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9.0 INTRODUCTION

Most of the high performance resins having high curing process and are costly. Epoxy and Novolac both are used in space and aviation as a structural adhesive due to their superior thermal and mechanical properties. However, novolac is in powder form with very high melt viscosity, which is too high to allow its processing by conventional manufacturing technique. Therefore the processing of novolac itself is a real challenge. Most of the novolac resin applications are found in the form of molded parts. Due to high processing temperature and pressure requirement novolac is yet attractive for many applications. Due to its high thermal stability novolac has great potential to be used for high temperature applications. Therefore, the objective of this work is to optimize and synthesis of IPN adhesive by using novolac and epoxy resins. The two resins are mixed with their hardener and cured simultaneously. For spacecraft application, the adhesive should resist to the environmental (high temperature, corrosive and humid) condition. Therefore, it is the need of the time to introduce high temperature resistance adhesive, which is thermally more stable and can withstand the space climatic condition. Epoxy-novolac adhesive composite which is synthesized by introducing novel interpenetrating polymer network (IPN) technique can be useful due to the formation of strong cross-linking polymer network. Due to this cross-linking polymer network, when this adhesive is applied to laminate the polymers and titanium, the laminar nanocomposite shows high performance under different environmental conditions, which is shown in present work.
9.1 CONCLUSIONS

9.1.1 Epoxy-Novolac IPN Adhesive Systems

Synthesized epoxy-novolac IPN adhesives and their various characterization techniques can be concluded that

(i) Full IPN technique is used for synthesis of epoxy-novolac IPN adhesive with different blend ratio of epoxy and novolac. Therefore, the IPN adhesive is called full IPN.

(ii) Swelling study of epoxy-novolac IPN adhesive systems in twelve different solvents confirms the epoxy-novolac IPN adhesive.

(iii) Maximum swelling characteristics of epoxy-novolac IPN adhesives in acetone concludes that acetone is a good solvent in which epoxy-novolac IPN adhesive is swelled.

(iv) Epoxy-novolac IPN adhesive systems have solubility parameter, which is very close to acetone. Therefore, it is one of most important solvent in which epoxy-novolac IPN adhesive systems are swelled.

(v) Minimum swelling of epoxy-novolac (4:1) IPN adhesive in acetone confirms higher interpenetration network in compared to other epoxy-novolac IPN adhesive systems.

(vi) Maximum cross-linked density of epoxy-novolac (4:1) IPN adhesive system confirms the formation of highly cross-linked network in epoxy-novolac (4:1) IPN adhesive system.
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(vii) It is confirmed from creep study that the interwinding network is very high in the case of epoxy-novolac (4:1) IPN adhesive system.

(viii) The minimum strain of epoxy-novolac (4:1) IPN adhesive confirms low deformation compared to basic epoxy adhesive and novolac adhesive.

(ix) Higher storage modulus and loss modulus of epoxy-novolac (4:1) IPN adhesive confirms higher viscoelastic properties of epoxy-novolac (4:1) IPN adhesive.

(x) Higher glass transition temperature confirms the lower rubbery character of epoxy-novolac IPN adhesive systems in compared to basic epoxy adhesive and novolac adhesive.

(xi) Low $T_g$ of epoxy-novolac (4:1) and (4:2) IPN adhesive systems reveal higher rubbery character in compared to epoxy-novolac (4:3) and (1:1) IPN adhesive systems.

(xii) Two $T_g$ in epoxy-novolac (4:3) and (1:1) IPN adhesive systems indicates the gross phase separation of epoxy and novolac in IPN adhesive systems during synthesis of epoxy-novolac IPN adhesive.

(xiii) TGA study concludes that epoxy-novolac (4:1) IPN adhesive has higher thermal stability in compared to others adhesive systems at high temperature.

(xiv) Ultimate tensile strength results of different adhesive systems conclude that the epoxy-novolac (4:1) IPN adhesive has higher strength in compared to others adhesive systems.
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(xv) AFM topography and SEM morphology confirms the phase separation of epoxy and novolac in epoxy-novolac (4:1) IPN adhesive system.

(xvi) FTIR spectra confirm that synthesis of epoxy-novolac (4:1) IPN adhesive is simultaneously. Therefore, the epoxy-novolac (4:1) IPN adhesive is called simultaneous IPN adhesive, which is synthesized by full IPN technique.

9.1.2 Surface Modification of Polyether Imide and Polyether Ether Ketone

The surface characteristics of polymers are very important for application of polymers. Polyether imide (PEI) and polyether ether ketone (PEEK) both the polymers show hydrophobic surface in nature. Due to hydrophobic nature of polymers, adhesive bonding of these polymers are limited. Therefore, there is necessity to alter surface characteristics of these polymers. Plasma technique is an emerging technique, which can alter the polymer surface from hydrophobic to hydrophilic. In this study, conclusion on low-pressure DC glow discharge plasma treatment of polyether imide and polyether ether ketone and their surface characteristics are as follows.

(i) Low-pressure plasma treatment on PEI and PEEK changes the surfaces of polymers from hydrophobic to hydrophilic.

(ii) XPS analysis reveals incorporation of oxygen functional groups on PEI and PEEK surfaces after low-pressure plasma treatment.

(iii) Increasing ratio of oxygen/carbon concludes that plasma treatment increases oxygen in terms of oxide onto the surfaces of PEI and PEEK.
(iv) Energy dispersive Spectra (EDS) also confirmed the presence of oxygen functional groups on surface modified PEI and PEEK.

(v) The changes of surfaces of PEI and PEEK from SEM morphology conclude that due to the plasma treatment, the surfaces of PEI and PEEK are damaged and grain boundaries are observed.

(vi) The results of contact angles of water and formamide conclude that due to the plasma treatment, the surfaces of PEI and PEEK contains polar functional group such as oxygen and exhibits lower contact angle.

(vii) Plasma treatment on surfaces of PEI and PEEK increases the polar component as well as surface energy of the PEI and PEEK. This higher surface energy of these polymers attributes better adhesion characteristics.

9.1.3 Surface Modification of Titanium

Proper surface treatment of titanium is necessary to remove the dust, dirt and all sorts of contaminants, which can stand as barrier for intimacy between the adhesive and the adherend. Plasma treatment and sodium hydroxide anodization treatment are carried out to achieve desired surface properties of titanium. The conclusions of these investigations are as follows.

(i) Anodization forms oxide layer on the titanium surface whereas plasma nitriding forms nitrided layer on the surface of titanium.
(ii) From the results of XPS and EDS, it is concluded that NaOH anodization forms oxide layer and plasma nitriding technique forms nitrided layer on the surface of titanium.

(iii) The SEM morphology that due to surface treatment of titanium by anodization and plasma nitriding, the morphology of titanium surfaces are changed.

(iv) AFM topography concludes that due to surface treatment of titanium by anodization and plasma nitriding, the peaks and valleys of titanium surfaces are uniformed.

(v) Higher roughness value of anodized and plasma nitrided titanium than untreated titanium concludes that due to surface treatment, the roughness of titanium is increased.

(vi) The increasing value of hardness of surface modified titanium concludes that due to surface treatment of titanium, the metal surfaces are hardened than untreated titanium.

(vii) Anodization and plasma nitriding on titanium surface essentially increase polarity of the titanium surfaces.

(viii) Surface energy of titanium increases considerably due to anodization and plasma nitriding.
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9.1.4 Adhesive Bonding of Polyether Imide to Titanium and Polyether Ether Ketone to Titanium

Adhesive bonding of polymer to metal is a major problem due to the different surface nature of polymer and metal. Polymeric materials show hydrophobic surface whereas metal surface shows hydrophilic in nature. Hydrophilic surfaces of material exhibits strong adhesive bond. Therefore, surface treatment of polymeric materials is necessary to transform surface of polymeric materials from hydrophobic to hydrophilic. Low-pressure plasma treatment is used for surface modification of polyether imide and polyether ether ketone, which changes the surfaces of PEI and PEEK from hydrophobic to hydrophilic. Both the surface modified polymers such as PEI and PEEK shows high bond strength when the surfaces of PEI and PEEK are joined with surface modified titanium. The following conclusions are shown from this study:

(i) Epoxy-novolac (4:1) IPN adhesive exhibits higher adhesive bond strength when plasma treated PEI, PEEK, titanium and anodized titanium are joined by epoxy-novolac (4:1) IPN adhesive.

(ii) Due to low-pressure plasma treatment of PEI and PEEK, higher adhesive joint strength is observed when the surfaces of PEI and PEEK are joined by adhesive.

(ii) Anodized titanium to anodized titanium and plasma nitrided titanium to plasma nitrided titanium adhesive joint shows higher joint strength in compared to untreated titanium adhesive joints.
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(iv) In comparison to adhesive bonding of untreated surfaces of PEI, PEEK and titanium, the untreated to surface treated PEI, PEEK and titanium exhibits strong adhesive joint strength.

(v) Adhesive bonding of anodized titanium to plasma treated PEI and PEEK shows higher adhesive joint strength than plasma nitrided titanium to plasma treated PEI and PEEK adhesive joints.

(vi) Surface modification of PEI, PEEK and titanium exhibits cohesive failure whereas untreated PEI, PEEK and titanium shows interfacial adhesion failure.

(vii) Fracture surfaces of untreated to surface treated PEI, PEEK and titanium exhibits mixed failure

9.1.5 Durability of Adhesive Joints under Environmental Conditions

This dissertation reveals that enhancement of durability of epoxy-novolac (4:1) IPN adhesive bonding of PEI to titanium and PEEK to titanium under aggressive environmental conditions. In ambient condition, the adhesive bond strength of anodized titanium to plasma treated PEI and PEEK joint shows high bond strength. But when the joints are exposed under elevated temperature condition, Ringer’s solution and humid condition the mechanical strength of anodized titanium to plasma treated PEI and PEEK joints deteriorated. From this study it can be concluded that

(i) Surface modified PEI, PEEK and titanium shows higher adhesive joint strength in compared to untreated surfaces of PEI, PEEK and titanium under aggressive environmental condition.
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(ii) Untreated to surface treated PEI, PEEK and titanium adhesive bonded surface also shows the higher adhesive joint strength in compared to untreated one.

(iii) Plasma nitrided titanium to plasma treated PEI and PEEK adhesive bonded surfaces shows higher adhesive joint strength in compared to anodized titanium to plasma treated PEI and PEEK adhesive joints under aggressive environmental condition.

9.2 RECOMMENDATIONS FOR FUTURE WORK

In this dissertation work, synthesis of epoxy-novolac IPN adhesive systems and their characterization techniques clarify that epoxy-novolac (4:1) IPN adhesive is better in compared to others. Lap-shear tensile strength results reveal that when epoxy-novolac (4:1) IPN adhesive is used for joining of plasma treated polyether imide and polyether ether ketone to anodized and plasma nitrided titanium and exposed to environmental conditions such as elevated temperature condition (200 °C for 100 hrs.), Ringer’s solution (40 °C for 2 weeks) and humid condition (50 °C, 99 % R.H. for 100 hrs.), the adhesive joint shows high adhesive bond strength. The adhesive strength is also retained when 2 % CNF is added into the epoxy-novolac (4:1) IPN adhesive and adhesive joints are exposed to above mentioned aggressive environmental conditions. The recommendation for future works is outlined.

9.2.1 Epoxy-Novolac IPN Adhesive Systems

In the present work Epoxy-novolac IPN adhesive is synthesized simultaneously with the help of full IPN techniques. In this technique both the cross-linker of epoxy and novolac is added and cured. IPN is also synthesized sequentially with the help of
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semi IPN. In this technique one cross-linker of any one resin is absent. Therefore, the present work is recommended for synthesis of epoxy-novolac IPN adhesive by sequential method with the help of semi IPN technique and compares the properties of this type IPN adhesive with simultaneous epoxy-novolac IPN adhesive.

9.2.2 Carbon Nanofiber (CNF) Reinforced IPN Adhesive Systems

In this dissertation work, CNF is only dispersed into epoxy-novolac (4:1) IPN adhesive system. The aim of this work is to find out the durability of epoxy-novolac (4:1) IPN adhesive bonded polyether imide to titanium and polyether ether ketone to titanium at elevated temperature condition, Ringer’s solution condition as well as in humid condition. The results of lap-shear tensile strength clearly indicate that due to reinforcement of CNF into epoxy-novolac (4:1) IPN adhesive, the adhesive bond strength is improved under above-mentioned environmental conditions. The physico-chemical, thermal and mechanical properties of CNF reinforced epoxy-novolac (4:1) IPN adhesive systems is not considered in the present work. Therefore, It is recommended to examine the effect of CNF into the physico-chemical, thermal and mechanical properties of the epoxy-novolac (4:1) IPN adhesive. It is also recommended to find out the effects of CNF into the physico-chemical, thermal and mechanical properties of the other epoxy-novolac IPN adhesive systems.

Only 2% CNF is used as a reinforcement agent of epoxy-novolac (4:1) IPN adhesive system. To check proper ratio of CNF and adhesive, the work is explored to addition of different ratio of CNF into the epoxy-novolac (4:1) IPN adhesive.
Epoxy-novolac (1:1) IPN adhesive shows poor thermal and mechanical properties in the present study. The incorporation of CNF improves the mechanical properties of the epoxy-novolac (4:1) IPN adhesive system under different environmental conditions. Therefore, the present work also recommended to addition of CNF into the epoxy-novolac (1:1) IPN adhesive and to investigate checks the mechanical properties of the epoxy-novolac (1:1) IPN adhesive under different environmental conditions.

9.2.3 Surface Modification and Adhesive Bonding of Polymers

Experimental results of adhesive bonding of low-pressure DC glow-discharge plasma treated PEI-to-PEI and PEEK-to-PEEK exhibits higher adhesive joint strength in compared to adhesive bonding of untreated PEI to PEI and PEEK-to-PEEK. This result is clearly mentioned that due to low-pressure plasma treatment on the surface of PEI and PEEK, oxygen functional group in terms of oxide, incorporates on the surface of PEI and PEEK. This oxide functional group increases the surface polarity and surface energy, which makes a strong connection with adhesive, when adhesive is applied for joining of plasma treated PEI-to-PEI and PEEK-to-PEEK. The main purpose of the study is surface modification of PEI and PEEK in one side and measured the adhesive bond strength of PEI-to-PEI and PEEK-to-PEEK in another side. There is no comparative study of surface properties in between PEI and PEEK. Therefore, it is recommended for comparative study in between PEI and PEEK to find out the best polymer, which shows high surface properties and high adhesive joint strength after plasma treatment.
9.2.4 Surface Modification and Adhesive bonding of Titanium

The correlation of experimental results of surface energy and adhesive bonding of anodized titanium is concluded that due to the oxide layer on the surface of titanium, which is formed in the treatment of NaOH anodization technique, improves the adhesive bond strength of titanium. But when the adhesive joints are exposed to aggressive environmental conditions such as elevated temperature condition (200 °C for 100 hrs.), Ringer’s solution (40 °C for 2 weeks) and humid condition (50 °C, 99 % R.H. for 100 hrs.), poor mechanical strength is observed. To find out the reason behind this, it is found that oxide layers are enhanced the brittle characteristics of materials and showed poor mechanical strength under aggressive environments. Therefore, to improve adhesive bond strength of titanium under aggressive environmental conditions, there is a necessity to investigate other anodization techniques for modification of titanium.

Plasma nitriding was used to improve the adhesion properties of the titanium adhesive joints and its retention under environmental condition. Results obtained from contact angle measurement after plasma nitriding treatment shows that plasma nitriding has improved the wetting properties of titanium surface. Another important observation of this study is that surface topography of titanium is another crucial factor to achieve high bond strength. Due to plasma treatment, surface roughness of titanium increased. The increase in surface roughness is correlated with the increase in bond strength of plasma nitrided titanium. These results indicate that performances of bonded joints not only depend on the properties of the adhesive but it also depend on physico-chemical properties of substrates. But the experimental result of surface
energy reveals that due to plasma treatment of the titanium surface, surface energy of
the titanium is relatively low in respect of anodized titanium. This is because of the
less polarity of nitrogen than oxygen. Therefore, it is recommended that the work is
explored to the surface treatment of titanium by oxygen plasma treatment and
incorporates oxide layer on the surface of titanium.

9.2.5 Durability of Adhesive Bonding of Polymer to Titanium under Aggressive
Environmental Conditions

The present work is explored only epoxy-novolac (4:1) IPN adhesive and its
joining performance under aggressive environmental conditions. There is no detailing
mentioned about others epoxy-novolac IPN adhesive systems and their joining
performance under aggressive environmental conditions. Therefore, it is
recommended to check the adhesive joint strength of epoxy-novolac (4:2); (4:3); and
(1:1) IPN adhesive bonded plasma treated polyether imide to titanium and polyether
ether ketone to titanium under aggressive environmental conditions such as elevated
temperature condition (200 °C for 100 hrs.), Ringer’s solution (40 °C for 2 weeks) and
humid condition (50 °C, 99 % R.H. for 100 hrs.).