

THE DETECTION METHOD OF PARTICLE DISTRIBUTION IN TERNARY COMPOSITES CONSISTING OF PARTICLES, RESIN MATRIX AND 3-D WOVEN REINFORCEMENT

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ABSTRACT

Recently, with the increasing demands and requirements for thermostabilities and mechanical properties, traditional ablation resistant composites face new challenges. Adding the heat-resistant metal compounds to the three-dimensional woven-preforms was taken to promote the high-temperature performance of the composites, such as glass fibre reinforced composites of phenolic and carbon-carbon composites used in the aviation and aerospace.

Herein ternary composites of TiC particles / three-dimensional woven glass fibre (fine weave pierced fabric) / resin matrix was fabricated with the liquid phase infiltration method. Several particle detection methods were investigated to analyze the distribution of TiC particles within the composite, which is important for process optimal to improve the performance of the composites. Microscopic methods such as metallographic photography and Electron probe micro-analyser (EPMA) were taken to prove whether the particles could enter the preforms or not. Macroscopic methods such as the method based on calculations of the density, chemical analysis and physical analysis were investigated by studying their feasibility and accuracy.

The comparisons of the detection methods laid the foundation of analysis of process and enabled the optimizing the structure and performance of ternary composites. And at present, only final composite parts can be analyzed with those off-line particle detection methods. Developing a new on-line method or facility will be of great importance to the future research and manufacture of high-performance ternary ablation resistant composites.

1 INTRODUCTION

The fibre reinforce polymer composites, as one of the advanced composites, are widely applied in the aeronautics and astronautics as a result of their high strength rate, high modulus rate and excellent mechanical performance. Especially in some service environments that is high-temperature, the ablation resistant composite is one of the best choices besides superalloys. And at the circumstances where the stagnation temperature is more than 2000 °C, the exclusively appropriate option is the carbon-carbon composite, which can be converted from fibre reinforce polymer with the process of pyrolysis. However, the interlayer reaction in the composites is so weak that forbids the improvement the thermostabilities and mechanical performance which is imperative to fulfil the more and more requirements of the vehicles which are faster and higher.

Therefore the 3-D wovens were developed as the reinforcements which contained fibres perpendicular to the in-plane direction of traditional 2-D fabrics [1-4]. 3-D textile composites had a vast range of properties that are superior to traditional 2D laminates [5], nevertheless, which were not satisfied enough to the future requirements of high-temperature environments in the aviation and aerospace. High-melting-point particles were considered to be added to the polymer reinforce composites and carbon-carbon composites, expecting to improve the thermostabilities, which brought new challenges to researchers and engineers.

It is believed that the distributions of particles including contents and locations are the critical factors of thermostabilities and mechanical performance of the ternary composites with Liquid Composite Moulding, in which preforms are permeated with the blend of resins and particles. Efforts have been done to research the methods of analysing the particles in the processes and in the products. M Nordlund et al. [6] developed an apparatus that taking high resolution camera to track the movement of particles through a transparent mould, which can obtain the distributions in real time. However, this optical method was strictly limited by the transmission of light with specimens. Many other means were taken to analyze the final consequence in composites. M Chohra et al. [7] and D Lefevre et al. [8] discussed the ways that adopted washing or ablation to separate the different phases in the composites. As well as the electron probe micro-analyzer (EPMA) was employed to study the distributions in a microscopic scale [9].

However, many difficulties appeared in the attempts of distinguishing the different phases in the ternary composites by the above means. As a consequence, a new way that took centrifugal separation to conduct the physical analysis was developed in this paper. Advantages and disadvantages of centrifugal separation and other four kinds of detection methods of particles were discussed.

2 EXPERIMENTAL

In order to investigate the detection method of particle distribution, the fabrication of ternary composites consisting of particles, resin matrix and 3-D woven reinforcement was discussed in this paragraph, which was divided into two parts: preform preparations and infiltrations.

2.1 Preform Preparations

Satin glass fibre wovens were sown up with cotton threads which were easily removed by heat. Sown wovens sized of 50×50×5 mm were overlaid to the thickness of nearly 30 mm, which showed the same structure with fine weave pierced fabric. The suture lines in the fabrics were arranged as an array with a spacing of 2 mm.

The directions of glass fibre in Satin wovens were defined as x-direction and y-direction, which were almost equivalent owing to the structure of fabrics. The direction of cotton threads was defined as z-direction, representing the pierce-direction of fine weave pierced fabric.

Boundary effects that mixtures of particles and resin flow along the edges between the preform and the mould were eliminated by stuffing the margins of preforms with epoxy resin (Fig.1).

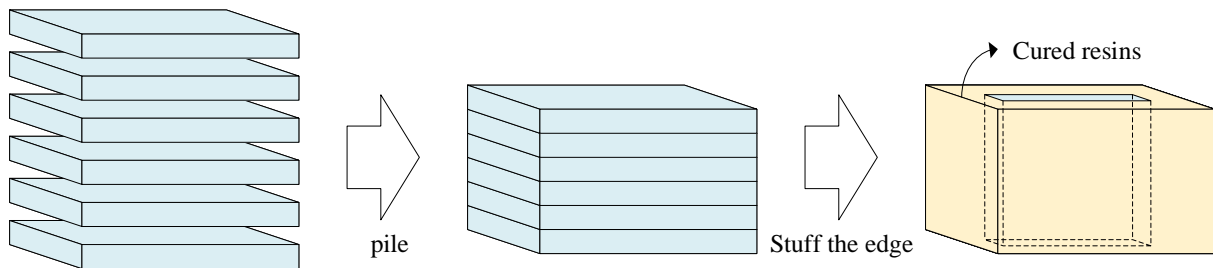


Figure 1: Process of the preform treatment.

2.2 Infiltrations

The VARI method was taken to conduct the infiltration with the preform of Fig.2. The vacuum regulator was used to ensure the driving pressure in the preform was exactly controlled (0.1 MPa and 0.05 MPa). Combinations of two kinds of TiC particles (diameters of 700 nm and 1400nm) and two kinds of epoxy resin (viscosities of 0.1 Pa·s and 0.5 Pa·s) were considered as the precursor of the matrix of composites. The flow direction was along the pierce lines.

After the preform was completely impregnated, a saturated flow of the blends continued allowing more particles could enter the preform. The volume of void in the preforms was nearly 60 cm³ while the gross volume of the combinations getting into the preforms was nearly 300 ml.

After infiltrating, 3-D preforms with resins and particles were cured, ready for analysing the distribution of particles.

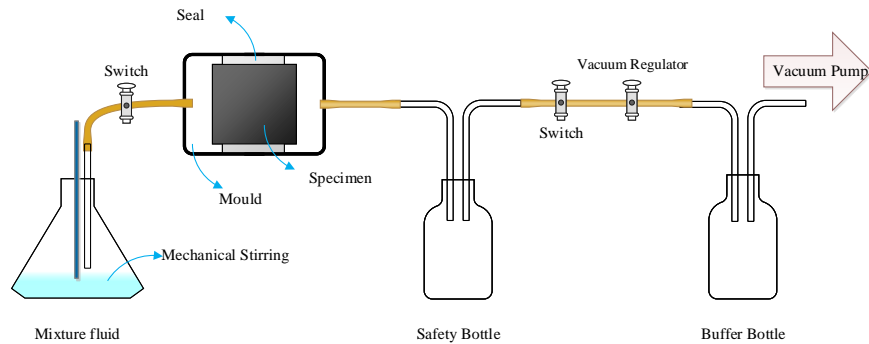


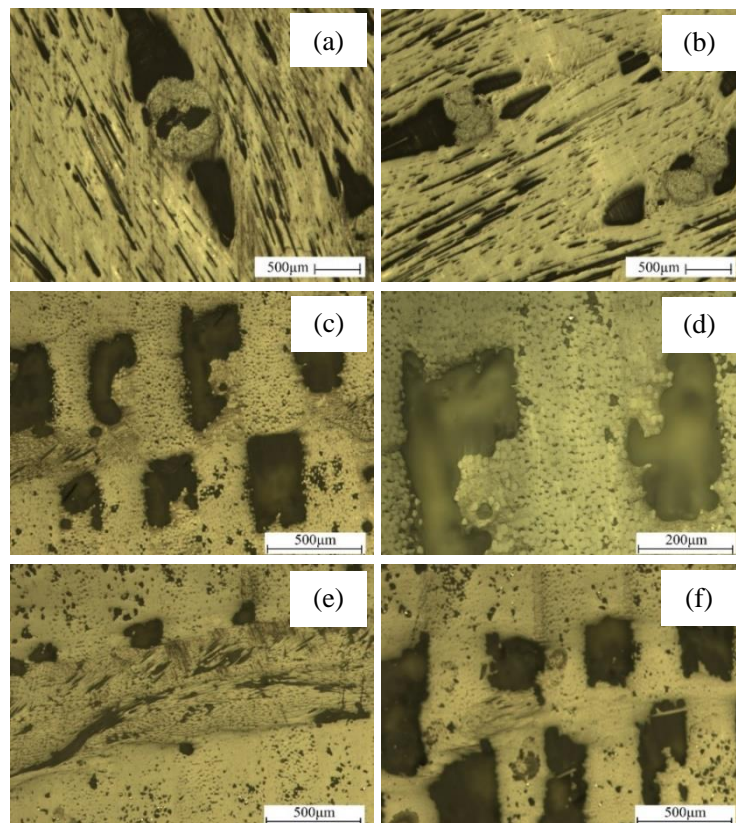
Figure 2: Sketch of facilities used for infiltrations.

3 DISCUSSION OF MICROSCOPIC METHODS

Microscopic methods had a scope only covered several bundles in the preforms, which mainly focused on the possibility for particles to entering the preforms. Based on the structure analysis and the element analysis, two methods were discussed for their applicabilities in ternary composites.

3.1 Metallographic photography

The structures of preforms in three directions which were defined in section 2.1 were showed in Fig.3. Photos were obtained by the metalloscope LEICA DM4000M.



(a and b were in xy-direction, c and d were in xz-direction, e and f were in yz-direction)

Figure 3: Metallographic photography of fabrics in different directions.

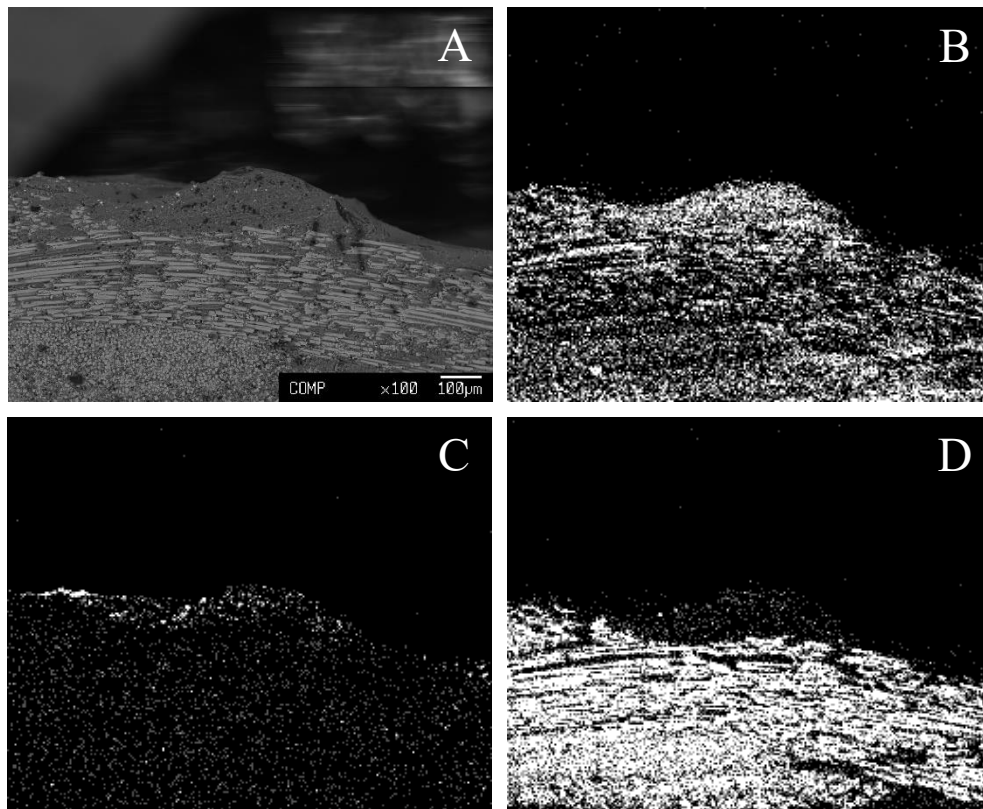
The lighter parts in Fig.3 were glass fibres and the darker parts were epoxy resins. TiC particles were not added to the composites in the section.

It was proved that introduction of z-direction fibres led to voids of diameter larger than 500 μm by metallographic photography in xy-direction. The metallographic photography in xz-direction and yz-direction presented that interlayer voids whose sizes were around 200 μm were concentrated nearby the pierce-fibres. The voids between bundles as well as voids in tows (nearly 50 μm) provided the channels allowing the particles (diameter of 700 nm and 1400nm) getting through the preforms.

The metallographic photography can be used to analyze the structure of preform if it was possible for the other two phases entering the fabric. It was a fundamental way to judging the distribution of particles in the woven with low cost: No particles would get into the preforms if there were no space for them.

3.2 Electron probe micro-analyzer (EPMA)

It is known that there are two kinds of voids in the preforms: The larger one is between bundles, and the smaller one is in tows. The different sizes of voids lead to the different possibilities for particles to access, which can be evaluated by means of EPMA (JEOL JXA-8100).



(A: morphology of the edge of sample; B: distribution of element Carbon;
C: distribution of element Titanium; D: distribution of element Silicon)

Figure 4: The results (map scanning) of elemental analyses by EPMA at the edge of sample.

The results of EPMA (Fig. 4) showed the morphology and element distributions of the edge of sample in which mixture of TiC and resins entered the fabric. The element of Carbon mainly existed in resins and particles, while the element of Titanium only existed in particles. The element of Silicon stood for fibres, in which area there was Titanium existing, confirming that the particles had the ability to enter in-tow-voids of 3-D woven with the infiltration of mixtures.

4 DISCUSSION OF MACROSCOPIC METHODS

Macroscopic methods were classified by the methods of separating different phases. Owing to the

epoxy resins in the composites were easily removed in the furnace, meanwhile the z-direction cotton threads were obliterated which was probable to segregate the whole composites into isolate sections. The particle distribution could be inferred with the mass fractions of each section. Consequently, only distinguishing the particles and wovens was concerned in the paragraph.

After attempted, three methods analyzing the distribution of particles in a macroscopic scale were much more feasible.

4.1 Method based on calculations of the density

The phases particles and 3-D woven reinforcements in ternary composites had different densities. The mass fraction of particles was able to be calculated with results of mass and volume measurement by Eq.1. The accuracies of measurement were up to 0.01 mm with sizes and 0.0001 g with mass in the experiments.

$$MassFraction_{particles} = \frac{\frac{Mass_{Total}}{Volume_{Total}} - Density_{Fabrics}}{Density_{Particles}} \quad (1)$$

Results of particle distribution with the method based on the density showed in Fig.5, in which the direction of infiltration was along the x-axis positions. It was presented the higher driving pressure, higher viscosity and smaller particle would lead to the higher content of TiC in the preforms, and none particles access to the fabrics at the situation of 0.1 Pa·s, 0.05 MPa and 1400nm.

However, the consequences were not precise ideally owing to the hardship in measurement, and even negative value could be observed in the figures. Hence the accuracy of the method based on the density should be discussed in this part. The valid area of each specimen was nearly 6×20×6 mm, whose mass was nearly 4 g. The densities of preforms and TiC particles were 1.2 g/cm³ and 4.93 g/cm³ separately. A fluctuation of 0.0001 g in mass measurement would lead to a change in mass fraction of 0.04%(absolutely value), while a fluctuation of 0.01 mm in size measurement would lead to a change in mass fraction of 0.6%~2.6% (absolutely value) at the circumstance of the content of TiC was about 1%(absolutely value). Obviously, the error in size was the critical factor resulting in the unacceptable content. Concurrently a fluctuation of 0.0001 mm (0.1 μm) in size measurement could lead to an identical precision with mass (absolutely value of 0.04% in mass fraction) which was impractical in experiments.

4.2 Chemical analysis

Chemical analysis could be employed to distinguish the TiC and glass fibre with the different reactions to the solvent or acid, which was usually adopted in testing soluble ingredients.

TiC could be eroded by Nitric acid or nitrohydrochloric acid while the glass fibre hardly, which were inapplicable after attempted because scarcely any variations in mass were observed.

As a result, hydrofluoric acid was attempted, which would corrode glass fibre and TiC in different rates. After treatment in hydrofluoric acid for 30 min and rinsing in distilled water, weight of glass fibres and TiC reduced for 60% and 21% separately. Corresponding the mass fraction of particles in the composites could be calculated by Eq.2.

$$\begin{cases} Mass_{GlassFibre} + Mass_{TiC} = Mass_{Total} \\ 0.40 \times Mass_{GlassFibre} + 0.79 \times Mass_{TiC} = Mass_{Remainder} \end{cases} \quad (2)$$

In section 4.1, for specimens infiltrated with 1400 mm TiC, only near the inlet of mixed liquid in the preforms could discover particles filling. Therefore, only the inlet parts of fabric were analyzed with chemical analysis(Fig.6).

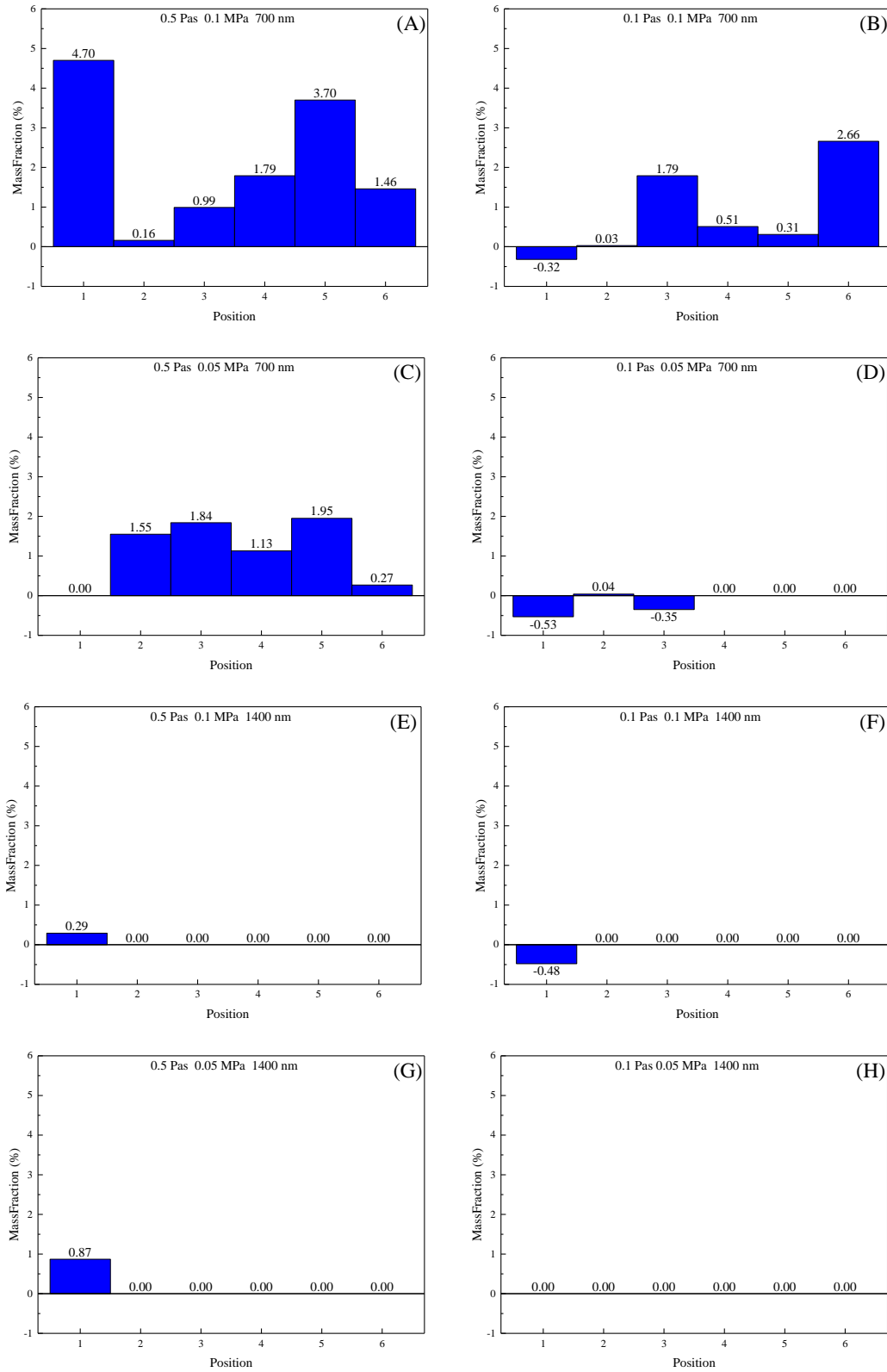


Figure 5: The results with the methods based on the density (mass fraction distribution in the sample).

It was pointed out that the quantity of 1400 nm TiC which entered the wovens deepened on the viscosity and pressure: when 0.1 MPa was taken, more particles would access the voids in the preforms with lower viscosity which led to the faster speed of mixture; when 0.05 MPa was employed, a lower

viscosity meant a weaker ability for liquid to transport the TiC, which brought about none TiC existed in preforms.

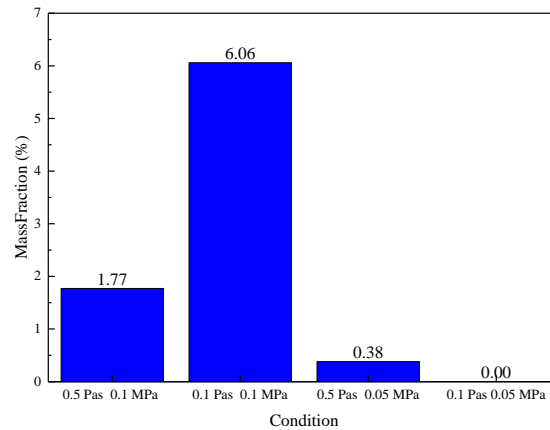


Figure 6: The results with the methods of chemical analysis (mass fraction distribution in the sample).

The accuracy of chemical analysis was largely effected by the measurement of mass reductions after treated in hydrofluoric acid. A fluctuation of 1% in mass reduction of TiC would lead to a change in mass fraction of 0.05%(absolutely value), while a fluctuation of 1% in mass reduction of glass fibre would lead to a change in mass fraction of 0.1% (absolutely value), which was relatively acceptable in the detection of ternary composites. Nevertheless, reagents with corrosivity and neurovirulence were adopted in chemical analysis which were so dangerous that obstructed the appliance in the large-scale experiments.

4.3 Physical analysis

The difficulty of method based on calculations of the density was imprecision in size measurement, which could be overcome with taking other methods instead of size measurement. The physical analysis based on centrifugal separation was attempted to distinguish the TiC and glass fibres with their different densities. The centrifugal machine adopted was TG1650-WS produced by Shanghai Lu Xiangyi centrifuge instrument Co., Ltd (FDA number:3010704506).

Glass fibres had a density of about 2.5~2.7 g/cm³, and TiC was 4.93 g/cm³ around. Tetrabromoethane whose density was 2.97 g/cm³ as a kind of heavy liquid was employed to separate the two phases. Obviously, glass fibres would float on the surface of heavy liquid which was convenient to collecting and particles would sink to the bottom. After centrifuging at a rate of 6000 rpm for 15 min, TiC was weighted with the removal of fibres.

As can be seen in Fig.7, 700 nm particles would get through the preforms at a higher viscosity or a higher driving pressure, which was the same with section 4.1. Results from physical analysis were much more credible because method based on calculations of the density had a low accuracy.

Errors in physical analysis were sample losing in transfer process from different vessels. Under the value of particle mass fractions and previous experiments, accuracy of physical analysis could be up to 0.1%~1%, which was acceptable in this occasion.

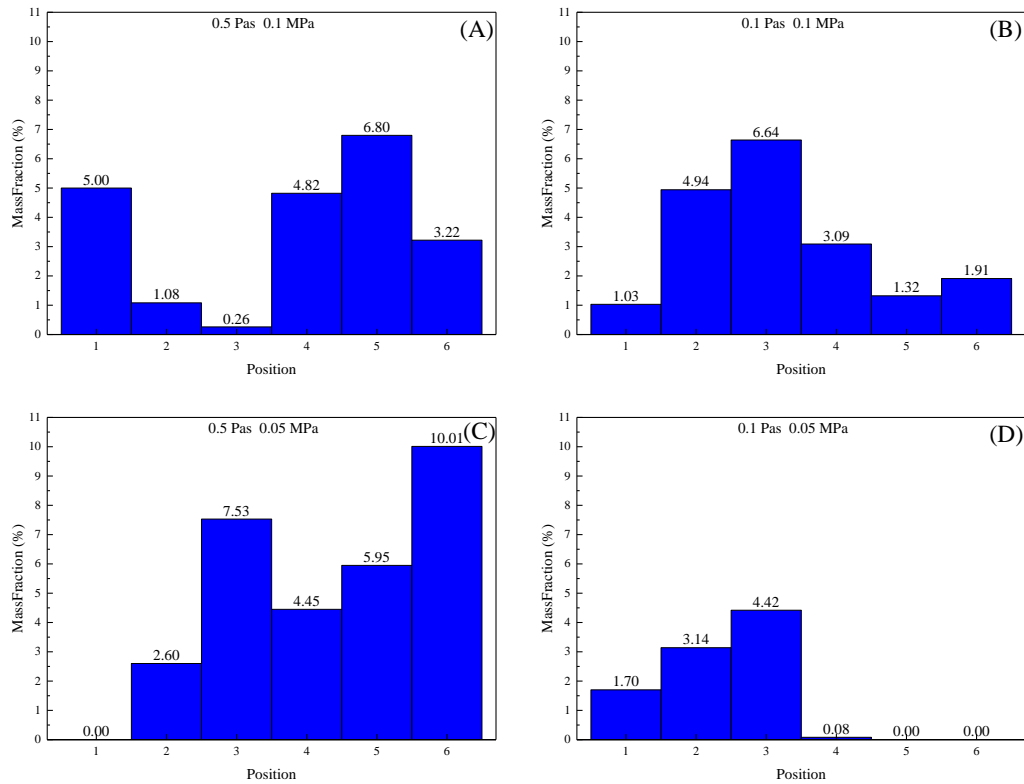


Figure 7: The results with the methods of physical analysis (mass fraction distribution in the sample).

5 CONCLUSION

Two kinds of microscopic methods were discussed in this paper. Based on the result of metallographic photography, there were channels (nearly 200 μm between bundles and 50 μm in tows) that allowed the infiltration of particles and resins within the preforms. The results of EPMA confirmed that the particles could enter 3-D woven with the infiltration of mixture. Both methods could be used in the qualitative analyses of ternary composites.

Three kinds of macroscopic methods were compared at ternary composites. Methods based on calculations of the density were imprecise because the accuracy of size measurement could not meet the requirements. Methods of chemical analysis based on one phase or some phases dissolved by acid or other corrosive reagents in different rates were theoretically feasible. However, because of the high stability of TiC or glass fibres, health-damaging strong acid or strong corrosive reagents were usually employed, which was dangerous in experiments. Methods of physical analysis based on centrifugal separation were also attempted. Different distributions of particles were measured in parts manufactured with different combination of resins and particles. After comparison, physical analysis method received priority for its acceptable accuracy and better feasibility.

This paper proposes the analyses methods of particle distributions in ternary composites. Only the final composite parts can be analyzed with those detection methods. The proceeding in the infiltrations remains unclear to researchers which was necessary to be eliminated. Developing a new on-line method or facility will be of great importance to the future research and manufacture of high-performance ternary ablation resistant composites. And the distributions of particles in the 3-D woven reinforcement shows a complex pattern which need further studies as well.

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