

**STUDIES ON GLASS FIBRE FABRIC/EPOXY
SELF-HEALING COMPOSITES**

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**DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI
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SELF-HEALING COMPOSITES**

by

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Department of Materials Science and Engineering

Submitted

in fulfilment of the requirements of the degree of Doctor of Philosophy

to the



**Indian Institute of Technology Delhi
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Dedicated to my family

CERTIFICATE

This is to certify that the thesis entitled, “**Studies on glass fibre fabric/epoxy self-healing composites**” being submitted by **Ms. Shilpi Sharma** to the Indian Institute of Technology Delhi, for the award of degree of **Doctor of Philosophy** is a record of bonafide research work carried out by her under our supervision. This thesis has been prepared in conformity with the rules and regulations of the Indian Institute of Technology Delhi, New Delhi. We further certify that the thesis has reached the requisite standard for a Ph.D. degree of this Institute. The results contained in this thesis are original and have not been submitted, in part or full, to any other University or Institute for the award of any other degree or diploma.

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Abstract

The present research work was focused upon the fabrication of glass fibre fabric/epoxy self-healing composites, where the healing functionality is bestowed by the inclusion of healant loaded microcapsules/or hollow glass fibre fabric. Healant loaded microcapsules have been prepared by in-situ polymerization using emulsion technique which resulted in microcapsules with poly(melamine-formaldehyde) [PMF] shell and by solvent evaporation technique which resulted in microcapsules with poly(methyl methacrylate) [PMMA] shell. In the development of epoxy loaded PMF/PMMA microcapsules, percent yield, core content and controlling the shell wall thickness, stability, smooth and stable morphology of microcapsules are the key issues. Thus, the aim of this work is to study the influence of various parameters on the properties of epoxy loaded PMF and PMMA microcapsules. The resulting epoxy loaded/amine loaded microcapsules were characterized by Fourier-transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$), optical microscopy (OM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), particle size analyser for mean particle size and particle size distribution (PSD) and differential scanning calorimeter (DSC) etc.

The effect of reaction parameters such as microencapsulation temperature, melamine-to-formaldehyde (M/F) ratio, surfactant concentration and core-to-shell ratio taken in the synthesis of epoxy loaded PMF microcapsules on percent yield, core content, shell wall thickness, shell wall stability etc. was investigated by one-at-a-time approach and optimized. The effect of various process parameters, such as surfactant concentration, core-to-shell ratio taken in the initial feed, temperature and agitation speed in the synthesis of epoxy loaded PMMA microcapsules were investigated by statistical method. Taguchi orthogonal array with L_{25} matrix was implemented to optimize the experimental parameters for such microcapsules.

The signal-to-noise ratio (SNR) and analysis of variance (ANOVA) were also performed to determine the optimum parameters and significance of various parameters. FTIR and ¹H-NMR spectra confirmed the presence of epoxy as the core material in PMF/PMMA microcapsules. From these studies, the optimum process conditions for the preparation of epoxy filled PMF microcapsules were 80 °C temperature , 1:9 melamine-to-formaldehyde ratio, 5 wt% surfactant concentration and 1:1 core-to-shell ratio (in moles). SNR analysis identified the optimum levels of various parameters for the preparation of epoxy filled PMMA microcapsules as: surfactant concentration-10 wt%, core-to-shell ratio-3:1, temperature-40 °C and agitation speed-300 rpm. ANOVA analysis showed that surfactant concentration was the most significant parameter in improving the core content of epoxy filled PMMA microcapsules.

The effect of inclusion of healant loaded hollow glass fibre fabric/PMF/PMMA microcapsules or their combination on the mechanical, morphological and self-healing properties of glass fibre fabric/epoxy composites was also carried out in the present research work. All composites were prepared using eleven layers of fabric with warp fibres alignment by hand lay-up (HLU) method. Fiber content of all the composites was determined using ignition loss method. The mechanical (impact, flexural and dynamic mechanical analysis) and self-healing test of composites were carried out and the effects of inclusion of healant loaded hollow glass fibre fabric/healant loaded microcapsules were analyzed. The inclusion of epoxy and amine loaded hollow glass fibre fabric in the epoxy composites resulted in a significant ~82.3% improvement in impact strength. The morphological analysis of impact fractured samples showed the oozing out of healing agent from the glass fibres and curing of healing agents at the surface of the fibres. The surface morphology of the healed samples showed that the healing agent leaks into the crack region and heal this region by initiation of curing reactions. These studies showed that PMF and PMMA microcapsules at 2.5 and 5 wt%

could be used as an effective self-healing material, respectively. PMMA microcapsules based self-healing composites showed better performance as compared to PMF microcapsules based compositions. This study clearly demonstrated that the inclusion of healant (epoxy and amine) loaded PMF, PMMA microcapsules and hollow glass fibre fabric meet the fundamental requirements of the commercial applications such as aerospace and marine industries.

सार

वर्तमान शोध कार्य ग्लास फाइबर फ़ैब्रिक/एपॉक्सी सेल्फ-हीलिंग कंपोजिट्स के निर्माण पर केंद्रित था, जहां हील लोडेड माइक्रोसेपल्स/या खोखले ग्लास फाइबर फ़ैब्रिक के समावेश द्वारा हीलिंग की कार्यक्षमता को पूरा किया जाता है। हीलेंट लोडेड माइक्रोकैप्सल्स को इमल्शन तकनीक का उपयोग करके इन-सीटू पोलीमराइजेशन द्वारा तैयार किया गया है, जिसके परिणामस्वरूप पॉली (मेलामाइन-फॉर्मल्डिहाइड) [पीएमएफ] शेल के साथ माइक्रोकैप्सल्स और विलायक वाष्पीकरण तकनीक के परिणामस्वरूप पॉली (मिथाइल मेथैक्रिलेट) [पीएमएमए] शेल के साथ माइक्रोकैप्सूल का परिणाम हुआ। एपॉक्सी भरी हुई पीएमएफ/पीएमएमए माइक्रोकैप्सुलस के विकास में प्रतिशत उपज, कोर सामग्री और शेल दीवार की मोटाई को नियंत्रित करना, माइक्रोकैप्सल्स की स्थिरता, चिकनी और स्थिर आकृति विज्ञान प्रमुख मुद्दे हैं। इस प्रकार, इस काम का उद्देश्य एपॉक्सी लोड पीएमएफ और पीएमएमए माइक्रोकैप्सुल के गुणों पर विभिन्न मापदंडों के प्रभाव का अध्ययन करना है। परिणामस्वरूप एपॉक्सी लोडेड/एमआइन लोडेड माइक्रोकैप्सल्स को फूरियर-ट्रांसफॉर्म इंफ्रारेड स्पेक्ट्रोस्कोपी (एफटीआईआर), परमाणु चुंबकीय अनुनाद स्पेक्ट्रोस्कोपी (¹एच-एनएमआर), ऑप्टिकल माइक्रोस्कोपी (ओएम), स्कैनिंग इलेक्ट्रॉन माइक्रोस्कोपी (एसईएम), ट्रांसमिशन इलेक्ट्रॉन माइक्रोस्कोपी (टीईएम) की विशेषता थी। माध्य कण आकार और कण आकार वितरण (पीएसडी) और अंतर स्कैनिंग कैलोरीमीटर (डीएससी) आदि के लिए कण आकार विश्लेषक।

प्रतिक्रिया मापदंडों का प्रभाव जैसे कि माइक्रोएन्कैप्सुलेशन तापमान, मेलामाइन-टू-फॉर्मल्डिहाइड (एम/एफ) अनुपात, सर्फैक्टेंट एकाग्रता और कोर-से-शेल अनुपात प्रतिशत उपज, कोर सामग्री, शेल की दीवार की मोटाई पर एपॉक्सी लोड पीएमएफ माइक्रोकैप्सुलस के संश्लेषण में लिया गया है। शेल दीवार स्थिरता आदि की जांच एक बार के दृष्टिकोण और अनुकूलित द्वारा की गई थी। विभिन्न प्रक्रिया मापदंडों के प्रभाव, जैसे कि सर्फैक्टेंट एकाग्रता, प्रारंभिक फीड में लिया गया कोर-टू-शेल अनुपात, एपॉक्सी लोड पीएमएमए माइक्रोकैप्सुलस के संश्लेषण में तापमान और आंदोलन

की गति सांख्यिकीय विधि द्वारा जांच की गई थी। ल_{२५} मैट्रिक्स के साथ टैगुचि ऑर्थोगोनल सरणी को ऐसे माइक्रोसेप्स्यूल के लिए प्रयोगात्मक मापदंडों को अनुकूलित करने के लिए लागू किया गया था। विभिन्न मापदंडों के इष्टतम मापदंडों और महत्व को निर्धारित करने के लिए संकेत-टू-शोर अनुपात (एसएनआर) और विचरण (एनोवा) का विश्लेषण भी किया गया था। एफटीआईआर और ^१एच-एनएमआर स्पेक्ट्रा ने पीएमएफ/पीएमएमए माइक्रोकैप्सूल में मुख्य सामग्री के रूप में एपॉक्सी की उपस्थिति की पुष्टि की। इन अध्ययनों से, एपॉक्सी से भरे पीएमएफ माइक्रोकैप्सूल की तैयारी के लिए इष्टतम प्रक्रिया की स्थिति ८० डिग्री सेल्सियस तापमान, १:९ मेलामाइन-टू-फॉर्मलडिहाइड अनुपात, ५ वट% सर्फैक्टेंट एकाग्रता और १:१ कोर-टू-शेल अनुपात (मोल्स में)। एसएनआर विश्लेषण ने एपॉक्सी से भरे पीएमएमए माइक्रोकैप्सूल की तैयारी के लिए विभिन्न मापदंडों के इष्टतम स्तरों की पहचान की: सर्फैक्टेंट सघनता-१० वट%, कोर-टू-शेल अनुपात-३:१, तापमान-४० डिग्री सेल्सियस और आंदोलन की गति-३०० आरपीएम। एनोवा विश्लेषण से पता चला है कि एपॉक्सी से भरे पीएमएमए माइक्रोकैप्सुल्स की मुख्य सामग्री को बेहतर बनाने में सर्फैक्टेंट एकाग्रता सबसे महत्वपूर्ण पैरामीटर था।

हील लोडेड खोखले ग्लास फाइबर फैब्रिक/पीएमएफ/पीएमएमए माइक्रोकैप्सुल्स या ग्लास फाइबर फैब्रिक/एपॉक्सी कंपोजिट के मैकेनिकल, रूपात्मक और स्व-चिकित्सा गुणों पर उनके संयोजन के प्रभाव को भी वर्तमान शोध कार्य में शामिल किया गया था। सभी कंपोजिट्स को हैंड ले-अप (हलु) विधि द्वारा ताना-बाना संरेखण के साथ कपड़े की ग्यारह परतों का उपयोग करके तैयार किया गया था। सभी कंपोजिट की फाइबर सामग्री इग्निशन लॉस विधि का उपयोग करके निर्धारित की गई थी। यांत्रिक (प्रभाव, फ्लेक्सुरल और गतिशील यांत्रिक विश्लेषण) और कंपोजिट के आत्म-चिकित्सा परीक्षण किए गए थे और हीलेंट लोड किए गए खोखले ग्लास फाइबर फैब्रिक/हीलेंट लोडेड माइक्रोकैप्सुल्स के शामिल किए जाने के प्रभावों का विश्लेषण किया गया था। एपॉक्सी कंपोजिट में एपॉक्सी और अमाइन लोड खोखले ग्लास फाइबर फैब्रिक को शामिल करने से प्रभाव शक्ति में एक महत्वपूर्ण ~८२.३% सुधार हुआ। प्रभाव खंडित नमूनों के रूपात्मक

विश्लेषण ने ग्लास फाइबर से हीलिंग एजेंट के बाहर निकलने और फाइबर की सतह पर हीलिंग एजेंटों के इलाज का पता लगाया। चंगा नमूनों की सतह आकारिकी ने दिखाया कि उपचार एजेंट दरार क्षेत्र में लीक करता है और प्रतिक्रियाओं को ठीक करने की दीक्षा द्वारा इस क्षेत्र को ठीक करता है। इन अध्ययनों से पता चला कि क्रमशः २.५ और ५ वट% पर पीएमएफ और पीएमएमए माइक्रोकैप्सल्स को एक प्रभावी आत्म-चिकित्सा सामग्री के रूप में इस्तेमाल किया जा सकता है। पीएमएमए माइक्रोकैप्सल्स आधारित सेल्फ-हीलिंग कंपोजिट्स ने पीएमएफ माइक्रोकैप्सल्स आधारित रचनाओं की तुलना में बेहतर प्रदर्शन दिखाया। इस अध्ययन ने स्पष्ट रूप से प्रदर्शित किया कि हीलेंट (एपाॅक्सी और अमाइन) को शामिल करने से पीएमएफ, पीएमएमए माइक्रोकैप्सल्स और खोखले ग्लास फाइबर फैब्रिक लोड होते हैं, जो एयरोस्पेस और समुद्री उद्योगों जैसे वाणिज्यिक अनुप्रयोगों की मूलभूत आवश्यकताओं को पूरा करते हैं।

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List of Symbols

M_n	Number average molecular weight
M_w	Weight average molecular weight
ρ_c	Density of composite
ρ_w	Density of water
η	Healing efficiency
K_{IC}	Critical stress intensity factor
E'	Dynamic storage modulus
E''	Loss modulus
$\tan \delta$	Mechanical loss factor
T_g	Glass transition temperature
T_i	Temperature at which the curing exotherm starts
T_{peak}	Peak exotherm temperature
T_{end}	Temperature at which the curing exotherm ends
T_d	Decomposition temperature
W_f	Weight percent of fiber
P_h	Flexural strength of the self-healed composite
P_v	Flexural strength of the virgin sample (without self-healing)

List of Abbreviations

DGEBA	Diglycidyl ether of bisphenol-A
TETA	Triethylene tetramine
PMF	Poly(melamine-formaldehyde)
PMMA	Poly(methyl methacrylate)
TEA	Triethanolamine
SLS	Sodium lauryl sulphate
PVA	Poly(vinyl alcohol)
DCM	Dichloromethane
HGF	Hollow glass fibre
FTIR	Fourier transforms infrared spectroscopy
¹H-NMR	Nuclear magnetic resonance spectroscopy
OM	Optical microscopy
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
PSD	Particle size distribution
TGA	Thermal gravimetric analysis
DSC	Differential scanning calorimetry
DMA	Dynamic mechanical analysis
GPC	Gel permeation chromatography
SNR	Signal-to-noise ratio
OA	Taguchi orthogonal array
ANOVA	Analysis of variance
NIIS	Notched Izod impact strength
SENB	Single edge notch beam