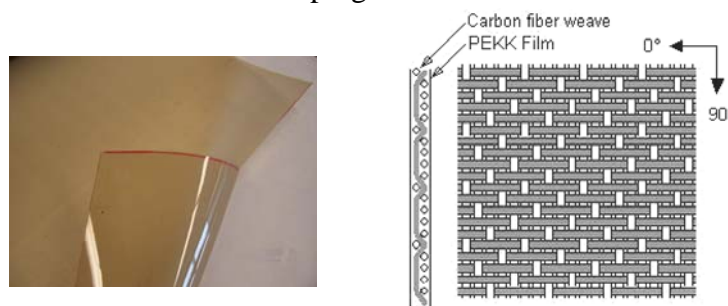


Fig. 1 PEKK polymer film and schematic of Carbon/PEKK 5 harness weave semipreg [13].

The manufacturer and supplier of these materials is CYTEC Engineered Materials, USA. Fig. 1 shows PEKK resin film and the schematic of the Carbon/PEKK semipreg. Because of its high

glass transition temperature (156°C, higher than PEEK - 143°C), PEKK based composites can be used for high temperature applications [1, 3].

PEKK POLYMER CHARACTERIZATION

Rheological Measurements

Rheological measurement of polymer such as determination of viscosity is important to obtain the polymer flow behavior at different processing temperatures. Keeping in mind the typical processing temperature of PEKK resin (~340°C) [3], the viscosity of the polymer was determined at temperatures 320, 340 and 360°C. Standard method of determining viscosity is by Shear Test of polymer melt using a Rotational Rheometer. Parallel plate fixture was used for melts. A nitrogen flow was kept during the experiment for an inert environment.

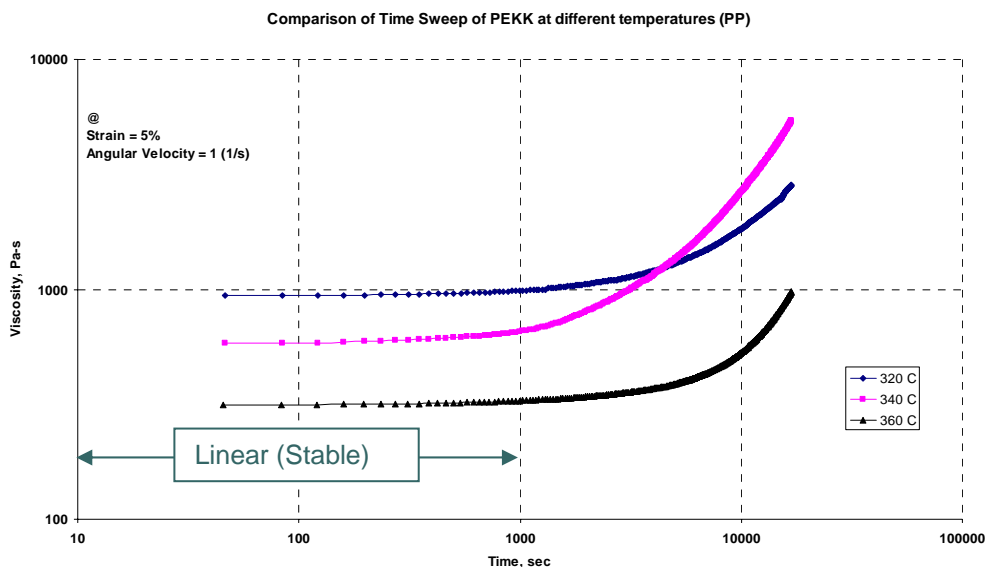


Fig. 2 Time sweep of PEKK at different temperatures.

Time sweep experiment was performed to determine the total amount of time up to which the polymer remains stable (no degradation or significant change in viscosity). Fig. 2 shows the variation of viscosity with respect to time for temperatures 320, 340 & 360°C. It is obvious from Fig. 2 that the polymer viscosity is linear up to 16 minutes for all the three temperatures. It is to be noted that prior to the first measurement; polymer was exposed to the target temperature for another 12-14 minutes for experimental preparation. Hence, the polymer viscosity remains unchanged for an approximate total of 30 minutes within the above mentioned temperature range. Afterwards, viscosity increases significantly with time, even though PEKK has a degradation temperature of 400°C [3]. A TGA (Thermo Gravimetric Analysis) experiment result in Fig. 3 below also confirms this. This experiment was performed at two different heating rates to check for variation in results. But it is obvious that within the stable temperature range, it has no effect.

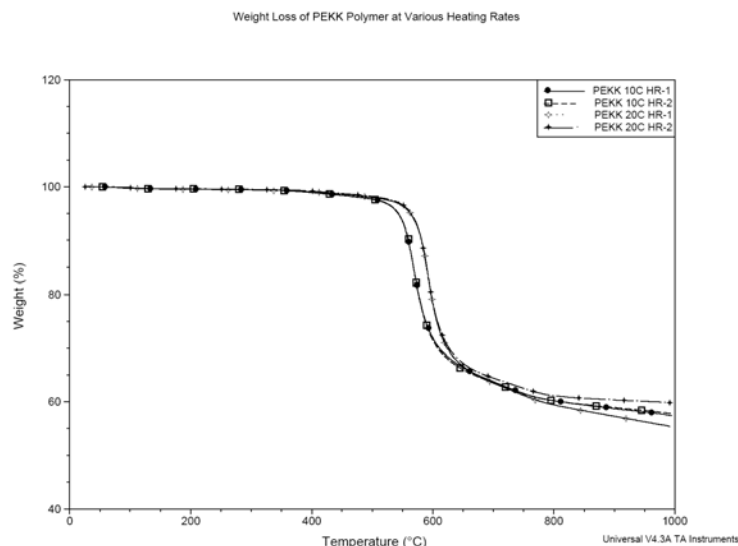


Fig. 3 Weight loss (degradation) of PEKK polymer with temperature at various heating rates.

A literature survey on this issue reveals that there are possibilities of cross-linking at higher temperatures. A similar phenomenon was observed for the case of PEEK [14]. The increase in viscosity with time is explained in terms of chain scission and cross-linking. Fig. 4 shows the chemical structure of PEKK monomer. A long chain of PEKK polymer consists of many monomers as shown below.

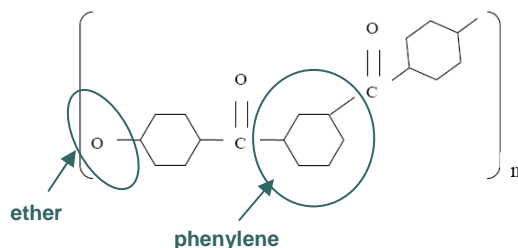


Fig. 4 Monomer of PEKK [3].

During the experiment, extended exposure at high temperature initiates the instability in either at ether (R-O-R) or at phenylene bonds resulting in chain scission at the end of the chain. As a result of the chain scission the produced radicals extract hydrogen from phenylene units to form cross-links with the adjacent broken chain, hence increasing the viscosity of the polymer [14]. To confirm this issue, whether or not the PEKK polymer is cross-linking during viscosity tests, a few DSC experiments were performed.

DSC Study

A similar situation as in the viscosity test, i.e. polymer was exposed to high temperature for longer time, was simulated for the DSC tests. After a regular heating cycle, PEKK was kept at 360°C for few hours and then allowed to cool. But the cooling cycle did not generate any crystallization valley. Subsequently this polymer was heated again and it revealed no

crystallization and melting regions in the thermograms which are shown in Fig. 5. This behavior proves that extended exposure at high temperature caused all the polymer chains to crosslink and allows no free chains left for forming new crystals. Curves in Fig. 5 are superposed; the bold curves are active among the rest.

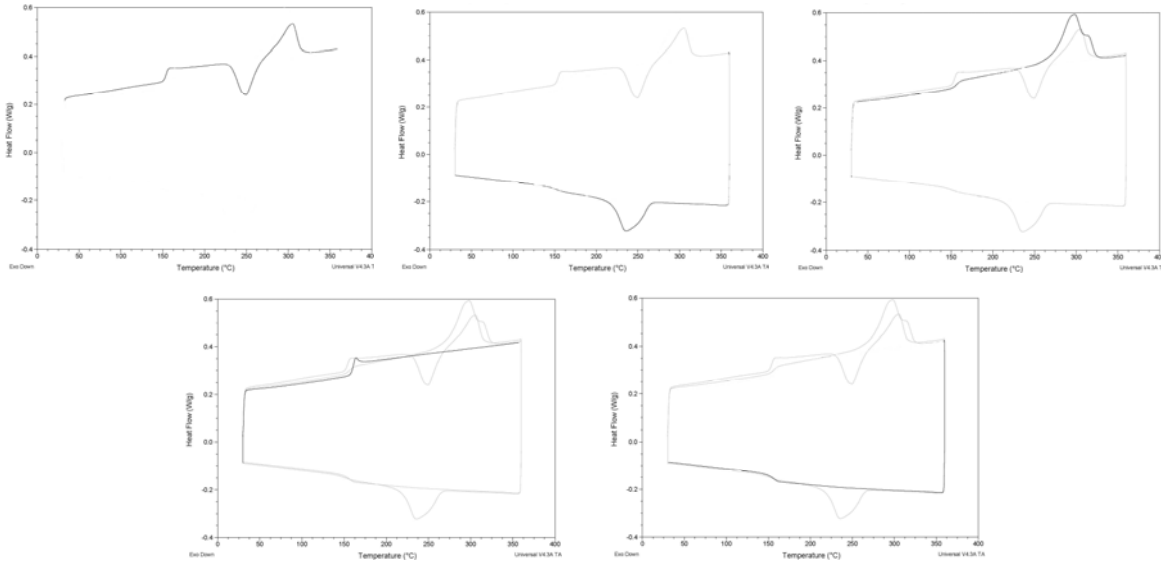


Fig. 5 DSC thermograms clockwise: 1st heating up to 360°C ; 1st cooling curve; 2nd heating up to 360°C; hold few hours at 360°C and then 2nd cooling (no crystallization dip); 3rd heating (no crystallization dip or melting peak).

The DSC results confirm that crosslinking exists when material is exposed to longer period of time at high temperature. From the viscosity and DSC tests it can be concluded that processing time of PEKK within a temperature range of 320 to 360°C should not exceed 30 minutes.

INFLUENCE OF PROCESSING PARAMETERS ON THE FLOW THROUGH THE FIBER NETWORK OF THE COMPOSITE LAMINATE

The adapted manufacturing technique to process the Carbon/PEKK semipreg was compression molding. The applied pressure is the driving force causing the semipreg ply interfaces to coalesce. The elevated temperature controls the rate at which the ply interfaces bond together by influencing the mobility of the molecular chains of the polymer. The temperature and pressure also affect the polymer flow through the fiber arrangement. So it is important to address issues like the consolidation of the ply interfaces to one another and the permeability of polymer through the fibrous media. Fig. 6 schematically shows the various stages of laminate deformation during consolidation cycle. Initially, the layers have bulk interply and intraply spacing between them which is reduced by application of pressure. Once heated above melting point, the resin starts to flow within the fiber network under pressure, resulting in a compact final configuration of a laminate composite. To understand these different stages of laminate deformation during processing, few laminates are manufactured (using various processing conditions) and their cross-sections are analyzed through microscopic observation. The various processing conditions used for different laminates are listed in Table 1.

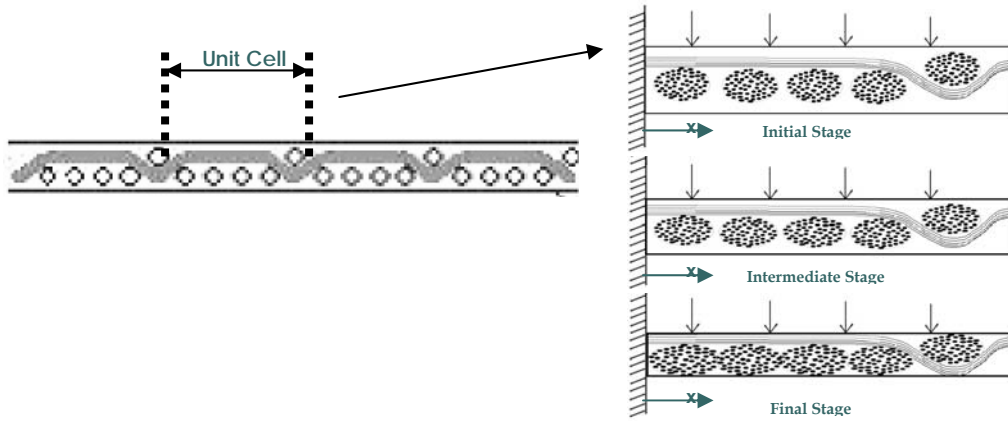


Fig. 6 Different stages of deformation of Carbon/PEKK semipreg under compression loading.

All samples are heated up to the consolidation temperature before applying desired pressure. At the end of the dwell time, samples are quenched to freeze their internal condition of that moment. This condition of the laminate is then observed under microscope to understand the different stages of consolidation, i.e. effect of the processing variables.

Table 1 Processing variables of Carbon/PEKK semipreg laminates

| Sample # | Pressure, MPa | Dwell Time, min | Temperature, °C |
|----------|---------------|-----------------|-----------------|
| CPM 1 | 2.2 | <1 | 360 |
| CPM 2 | 2.2 | 6 | 360 |
| CPM 3 | 2.2 | 12 | 360 |
| CPM 4 | 1.1 | 12 | 360 |
| CPM 5 | 1.1 | 6 | 360 |
| CPM 6 | 1.1 | <1 | 360 |

As described in Table 1, sample numbers CPM 1 & CPM 6 have all the parameters same except for pressure, which is half the amount of the initial value. Same relation prevails in other pairs such as, CPM 2 & 5 and CPM 3 & 4. Fig. 7, 8 & 9 below show the qualitative comparison of different laminate cross-sections due to the variable processing conditions. All the laminates have three layers of semipreg and are shown at the center of the micrographs. The grey area on both sides of each laminate micrograph is epoxy mounting, which facilitated the polishing procedure of the samples. Each sample is measured at different sections for the thicknesses of single tow/layer and whole laminate. The significant difference between laminates CPM 1 and 6, which can be observed from Fig. 7, is the change in thickness due to the change in pressure during consolidation. The change in laminate thickness is about 11% as the pressure is reduced to half the amount. This confirms the squeezing of the bulk space and merging of multiple layers. Apart from that, the qualitative void content is obvious in both the laminates which can be attributed to the application of pressure for a very short period of time. Significant improvement in laminate quality, in terms of void content, is observed when enough dwell time is allowed. This is shown in Fig. 8 and 9.

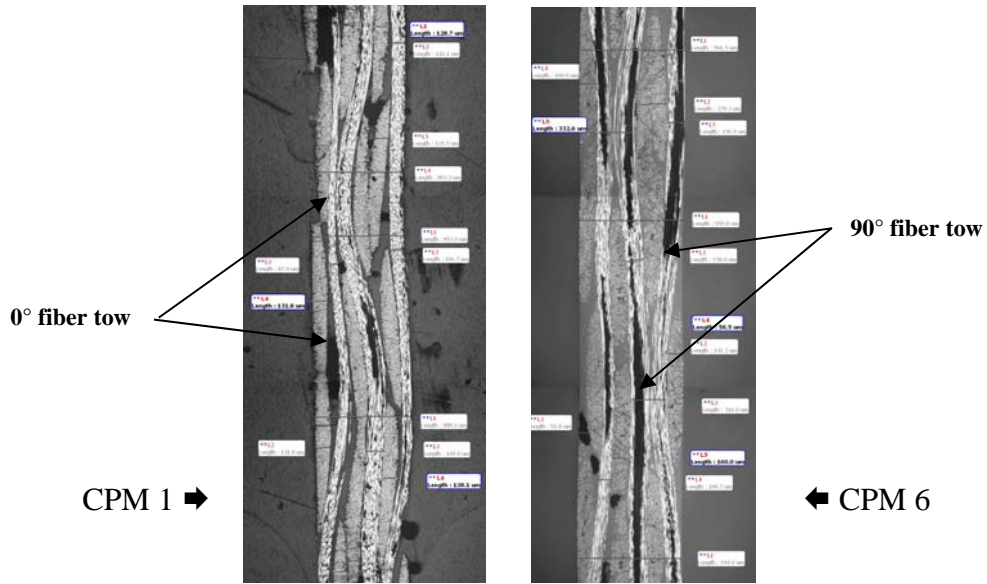


Fig. 7 Cross-sectional micrograph of laminates CPM 1 & CPM 6.

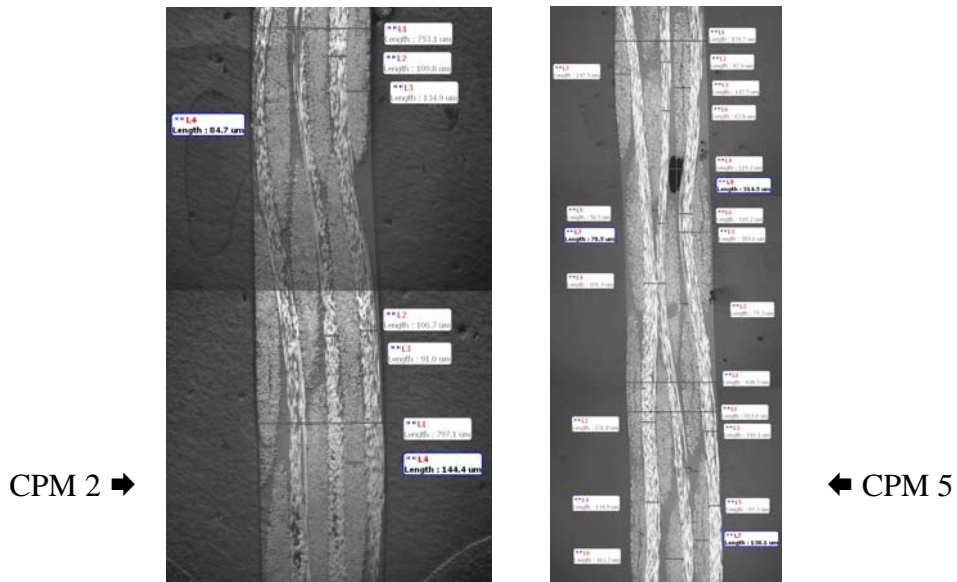


Fig. 8 Cross-sectional micrograph of laminates CPM 2 & CPM 5.

Similar to Fig. 7, Fig. 8 confirms the difference between laminates CPM 2 and 5 due to pressure change; only dwell time is higher in the latter Figure. Due to the fact that laminate CPM 5 was exposed to lower pressure (1.1 MPa), a little amount of void content is still noticeable, so is the increase in thickness (10%). CPM 3 and 4 laminates have identical conditions except for pressure which are shown in Fig. 9. As shown in the micrographs, sufficient dwell time improved the overall quality of these laminates compared to the rest. Specially, laminate CPM 3 looks more coalesce than CPM 4 due to the appropriate pressure (2.2 MPa) and dwell time.

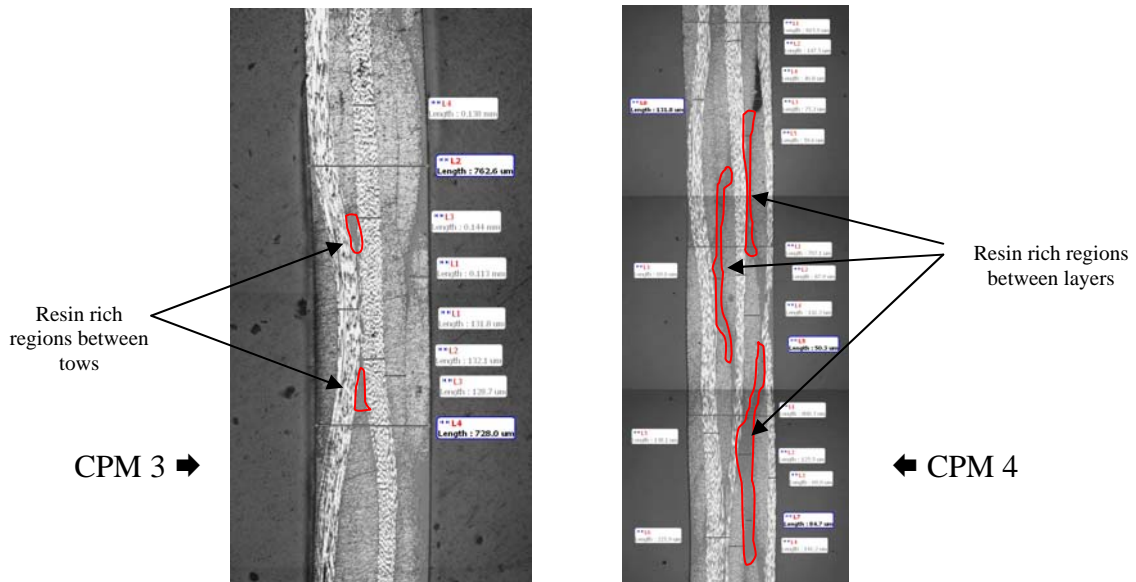


Fig. 9 Cross-sectional micrograph of laminates CPM 3 & CPM 4.

On the other hand, CPM 4 still contains some amount of void and continuous gaps or resin rich regions (marked by freeform lines) between layers. The resin rich regions of CPM 3 cannot be avoided because of the elliptical shape of the fiber tows after deformation. Hence, it can be concluded from the illustrations that processing parameters of sample CPM3 reveals the best quality laminate compared to the rest. This can be contributed to the combination of appropriate amount of pressure and dwell time.

CONCLUSIONS

The viscous behavior of the PEKK polymer has been observed and it is recommended not to process this polymer more than 30 minutes within a temperature range of 320 - 360°C to avoid degradation due to chain scission and cross-linking phenomena. As an initial work of developing a flow and permeability model, the conditions of Carbon/PEKK 5-harness satin weave semipreg under variable processing parameters have been demonstrated. The influence of these parameters on the final laminate quality has been understood. Some of the problem areas have been highlighted, such as the void content and resin rich regions. Their remedies have also been addressed. As a future work plan, these problem areas need to be quantified and must be integrated in a relationship by which it would be possible to predict their presence with the changing processing parameters. This would finally be applicable in the flow and permeability model for such type of material.

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