Behaviour of advanced polymer composites in erosive/corrosive environments

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The erosion/corrosion properties of the advanced polymer composites, PMR-15, BMI (Matrimid 5292) and PMR-II-20 have been studied. Specimens of these materials were exposed to jets of an erosion/corrosion medium consisting of salt, iron oxide, quartz and coarse desert dust dispersed in water. The jets impinged on the specimens perpendicular to the plane of the reinforcements for a period of approximately 2 months. The velocity of the jets was measured to be $10\ \mathrm{m\ s^{-1}}$. The damaged surfaces were examined both visually and under a scanning electron microscope. Damage mechanisms which are associated with this phenomenon are identified. Matrix microcracking, matrix removal and blister formation are the principal damage mechanisms observed. Deep cuts, cutting lines and rust deposition are the main features of the damaged surface. It is observed that BMI matrix composites display a large amount of matrix removal and consequently, fibre exposure. A large amount of scales of deposits are also observed. On the other hand, PMR-15 shows cutting lines, with less matrix removal than BMI. Large scale deposits are also observed on the surface of PMR-15 composite. The PMR-II composite displays the least amount of matrix removal, with brittle matrix microcracking. Blister formation is a dominant corrosive feature of the PMR-II composite.

(Keywords: composites; erosion/corrosion; polyimide)

INTRODUCTION

Advanced polymer composites are gaining wide acceptance, particularly in aerospace applications, owing to their low weight, high strength-to-weight ratios and their capability to withstand high temperatures. These composites can withstand temperatures up to about 600°F (300°C), beyond the capability of commonly used composites such as graphite/epoxy and Kevlar/epoxy. The resins finding wide acceptance are those from the polyimide group (PMRs) and the bismaleimides (BMI).

The erosive/corrosive resistance of advanced polymer composites is an important property in applications where components manufactured of these materials are exposed to such an environment. These applications include torpedo shells, pump casings, impellers and aircraft wings.

Erosion mechanisms of anisotropic materials such as polymer composites have been studied in some detail by earlier researchers. Tilly and Sage[1] investigated the sand erosion properties of glass/nylon, carbon/nylon, glass/epoxy and steel/epoxy composites and concluded that composite materials, in general, have poor erosion resistance. Zahavi and Schmitt[2] found that glass/epoxy laminates behave in a semiductile manner. Pool *et al.*[3] studied the erosion behaviour of graphite/polyimide, aramid/polyimide, aramid/epoxy and graphite/polyphenylene sulphide (PPS) composites. It was concluded that well-bonded ductile fibres in a thermoplastic matrix exhibit the lowest erosion rates. Tsiang[4] conducted extensive research on the sand erosion of both thermoplastic and thermoset matrix composites. Glass, graphite and aramid fibres in the forms of chopped mats, woven cloth and unidirectional tape in BMI, PPS, epoxy, PEEK and nylon matrices were studied. Graphite fibres show the least erosion resistance at both low (30°) and high angles (90°) of impingement. Glass fibres exhibit the least resistance at medium angles of impingement. Aramid fibres display superior erosion resistance properties. Glass and graphite fibres are brittle and rupture easily. Aramid fibres break into fibrils and absorb a large amount of energy before rupture. They display high erosion resistance. Fibre alignment also plays a role in determining the erosion resistance of the composites. Fibres aligned parallel to the impinging jet impart a lower erosion resistance to a composite than those aligned perpendicular to it. On the whole, randomly oriented fibres impart the best support.

Erosion mechanisms can be divided into two categories:

(1) Ductile erosion, in which maximum damage occurs at glancing angles of impact. Cutting wear and deformation are the two main damage mechanisms.

(2) Brittle erosion, in which maximum damage occurs at normal angles of impingement. Elastic cracking and material removal of fragments are the main damage mechanisms.

The process of erosion starts with matrix cracking and is followed by its removal. Subsequently, the reinforcements are exposed, broken down into fragments and removed from the erosion areas. Hence the erosion resistances of both the matrix material and the reinforcements are important factors determining the erosion resistance of the composites. Thermoplastic resins behave in a ductile manner, while thermosets behave in a brittle manner. Polyimide, BMI and epoxy matrices exhibit lower erosion resistance than PPS and PEEK.

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Polymer coatings have improved the erosion resistance capability of reinforced plastic structures. The most successful coatings are the fluoroelastomers and polyurethane. Hurley *et al.*[5] studied in detail the effect of rain erosion on polyurethane and fluoroelastomer-coated glass/epoxy, graphite/epoxy and quartz/polyimide composites. They found that the erosion rates are lower at small angles of impingement. Also graphite/epoxy composites exhibit lower erosion resistance; glass/epoxy showed the least damage. Among the two coatings examined, polyurethane provides better protection.

Frequently components manufactured from these composites are exposed to a corrosive environment. Pump blades, marine equipment, ship parts exposed to seawater etc. are a few examples. In such cases knowledge of their corrosion resistance assumes practical importance. Also the composites may be in contact with a metal, allowing galvanic coupling to occur. This may also lead to the degradation of the composites by the process of corrosion.

Graphite is very noble in the galvanic series and a very effective cathode. Hence when graphite fibres and metals are in contact in an electrolyte, rapid corrosion of the metals occurs. Also, the composites may degrade due to blister formation. Tucker *et al.*[6] studied the corrosion behaviour of graphite/vinyl ester composites coupled to pure grade titanium, aluminium-2014, stainless steel and monel. No degradation was observed in the case of the composites coupled to titanium. The composites coupled to aluminium were degraded severely by blister formation when active corrosion of the metal occurred. Tucker and Brown[7] studied blister formation on graphite composites coupled to steel in seawater. They studied graphite/vinyl ester and a special composite graphite/epoxy designated T300/5208. Water molecules diffuse into the polymer matrix and combine with water-soluble substances such as binder, promoters, etc. and reside in the voids and cracks. This solution sets up an osmotic pressure and water is drawn in continuously. The solution also has an hydrolytic effect, which can lead to decomposition of the matrix. At a certain stage, the internal pressure of the solution exceeds the failure pressure of the resin and a blister may occur. Also, the blisters may break in the later stages of the process and lead to severe loss of strength of the composites. Epoxy resins show lower degradation. It is also seen that galvanic coupling is essential for corrosion to occur. The greater the separation on the galvanic series, the faster the blister formation and the greater the number of corrosion events that occur.

As most of the structural materials in use today are either metals or metallic alloys, extensive work has been done on these materials. Very little study has been done on polymer composites, particularly the PMRs and BMI. However, as more and more composites are proposed for structural materials, knowledge about their erosive/corrosive resistance gains greater importance. Moreover, most studies are concerned with studying either corrosion or erosion separately. A combined erosion/corrosion study which simulates a real life problem, as far as is known, does not exist. In the present work the erosion/corrosion behaviour of graphite-reinforced advanced polymer composites such as PMR-15, BMI and PMR-II is studied. Jets of salt water containing contaminants are impinged on the specimens of these three materials. Scanning electron microscope (s.e.m.) work is carried out on the damaged surfaces to identify and understand the damage processes associated with this phenomenon.

EXPERIMENTAL

Three composites are considered for the present study. The resins are PMR-15, toughened BMI (Matrimid 5292) and PMR-II-20. The reinforcement is Celion G 30-500 carbon fabric with 3 K filaments per toe, 8 harness satin weave and epoxy sizing and is the same for the three materials. The fibre volume fraction is 0.6.

The erosion/corrosion apparatus which was specifically designed for the current investigation consists mainly of the following: a centrifugal pump; nozzles to direct the jets onto the specimens; specimen-holding fixtures; a stainless steel tank; piping systems, valves etc.

A schematic diagram of the experimental set-up is shown in *Figure 1*. A water-based erosive/corrosive medium was prepared in order to simulate a harsh environment, which components manufactured from these materials frequently experience in service. The contaminants include ferroso-ferric oxide (1.5 g/1000 gal), ferric oxide (29.0 g/1000 gal), crushed quartz (2.0 g/1000 gal), desert dust (8.0 g/1000 gal) and cotton linters (0.1 g/1000 gal). Salt was added to make a concentration equivalent to about 4 parts of salt in each 100 parts of salt water.

The specimens of PMR-15, BMI and PMR-II were firmly fixed in the fixtures. The jets were allowed to impinge on the specimens perpendicular to the plane of reinforcement (woven cloth). The fixtures could be moved, both vertically and horizontally, to facilitate the proper projection of the jets on to the specimens. The distance between the specimen and the nozzles was 100 mm. The jet velocity was measured to be 10 m s^{-1}. The contents of the tank were circulated in a closed-loop piping system. The specimens were checked for visual damage from time to time during the course of the experiment. The total duration of the exposure was 1500 h. S.e.m. work was carried out to identify the damage events present in both the polymeric matrices and the reinforcement.

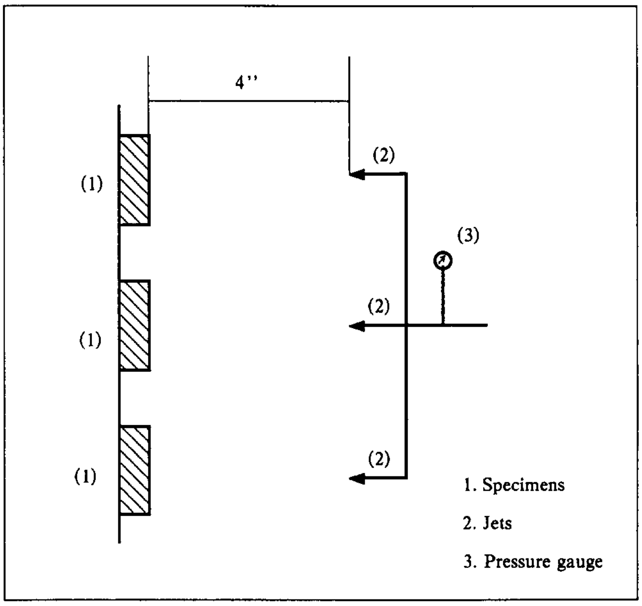

Figure 1 Schematic of the experimental set-up

RESULTS AND DISCUSSION

To examine the behaviour of these composites in an erosive/corrosive environment, scanning electron microscopy was used. This reveals the microstructural texture of the eroded/corroded surface and the damage mechanisms involved. Cutting lines, matrix cracking, fragmentation, fibre exposure, salt deposition etc. were some of the mechanisms identified during this examination.

The main damage mechanisms in the case of PMR-15 are surface roughening and matrix cutting lines, while for BMI, extensive matrix removal and fibre exposure is observed. In PMR-II-20 composite, blistering and matrix microcracking are the dominant features of the eroded/corroded surface.

To understand fully the erosive/corrosive damage mechanisms of these composites, knowledge of their mechanical performance is necessary. Recent investigations[8,9] into the mechanical performance of these composites reveal that the toughened BMI composite exhibits brittle behaviour. The PMR-II-20 also shows a linear response with a very slight yielding immediately before fracture. On the other hand, PMR-15 shows a considerable degree of yielding prior to fracture, which is indicative of higher matrix ductility than the other two composites. The flexural modulus of the PMR-15 is about 20% less than that of the PMR-II and BMI composites.

For PMR-15, a low magnification micrograph, *Figure 2*, shows manifestation of the damage in the form of both horizontal and vertical cutting lines. Further high magnification of the cutting lines reveals the microstructural texture of the eroded/corroded surface, *Figure 3*. The cuts are observed to run over the whole surface. This is the first stage of the damage process and further exposure to the erosive/corrosive environment could lead to fragmentation of the surface layer and its removal. Evidence of microcracks is observed at the centre of the impingement area, but to a lesser degree. Moreover, the cutting lines could themselves develop into microcracks in the later stages of the damage process. The scales of deposits in *Figure 2* are a brownish colour, and are a combination of rust, salt and other contaminants, as can be seen from the strand of cotton sticking to them, *Figure 4*.

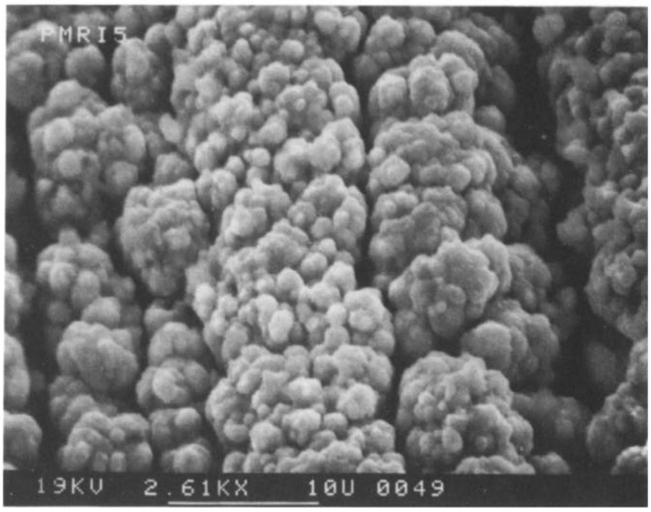

Figure 3 Higher magnification of the cutting lines of *Figure 2*

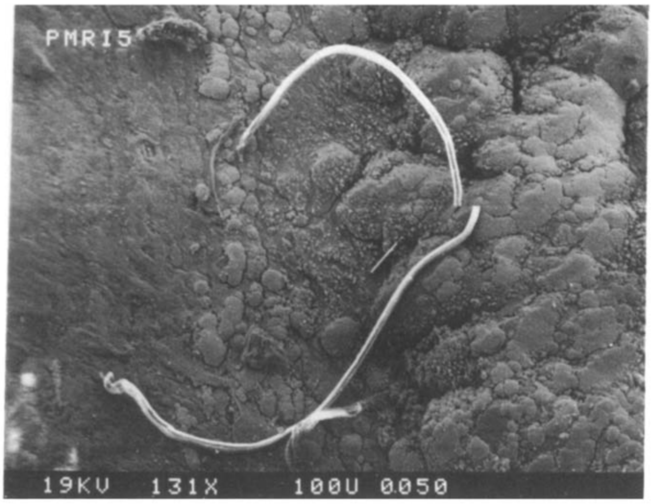

Figure 4 Scales of deposits on a PMR-15 specimen showing strands of cotton contaminant

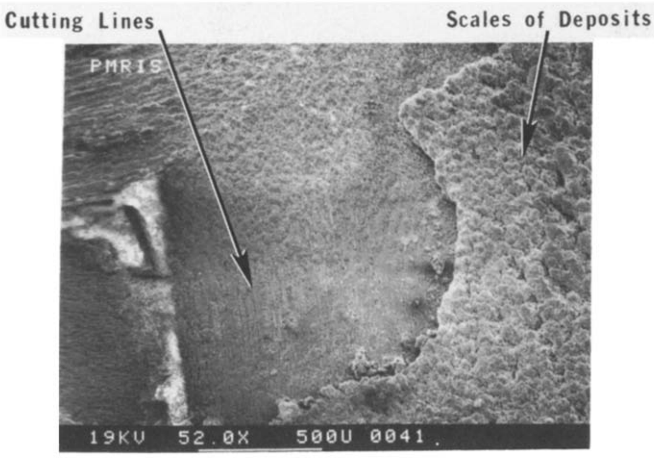

Figure 2 Micrograph of the jet impingement area of PMR-15 composite, showing cutting lines and scales of deposits

As the PMR-15 composite has the highest degree of yielding of the composites being tested, it is not surprising to see more cutting lines than pure microcracking; a 'ductile erosion' behaviour. The impinging particles tend to lose their energy upon impact and glance off the surface causing abrasive cutting line type wear.

The bismaleimide matrix composite shows the least resistance to the erosive/corrosive environment. An overview of the impingement area is shown in *Figure 5*. Further magnification of the impingement area shows the presence of deep cuts and the mechanism by which matrix is being removed, as shown in *Figure 6*. Microstructural details of some of the badly eroded area are shown in *Figure 7*. The brittle nature of the toughened BMI composite allows the impinging particles to cause elastic cracking which results in severe matrix removal. This drastic loss of matrix material causes the reinforcing fibres to become 'naked'. Clean individual fibres, indicative of weak matrix–fibre bonding, are observed. The direct exposure of the fibres to the erosive/corrosive environment could lead to their breakage and removal from the composite. This could lead to a drastic loss of strength. The time frame of the current study (approximately 2 months) was, however, not long enough for this to occur. Scales of deposits of rust, salt etc. are observed surrounding the jet impingement area.

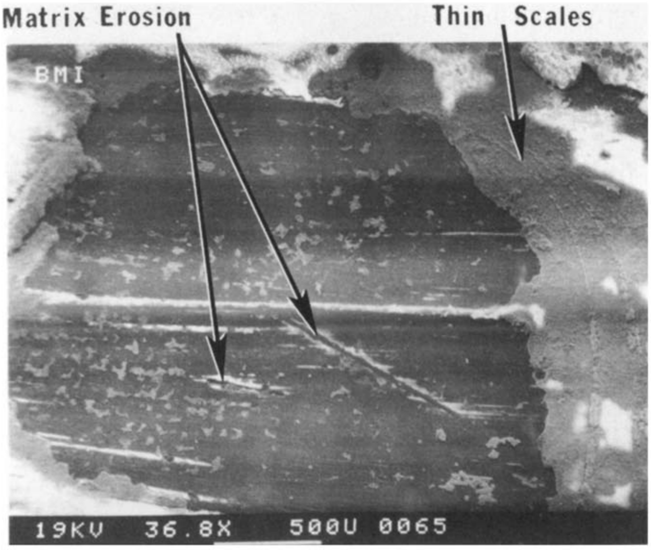

Figure 5 Micrograph showing an overview of the jet impingement area of the BMI (Matrimid 5292) composite

This layer is thinner than that observed in the case of PMR-15.

PMR-II-20 composite shows interesting erosive/corrosive damage features. These are elastic microcracking, *Figure 8*, and blister formation, *Figure 9*. Scales of deposits are also observed on the surface, but they are not as thick as in the case of PMR-15 and BMI composites.

The brittle nature of the PMR-II-20 matrix is manifested in the elastic microcracking damage which forms a type of network, *Figure 8*. In spite of the fact that PMR-II-20 displays almost the same flexural modulus as the toughened BMI composite, it is about 2.4 times stronger[8,9]. This implies higher resistance to fragmentation after the elastic microcracking has occurred. As a result no matrix removal has been observed in the case of PMR-II composites.

Water can diffuse into the polymer matrix, probably accelerated by the existence of microcracks, resulting in blister formation. At a later stage, the internal pressure of the solution, inside the blister, overcomes the ultimate

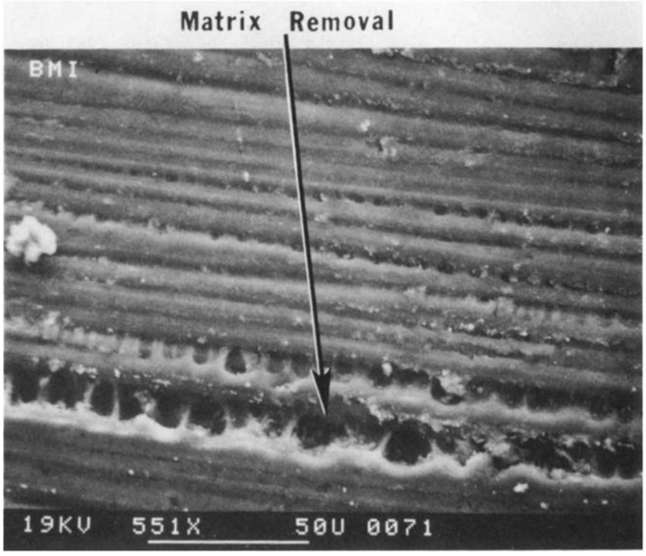

Figure 6 Micrograph of the eroded/corroded surface of the BMI (Matrimid 5292) composite showing evidence of matrix removal

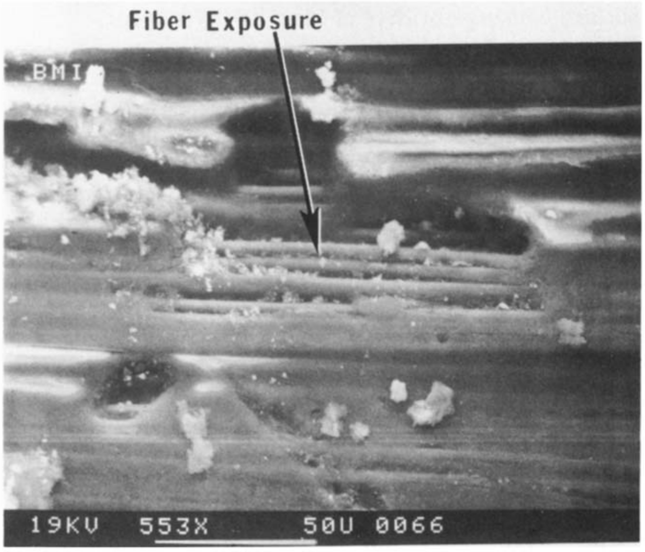

Figure 7 Micrograph of an area of exposed fibres indicative of severe matrix removal from the BMI (5292 Matrimid) composite

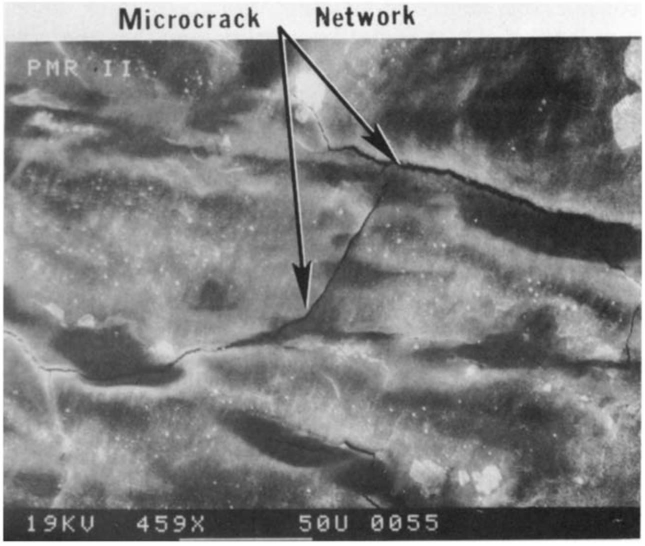

Figure 8 Micrograph of the eroded/corroded surface of the PMR-II-20 composite, revealing a matrix microcrack network

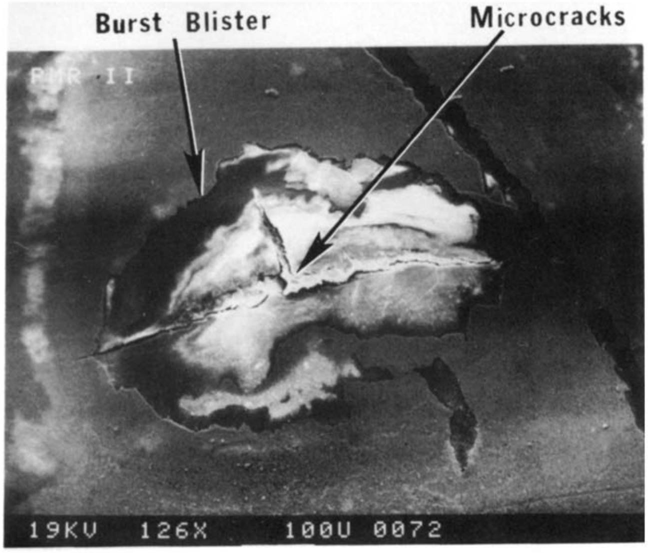

Figure 9 Microfeatures of the blisters on the PMR-II-20 composite

strength of the matrix causing the blister to burst. This can be observed from the microcracks which exist on the blister surface of *Figure 9*. Thus it could be the case that PMR-II-20 composite earns its superior resistance to the erosive/corrosive environment by the mechanism of blister formation. This is an energy dissipative process which can delay the fragmentation of the matrix and, hence, its removal. More research is needed to understand fully the interaction between elastic microcracking and blister formation. This is currently being undertaken.

CONCLUSIONS

The erosion/corrosion resistance of polyimide matrix graphite reinforced composites is largely dependent on the stiffness and strength of their matrices. This has been demonstrated by the current study conducted on PMR-15, BMI (Matrimid 5292) and PMR-II-20 composites.

(1) PMR-15 composite, which is the most compliant and exhibits the highest degree of yielding among the three composites studied, displays surface roughening and cutting lines under liquid jet impingement of erosive/corrosive medium.

(2) The BMI matrix composite shows the least resistance to the erosive/corrosive environment with severe matrix removal as a result of brittle elastic microcracking.

(3) The PMR-II-20 composite also displays elastic microcracking. However, matrix removal is resisted due to its superior strength. As a consequence, PMR-II-20 exhibits blister formation, owing to diffusion of the solution into the polymer matrix through the microcrack network.

(4) Matrix elasticity appears to control the thickness of the deposited layer of salt and contaminants surrounding the jet impingement area. PMR-15 composite, which has the most compliant matrix of those tested, shows the thickest layer of deposits. Both BMI and PMR-II-20 display thinner layers of deposits.

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