

A STUDY ON
POLYURETHENE NANOCOMPOSITE COATINGS FOR
IMPROVED WEATHER RESISTANCE AND
GAS BARRIER PROPERTIES

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by
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CERTIFICATE

This is to certify that the thesis entitled “A STUDY ON POLYURETHENE NANOCOMPOSITE COATINGS FOR IMPROVED WEATHER RESISTANCE AND GAS BARRIER PROPERTIES” being submitted by Mrs. Upashana Chatterjee to the Indian Institute of Technology Delhi is a record of bonafide research work carried out by her under our supervision and guidance. The thesis work, in our opinion, has reached the standard, fulfilling the requirements for DOCTOR OF PHILOSOPHY degree. The research report and results presented in this thesis have not been submitted, in part or full, to any University or Institute for the award of any degree or diploma.

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(Upashana Chatterjee)

ABSTRACT

‘Lighter-than-air (LTA)’ helium inflatables are receiving renewed attention in the scientific and research communities. These advanced inflatables are basically huge balloon kind of structure made up of impermeable coated textile and typically use helium gas to stay aloft for passive air defense and surveillance. Degradation due to the severe weathering stresses, mainly solar ultra-violet (UV) radiation, affects the barrier property of the inflatable envelope structure and thus limits the service life of the whole system causing a huge loss. Thus, one of the major concerns is to improve the barrier properties of the envelope system from the harmful weathering factors.

A typical inflatable envelope system consists of a strength layer generally made up of woven textiles, having high strength-to-weight-ratio, to provide a flexible high strength base to the structure and a protective layer which acts as a gas barrier layer for maintaining the inflated condition of the structure. Among various types of polymeric resins, Thermoplastic polyurethane (TPU) has recently attracted much interest as a protective layer or coating for such high end applications. However, similar to other polymeric materials, TPU is also considered to be susceptible to UV degradation on exposure to weather.

The present study is an attempt to investigate on a novel high performance TPU nanocomposite coatings having superior weathering resistance as well as good impermeability property for textile based advanced inflatables. Being a very versatile polymer in respect to its chemistry, the property of TPUs is known to vary significantly. In this study, the weathering behaviour of two chemically different types of TPUs has been studied in detail to understand the degradation trend thoroughly. In this regard, the

effect of various classes of conventional UV protective additives has also been considered.

These organic UV protective additives are found to suffer mainly from physical losses. To overcome these limitations the study has been extended to explore the effect of incorporation of advanced nanomaterials into the coating system. Nanomaterials seem to provide minimum physical loss, at the same time, they can provide additional functional properties such as resistance to permeability of gases etc. In this respect, the most common and potential nanofillers to improve the impermeability property of polymeric membranes are nano clay and graphene. Both of them, having two dimensional platelet geometry and high aspect ratio, have already been reported to act as diffusion barriers in polymeric membranes. In the present study, a combination of conventional UV protective additives as well as advanced nanomaterials such as nano clay and graphene has been investigated for a high performance, multifunctional nanocomposite coating. An optimal design of TPU based nanocomposite formulation has been explored in accordance with a mixture design for three components additives (UV stabilizer, nano clay and graphene).

Further, the above analysis has been extended to explore a novel multilayered coating where different layers contain a sequence of UV additives and different nanomaterials, apprehending further improvement in performance properties. A series of TPU nanocomposite based coating formulations have been synthesized and coated onto high strength polyester (PET) woven fabric targeting inflatable envelope systems and the performance properties have been analyzed in detail.

The weathering of materials has long been recognized as a natural fact and the extent of weathering is truly considered to be dependent upon the exposure conditions. However, the natural or outdoor weathering tests of the material take prolonged time, which is not acceptable in an industrial set up. Besides, natural conditions have too many

uncontrolled and unpredictable variables that make analysis difficult. Thus, in this study, the focus has been on artificial accelerated weathering where the exposure conditions are simulated inside the lab at an accelerated level and are maintained in a controlled manner. However, too much reliance on accelerated testing can be potentially misleading. In the present study, an attempt has also been made to study the degradation behaviour of the coatings under natural weathering condition, using a specially designed and in-house fabricated outdoor weathering rack.

The ultimate aim of a weathering test is to provide a prediction of the performance of the material under the in-service conditions. However, till date, no work has been reported so far for prediction of service life for the inflatable envelope materials. In the present study, a systematic approach of prediction of service life of the ultimate coated material has also been proposed based on mathematical model. A reliability model with two stress types (UV radiation and temperature) has been applied for the estimation of the service life of three different types of TPU coated systems based on the loss of helium gas barrier property. It has been found from the study that, in comparison to the neat TPU coating, nanocomposite based coatings have significant effect in enhancing the service lifetime of the product. Validation of the proposed model has also been made by performing natural weathering of the materials.

सार

'हवा-से-हल्का (एलटीए)' हीलियम इन्फैटेबल वैज्ञानिक और शोध समुदायों में नए सिरे से ध्यान प्राप्त कर रहे हैं। इन उन्नत इन्फैटेबलस, मूल रूप से विशाल गुब्बारा प्रकार की संरचना, अभेद्य लेपित कपड़ा से बना है और आमतौर पर ऊपर रहने के लिए निष्क्रिय वायु हेलियम गैस का उपयोग किया जाता है जो रक्षा और निगरानी के काम आता है। तीव्र मौसम संबंधित तनाव के कारण अवक्रमण, मुख्य रूप से सौर पराबैंगनी (यूवी) विकिरण, इन्फैटेबल लिफाफा संरचना की बाधा प्रदान करी गुण को प्रभावित करता है और इस प्रकार पूरे सिस्टम की कार्यकाल को सीमित करता है जिसके कारण एक भारी नुकसान होता है। इस प्रकार, प्रमुख चिंताओं में से एक है हानिकारक मौसम संबंधी कारकों से लिफाफा तंत्र की बाधा प्रदान करी गुणों में सुधार करना।

एक ठेठ इन्फैटेबल लिफाफा तंत्र में एक मज़बूती परत होती है जो आम तौर पर बने हुए वस्त्रों से बना होती है, उच्च मज़बूती-से-वजन-अनुपात वाले, संरचना को लचीला उच्च मज़बूत आधार और एक सुरक्षात्मक परत प्रदान करने के लिए जो एक गैस बाधा परत के रूप में कार्य करता है संरचना की फुलाया स्थिति बनाए रखने के लिए। विभिन्न प्रकार के पॉलिमर रेजिन में, थर्मोप्लास्टिक पॉलीयुरेथेन (टीपीयू) ने हाल ही में उच्च अंत अनुप्रयोगों के लिए एक सुरक्षात्मक परत या कोटिंग के रूप में बहुत रुचि आकर्षित किया। हालांकि, अन्य पोलिमरिक सामग्रियों के समान, टीपीयू को मौसम के संपर्क में यूवी अवक्रमण के लिए अतिसंवेदनशील माना जाता है।

वर्तमान अध्ययन एक नया उच्च प्रदर्शन टीपीयू नैनोकोमोसाइट कोटिंग्स की जांच करने का प्रयास है जो बेहतर मौसम प्रतिरोध के साथ-साथ कपड़ा आधारित उन्नत इन्फैटेबल के लिए अच्छा अभेद्यता की गुण भी है। अपने रसायन शास्त्र के संबंध में एक बहुत ही बहुमुखी बहुलक होने के नाते, टीपीयू की गुण को काफी भिन्नता के लिए जाना जाता है इस अध्ययन में, दो रासायनिक विभिन्न प्रकार के टीपीयू का मौसम व्यवहार का अध्ययन किया गया है ताकि अवक्रमण प्रवृत्ति को अच्छी तरह से समझ सकें। इस संबंध में, पारंपरिक यूवी सुरक्षात्मक योजक (एडिटिव) के विभिन्न वर्गों के प्रभाव को भी माना जाता है।

इन जैविक यूवी सुरक्षात्मक योजक मुख्यतः भौतिक नुकसान से ग्रस्त हैं। इन सीमाओं को दूर करने के लिए कोटिंग सिस्टम में उन्नत नैनोमिटेरियल्स को शामिल करने के प्रभाव का पता लगाने के लिए अध्ययन को बढ़ा दिया गया है। नैनो पदार्थ लगता है न्यूनतम भौतिक हानि प्रदान करता है, साथ ही, वे अतिरिक्त कार्यात्मक गुण प्रदान कर सकते हैं जैसे कि गैसों के पारगम्यता के प्रतिरोध आदि। इस संबंध में, सबसे सामान्य और संभावित नैनोफिलर्स, नैनोमिट्री और ग्राफीन की बहुलक झिल्ली की अभेद्यता गुण को सुधारने के लिए हैं। उन दोनों में, दो आयामी प्लेटलेट ज्यामिति और उच्च आस्पेक्ट अनुपात होने के कारण पहले से ही बहुलक झिल्ली में व्यापन बाधाओं के रूप में कार्य करने के लिए सूचित किया गया है। वर्तमान अध्ययन में, पारंपरिक यूवी सुरक्षात्मक योजक के साथ-साथ नैनो मिट्री और ग्रेफेन जैसे उन्नत नैनोमीटरों का एक उच्च प्रदर्शन, बहुक्रियात्मक नैनोकोमोसाइट कोटिंग के लिए जांच की गई है। टीपीयू आधारित नैनोकोमोसाइट तैयार करने का एक इष्टतम डिजाइन तीन घटकों के लिए एक मिश्रण डिजाइन के अनुसार खोजा गया है (यूवी स्टेबलाइज़र, नैनो मिट्री और ग्रेफेन)।

इसके अलावा, उपरोक्त विश्लेषण को एक नया बहु-स्तरीय कोटिंग का पता लगाने के लिए अन्वेषण किया गया है जहां विभिन्न परतों में यूवी योजक और विभिन्न नैनोमिटेरियल्स के अनुक्रम होते हैं, जो प्रदर्शन गुणों में और सुधार को प्राप्त करते हैं। टीपीयू नैनोकोमोसाइट पर आधारित कोटिंग सूत्रीकरण की एक श्रृंखला संश्लेषित तथा लेपित किया गया है और उच्च शक्ति पॉलिएस्टर (पीईटी) बुना हुआ कपड़े पर इन्फैटेबल लिफाफा सिस्टम को लक्षित करने और प्रदर्शन गुणों का विवरण विस्तार से किया गया है। सामग्रियों के मौसम को लंबे समय से एक प्राकृतिक तथ्य के रूप में पहचाना गया है और मौसम की माप वास्तव में जोखिम स्थितियों पर निर्भर

होने के लिए माना जाता है हालांकि, सामग्री के प्राकृतिक या आउटडोर मौसम परीक्षण एक लंबे समय तक लेते हैं, जो औद्योगिक सेट अप में स्वीकार्य नहीं है।

इसके अलावा, प्राकृतिक स्थितियों में बहुत अधिक अनियंत्रित और अप्रत्याशित वेरिएबल हैं जो विश्लेषण को मुश्किल बनाते हैं। इस प्रकार, इस अध्ययन में, फोकस कृत्रिम त्वरण वाले मौसम की स्थिति में किया गया है जहां एक्सपोजर की स्थिति एक त्वरित स्तर पर प्रयोगशाला के अंदर सिम्युलेटेड होती है और इसे नियंत्रित तरीके से बनाए रखा जाता है। हालांकि, त्वरित परीक्षण पर अधिक निर्भरता संभावित रूप से भ्रामक हो सकती है। वर्तमान अध्ययन में, विशेष रूप से डिजाइन किए और घर के बाहर निर्मित आउटडोर मौसम रैंक का उपयोग करते हुए, प्राकृतिक अपक्षय स्थिति के तहत कोटिंग्स के अवक्रमण व्यवहार का अध्ययन करने का प्रयास किया गया है।

एक अपक्षय परीक्षण का अंतिम उद्देश्य इन-सेवा शर्तों के तहत सामग्री के प्रदर्शन की भविष्यवाणी प्रदान करना है हालांकि, आज तक, इन्फैटेबल लिफाफा सामग्री के लिए कार्यकाल की भविष्यवाणी के लिए अभी तक कोई काम नहीं किया गया है। वर्तमान अध्ययन में, गणितीय मॉडल के आधार पर अंतिम लेपित सामग्री के कार्यकाल की भविष्यवाणी का एक व्यवस्थित दृष्टिकोण भी प्रस्तावित किया गया है। हीलियम गैस बाधा गुणों के नुकसान के आधार पर तीन प्रकार के टीपीयू लेपित सिस्टम के कार्यकाल के अनुमान के लिए दो तनाव प्रकार (यूवी विकिरण और तापमान) के साथ एक विश्वसनीयता मॉडल लागू किया गया है। यह अध्ययन से पाया गया है कि, स्वच्छ टीपीयू कोटिंग की तुलना में, नैनोकोमोसाइट आधारित कोटिंग्स उत्पाद के कार्यकाल को बढ़ाने में महत्वपूर्ण प्रभाव डालती हैं। प्रस्तावित मॉडल की मान्यता भी सामग्री की प्राकृतिक मौसम प्रदर्शन कर रही है।

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