

高韧性防雷击复合材料表面膜研究



肖万宝,李洪峰,曲春艳,王德志,张杨,杨海冬,王永强

黑龙江省科学院石油化学研究院,黑龙江 哈尔滨 150040

摘要:为增加防雷击复合材料表面膜韧性,本文采用双羟基聚苯醚增韧环氧树脂制备了一种高韧性防雷击复合材料表面膜,通过简支梁冲击试验机、电子拉力试验机和扫描电镜等对表面膜树脂固化物的力学性能和微观结构进行表征,通过模拟雷电流注入试验对铺贴该防雷击表面膜的复合材料层压板进行了雷击测试。结果表明,双羟基聚苯醚用量为10份时,表面膜树脂固化物缺口冲击强度为 17.5kJ/m^2 ,韧性提高73.3%。模拟雷击测试结果表明防雷击表面膜能有效降低雷电流对复合材料的雷击损伤。

关键词:复合材料;表面膜;防雷击;高韧性

中图分类号:TQ 323.5

文献标识码:A

DOI: 10.19452/j.issn1007-5453.2023.01.013

热固性树脂基复合材料(简称复合材料)制件表面最常见的缺陷是针孔、缺胶和贫胶。复合材料表面膜是一种用于复合材料制件外表面的树脂基膜状材料,它可以与预浸料共固化,解决复合材料制件表面缺陷、方便施工并可以节省传统打磨抛光试件的时间和劳力,且重量(质量)可控^[1-6]。复合材料结构件表面铺覆表面膜后,复合材料表面光滑致密。如图1所示,左半图复合材料表面呈现针孔等凹陷,右半图铺覆表面膜后表面平整无针孔现象。另外,复合材料表面膜的使用还可以赋予复合材料制件特殊的功能,如与金属网复合后具有防雷击等功能^[7-14]。由于复合材料导电性能较金属差,当复合材料遭受雷击时,很难将高能量的电流传出去,必然导致大能量的聚集,从而影响飞机的安全性能,因此必须对飞机复合材料部件进行有效的雷击防护。目前,飞机上复合材料雷击防护最行之有效的方法通常采用铺设金属网、表面喷铝、黏结金属箔或布置分流条等方式,其中铺设金属网的方式最为普遍,用量最大。带金属网的复合材料表面膜与预浸料共固化到复合材料结构上后,可承受200kA的电流,雷电流从飞机外表面沿金属网通过,复合材料内部损伤不严重,通常造成雷击点金属网烧蚀或浅层复材破损,维修人员在维修时只要将损坏的部分剥掉,重新修补就可完成^[15-23]。为匹配复合材料树脂体系,目前有环氧树脂、双马树脂、氰酸酯树脂及苯并噁嗪树脂为

主体树脂的复合材料表面膜^[24-30]。

本文研制了一种韧性环氧树脂复合材料表面膜,采用一种双羟基聚苯醚增韧改性环氧树脂,得到一种韧性环氧树脂体系,通过表面膜载体的优选,最后与金属网复合制备了一种防雷击复合材料表面膜,其有望在航空航天复合材料结构件中获得应用。

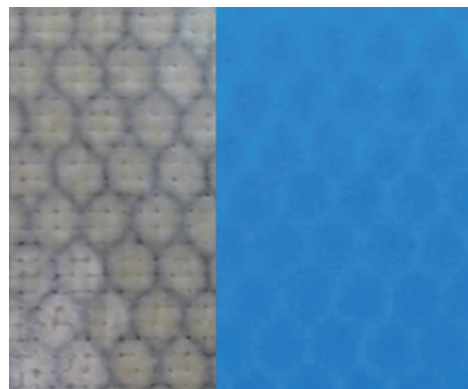


图1 铺附表面膜后复合材料表面对比

Fig.1 Surface contrast of composite material after surfacing film

1 试验部分

1.1 试验原料与试剂

试验中所采用的双酚A型环氧树脂(EP)为无锡环氧树

收稿日期:2022-06-08; 退修日期: 2022-11-02; 录用日期: 2022-12-05

基金项目: 航空科学基金(202000440X3001);黑龙江省自然科学基金研究团队项目(TD2020E003)

引用格式: Xiao Wanbao, Li Hongfeng, Qu Chunyan, et al. Research on high toughness lightning strike protection composite surfacing film[J]. Aeronautical Science & Technology, 2023, 34(01): 105-110. 肖万宝, 李洪峰, 曲春艳, 等. 高韧性防雷击复合材料表面膜研究[J]. 航空科学技术, 2023, 34(01): 105-110.

脂厂的产品;双羟基聚苯醚(MPPO)由郑州大学提供;载体购自阳江英普奇点五金制造有限公司;KKL系列防雷击金属网为航空工业合肥航太电物理技术有限公司的产品;固化剂混合物为自制。

1.2 试验过程

(1) 树脂试样制备

将环氧树脂置于容器中,升温至190℃,按配方(见表1)加入双羟基聚苯醚并不断搅拌,保温10min,搅拌均匀至完全溶解;降温130℃左右加入固化剂并不断搅拌,混合均匀后倒入预热的模具中;130℃真空脱泡,按照180℃×3h的固化工艺固化树脂浇铸体。

表1 试验配方

Table 1 Experimental formula

试验编号	EP/g	MPPO/g
0	100	0
1	100	5
2	100	10
3	100	15
4	100	20

(2) 表面膜制备

采用表1中树脂配方与载体和金属网通过热熔法成膜设备制备出防雷击复合材料表面膜,制备的表面膜厚度为0.13mm,面密度为150g/m²。

1.3 测试与表征

表面膜树脂固化物液氮冷冻后淬断面形貌通过荷兰Philips公司的XL30 ESEM型扫描电子显微镜(SEM)进行观察。表面膜的冲击强度采用河北承德材料试验机厂的Charpy XCJ-500型简支梁冲击试验机进行测定。表面膜树脂的玻璃化转变温度采用美国TA公司的DMA Q800型动态热机械分析仪(DMA)测试。

2 结果与讨论

2.1 表面膜树脂的韧性

本文采用冲击强度和断裂韧性衡量表面膜树脂固化物韧性。冲击强度试样采用无缺口冲击试样,冲击强度结果如图2所示,冲击强度随着MPPO用量的增加而增加,初始韧性增加明显,当用量超过10phr,增加趋势变缓。当MPPO用量为20phr时,缺口冲击强度达到最大值18.6kJ/m²,相比于未添加MPPO体系的10.1kJ/m²,冲击强度增加84.2%,表明表面膜树脂韧性得到明显提高。添加MPPO可以提高表面膜树脂的韧性,但要兼顾表面膜良好的工艺黏性以满足

表面膜树脂制造工艺的要求。从韧性增加趋势来看,本文选择10phr的MPPO增韧表面膜树脂,此时缺口冲击强度为17.5kJ/m²。

断裂韧性表征的是材料阻止裂纹扩展的能力,是度量材料的韧性好坏的一个定量指标,本文选用临界应力强度因子(KIC)来表征表面膜树脂的断裂韧性。KIC的计算公式如下。

$$K_{Ic} = \frac{P \cdot f(x)}{B \cdot W^{0.5}} \quad (1)$$

式中: P 为加载应力(N); B 为试样厚(mm); W 为试样宽(mm); ν 为泊松比,本文取 $\nu=0.40$; E 为弹性模量(MPa); $f(x)$ 为预裂纹长度和缺口深度之和 a 与试样宽度 W 的函数($x=a/W$),即

$$f(x) = 6x^{1/2} \frac{[1.99 - x(1-x)(2.15 - 3.93x + 2.71x^2)]}{(1+2x)(1-x)^{3/2}} \quad (2)$$

表面膜树脂固化物断裂韧性测试结果如图2所示,从图2中可知,随着MPPO的加入和用量的增加,表面膜树脂断裂韧性逐渐增加,当MPPO用量为20phr时,断裂韧性最大为1.42MPa·m^{0.5},断裂韧性与冲击强度的变化趋势相似。

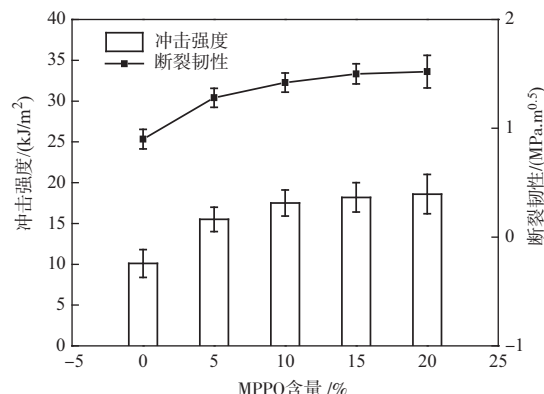
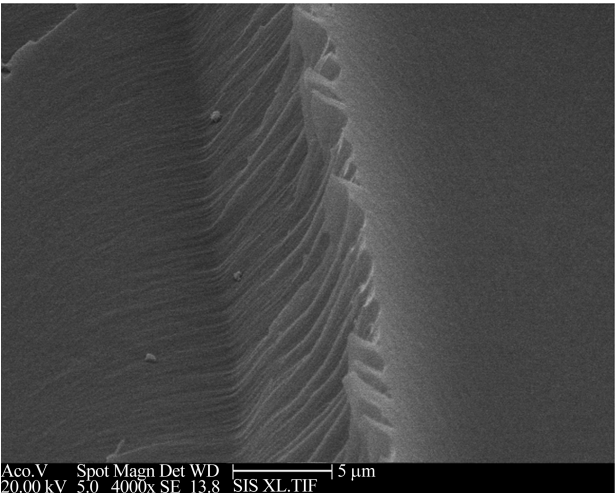


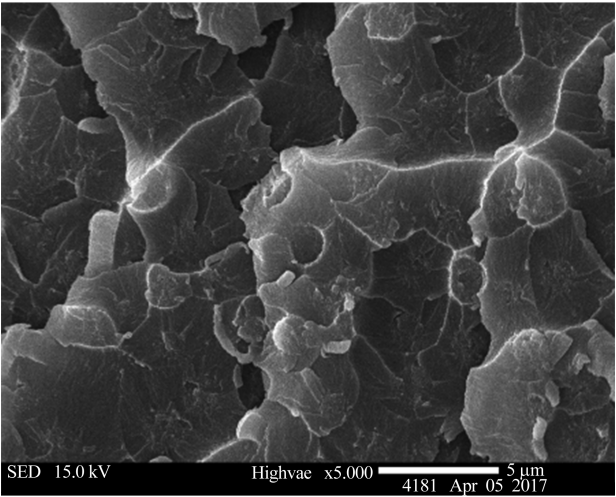
图2 表面膜树脂冲击强度和断裂韧性

Fig. 2 Impact strength and fracture toughness of surfacing film resin

图3为表面膜树脂固化物液氮冷冻后淬断面的SEM照片。图3(a)为未添加MPPO的树脂断面照片,断面平滑,为典型的脆性断裂形式;图3(b)为添加10份MPPO的树脂断面照片,可以观察到MPPO分散在环氧树脂基体的连续相中,形成环氧树脂基体中有许多白色环。这些白环结构起到了钉锚的作用,可以有效地阻止和抑制裂纹的扩散。此外,这种锚固结构可以缓解裂纹尖端的应力,降低环氧树脂基体的应力集中,从而产生韧性断裂。因此,环氧树脂基体



(a) MPPO-0%



(b) MPPO-10%

图3 表面膜树脂SEM照片

Fig. 3 SEM images of surfacing film resin

的韧性显著提高。

图4为表面膜树脂的玻璃化转变温度。从图4中可以看到,随着MPPO用量的增加,改性体系玻璃化转变温度保持在173℃左右小幅波动(如MPPO用量为0phr、5phr、10phr、15phr、20phr,玻璃化转变温度依次为 $T_0=173.23^{\circ}\text{C}$ 、 $T_5=172.9^{\circ}\text{C}$ 、 $T_{10}=174.8^{\circ}\text{C}$ 、 $T_{15}=173.4^{\circ}\text{C}$ 、 $T_{20}=170.5^{\circ}\text{C}$)。说明MPPO对表面膜耐热性基本没有影响。

2.2 表面膜防雷击性能

雷电在飞机表面不同的附着特征和传导特性将飞机表面大致划分成5个区域(1A、1B、2A、2B和3区)。雷电初始附着概率很高的表面为1区,雷电从初始附着点位置被气流吹移通过的概率很高的表面为2区,3区为1区和2区以外的所有飞机表面,该区域雷电流直接附着概率低,但可能成为雷电流传导的通道。A区是电弧在它上面悬停可能性

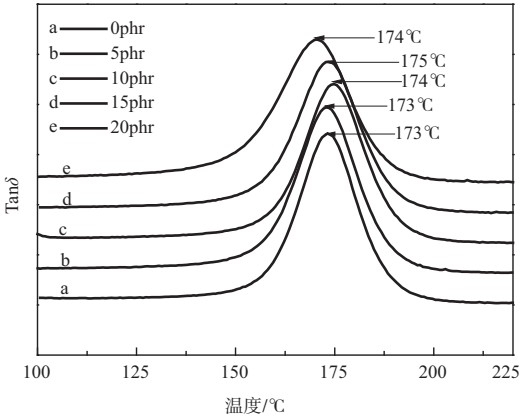


图4 表面膜树脂DMA曲线

Fig.4 DMA curves of surfacing film resin

较小的区域,B区是电弧在它上面悬停可能性较大的区域。

表面膜与防雷击金属网复合构成防雷击复合材料表面膜。73g/m²的铜网大多用于2A区和3区的防雷击,141g/m²的铜网大多用于1A区和2B区的防雷击,金属网规格可根据设计需求调整。金属网规格见表2,铜的电阻率为 $1.75\times 10^{-8}\Omega\cdot\text{m}$,密度为8.9g/cm³;铝的电阻率为 $2.83\times 10^{-8}\Omega\cdot\text{m}$,密度为2.7g/cm³;铜网导电性更优异,铝网价格便宜,质量轻,但易腐蚀,各具优势。

表2 几种常见金属网性能

Table 2 The performance of several common metal mesh

材质	单位面积质量/(g/m ²)	总厚度/mm	开放面积/%
Al	66	0.05	52
	78	0.10	71
	136	0.13	60
Cu	73	0.05	84
	107	0.05	84
	141	0.08	79
	195	0.08	70

对铺贴防雷击表面膜的复合材料层压板进行了2A区雷击试验,经模拟雷击B波平均电流1.80kA,持续时间5.28ms,库仑量9.52C;C波平均电流343.01kA,持续时间630.4ms,库仑量216.32C;D波峰值电流92.46kA,持续时间250.2μs,作用积分 $0.24\times 10^6\text{A}^2\text{s}$ 。试验结果如图5所示。图5(a)为未经防雷击表面膜保护的复合材料层压板,图中可以看到复合材料板出现碳纤维断裂、分层,复合材料内部出现损伤,图5(b)为铺贴防雷击表面膜的复合材料层压板,图中可以看到复合材料板出现金属网烧蚀,烧蚀面积约为直径φ16cm的圆,复合材料表面目测无损伤。试验结果说明防雷击表面膜有效降低雷电流对复合材料的雷击损伤。

下一步将开展铺贴防雷击表面膜的复合材料层压板进行不同雷击分区的雷击试验,并对模拟雷击后的复合材料层压板进行无损检测。

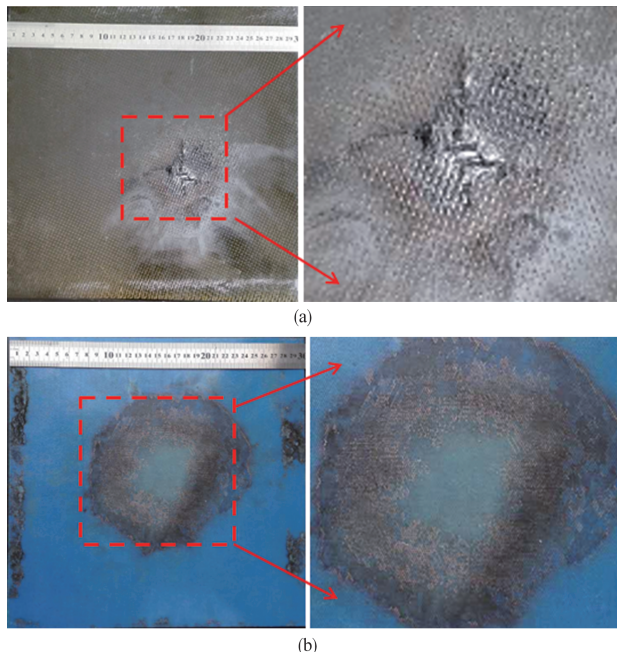


图5 复合材料表面膜2A区雷击后试验件

Fig.5 The specimen of composite surfacing film after 2A zone lightning strike

3 结论

复合材料表面膜树脂韧性随着双羟基聚苯醚(MPPO)用量的增加而提高,当MPPO用量为20phr时,缺口冲击强度达到最大值 18.6kJ/m^2 ,相比于未添加MPPO体系的冲击强度增加84.2%,表明表面膜树脂韧性得到明显提高,且对表面膜耐热性基本没有影响。防雷击表面膜能有效降低雷电流对复合材料的雷击损伤。

AST

参考文献

- [1] Wu S, Ladani R B, Zhang J, et al. Aligning multilayer graphene flakes with an external electric field to improve multifunctional properties of epoxy nanocomposites[J]. Carbon, 2015, 94:607-618.
- [2] Monetta T, Bellucci F, Acquesta A. Graphene/epoxy coating as multifunctional material for aircraft structures[J]. Aerospace, 2015, 2(2):423-434.
- [3] Katunin A, Krukiewicz K, Turczyn R, et al. Synthesis and characterization of the electrically conductive polymeric composite for lightning strike protection of aircraft structures [J]. Composite Structures, 2016, 159:773-783.
- [4] Kandare E, Khatibi A A, Yoo S, et al. Improving the through-thickness thermal and electrical conductivity of carbon fibre/epoxy laminates by exploiting synergy between graphene and silver nano-inclusions[J]. Composites Part A: Applied Science & Manufacturing, 2015, 69:72-82.
- [5] Khan F, Kausar A, Siddiq M. A review on properties and fabrication techniques of polymer/carbon nanotube composites and polymer intercalated buckypapers[J]. Polymer-Plastics Technology and Engineering, 2015, 54(14):1524-1539.
- [6] Reid L, Ransom J, Wehrmeister M. Grommet hole reinforcement and lightning strike protection in composite structural assembly[J]. Sae International Journal of Aerospace, 2011, 4(2):988-997.
- [7] Schueler R, Petermann J, Schulte K, et al. Agglomeration and electrical percolation behavior of carbon black dispersed in epoxy resin[J]. Journal of Applied Polymer Science, 1997, 63 (13):1741-1746.
- [8] Guadagno L, Vivo B D, Bartolomeo A D, et al. Effect of functionalization on the thermo-mechanical and electrical behavior of multi-wall carbon nanotube/epoxy composites[J]. Carbon, 2011, 49(6):1919-1930.
- [9] Yang K, Gu M, Guo Y, et al. Effects of carbon nanotube functionalization on the mechanical and thermal properties of epoxy composites[J]. Carbon, 2009, 47(7):1723-1737.
- [10] Pitalisky Z, Krontiras C A, Georga S N, et al. Effect of oxidation treatment of multiwalled carbon nanotubes on the mechanical and electrical properties of their epoxy composites [J]. Tumor Biology, 2002, 23(4):228-248.
- [11] Rosca I D, Hoa S V. Method for reducing contact resistivity of carbon nanotube-containing epoxy adhesives for aerospace applications[J]. Composites Science and Technology, 2011, 71 (2): 95-100.
- [12] Pal G, Kumar S. Modeling of carbon nanotubes and carbon nanotube-polymer composites[J]. Progress in Aerospace Sciences, 2016, 80: 33-58.
- [13] Jakubinek M B, Ashrafi B, Zhang Y, et al. Single-walled carbon nanotube-epoxy composites for structural and conductive aerospace adhesives[J]. Composites Part B:

- Engineering, 2015, 69: 87-93.
- [14] Han J, Zhang H, Chen M, et al. The combination of carbon nanotube buckypaper and insulating adhesive for lightning strike protection of the carbon fiber/epoxy laminates[J]. Carbon, 2015, 94: 101-113.
- [15] Prabhakaran R. Lightning strikes on metal and composite aircraft and their mitigation[J]. Journal of Aerospace Sciences and Technologies, 2011, 63(3): 208-222.
- [16] Iqbal H M S, Bhowmik S, Benedictus R. Process optimization of solvent based polybenzimidazole adhesive for aerospace applications[J]. International Journal of Adhesion and Adhesives, 2014, 48: 188-193.
- [17] Gagné M, Therriault D. Lightning strike protection of composites[J]. Progress in Aerospace Sciences, 2014, 64: 1-16.
- [18] Zhang D, Ye L, Deng S, et al. CF/EP composite laminates with carbon black and copper chloride for improved electrical conductivity and interlaminar fracture toughness[J]. Composites Science & Technology, 2012, 72(3):412-420.
- [19] Chakravarthi D K, Khabashesku V N, Vaidyanathan R, et al. Carbon fiber-bismaleimide composites filled with nickel-coated single-walled carbon nanotubes for lightning-strike protection[J]. Advanced Functional Materials, 2011, 21(13): 2527-2533.
- [20] Kawakami H, Feraboli P. Lightning strike damage resistance and tolerance of scarf-repaired mesh-protected carbon fiber composites[J]. Composites Part A: Applied Science and Manufacturing, 2011, 42(9): 1247-1262.
- [21] Li Y, Li R, Lu L, et al. Experimental study of damage characteristics of carbon woven fabric/epoxy laminates subjected to lightning strike[J]. Composites Part A: Applied Science and Manufacturing, 2015, 79: 164-175.
- [22] Katunin A, Krukiewicz K, Herega A, et al. Concept of a conducting composite material for lightning strike protection [J]. Advances in Materials Science, 2016, 16(2): 32-46.
- [23] Ennis B C, Pearce P J, Morris C E M. Aging and performance of structural film adhesives. III. Effect of humidity on a modern aerospace adhesive[J]. Journal of Applied Polymer Science, 2010, 37(1):15-32.
- [24] Lee S E, Park K Y, Oh K S, et al. The use of carbon/dielectric fiber woven fabrics as filters for electromagnetic radiation[J]. Carbon, 2009, 47(8): 1896-1904.
- [25] 刘辉平,段泽民,司晓亮,等.碳纤维复合材料雷电注入试验研究[J].电气应用,2016(14):74-77.
- Liu Huiping, Duan Zemin, Si Xiaoliang, et al. Experimental research on lightning injection of carbon fiber composites[J]. Electrotechnical Application,2016(14):74-77. (in Chinese)
- [26] 张杨,李洪峰,王德志,等.复合材料表面膜的研究进展[J].化学与粘合,2016,38(1):59-62.
- Zhang Yang, Li Hongfeng, Wang Dezhi, et al. Research progress in composite surface films[J]. Chemistry and Adhesion, 2016, 38(1):59-62. (in Chinese)
- [27] 胡静,巩翰林,司晓亮,等.碳纤维复合材料雷电防护特性仿真及试验研究[J].航空科学技术,2022,33(1):98-106.
- Hu Jing, Gong Hanlin, Si Xiaoliang, et al. Simulation and experimental research on lightning protection characteristics of carbon fiber composites[J]. Aeronautical Science & Technology, 2022,33(1):98-106. (in Chinese)
- [28] 曹景斌,王松,章强.树脂基复合材料湿热压缩性能研究[J].航空科学技术,2020,31(3):47-52.
- Cao Jingbin, Wang Song, Zhang Qiang. Research on resin composite hydrothermal compressive properties[J]. Aeronautical Science & Technology, 2020,31(3):47-52. (in Chinese)
- [29] 程健男,徐福泉,张体磊.树脂基复合材料在直升机的应用及其制造技术[J].航空科学技术,2021,32(1):109-114.
- Cheng Jiannan, Xu Fuquan, Zhang Tilei. Application and manufacturing technology of composites in helicopter[J]. Aeronautical Science & Technology, 2021,32(1): 109-114. (in Chinese)
- [30] 胡好,姚红,司晓亮,等.飞机复合材料板雷电损伤的试验研究[J].合肥工业大学学报(自然科学版),2014(4):402-406.
- Hu Hao, Yao Hong, Si Xiaoliang, et al. Experimental research on lightning damage of composite material plate of aircraft[J]. Journal of Hefei University of Technology(Natural Science), 2014(4):402-406. (in Chinese)

Research on High Toughness Lightning Strike Protection Composite Surfacing Film

Xiao Wanbao, Li Hongfeng, Qu Chunyan, Wang Dezhi, Zhang Yang, Yang Haidong, Wang Yongqiang

Institute of Petrochemistry Heilongjiang Academy of Sciences, Harbin 150040, China

Abstract: In order to increase the toughness of the lightning strike protection composite surface film, the high toughness lightning strike protection composite surface film is prepared by toughening epoxy resin with bis-hydroxy terminated polyphenylene oxide (MPPO). The mechanical properties and microstructure of the surface film cured resin are characterized by simple beam impact testing machine, electronic tensile testing machine and scanning electron microscope. The composite laminate laid on the lightning strike protection composite surface film were tested by the lightning injection test simulated. The results show that when the MPPO is 10phr, the impact strength of the surface film resin cured is 17.5kJ/m^2 , and the toughness increases by 73.3%. The lightning injection test simulated results show that the lightning protection surface film can effectively reduce the lightning damage to the composite material.

Key Words: composite material; surfacing film; lightning strike protection; high toughness

Received: 2022-06-08; **Revised:** 2022-11-02; **Accepted:** 2022-12-05

Foundation item: Aeronautical Science Foundation of China (202000440X3001) ; Natural Science Foundation of Heilongjiang Province Research Team(TD2020E003)