

**POLYURETHANE NANOCOMPOSITE BASED FILMS AND
LAMINATES WITH ENHANCED GAS BARRIER AND
WEATHER RESISTANCE PROPERTIES**

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WEATHER RESISTANCE PROPERTIES**

by

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Submitted

**in fulfillment of the requirements of the degree of Doctor of Philosophy
to the**



**INDIAN INSTITUTE OF TECHNOLOGY DELHI
OCTOBER 2019**

Dedicated to my parents

CERTIFICATE

This is to certify that the thesis entitled “**Polyurethane nanocomposite based films and laminates with enhanced gas barrier and weather resistance properties**” being submitted by **Mr. Bapan Adak** to the Indian Institute of Technology Delhi for the award of the degree of “**Doctor of Philosophy**” is a record of the authentic research work carried out by him under our guidance and supervision. He has fulfilled all the requirements for the submission of this thesis, which to the best of our knowledge has reached the required standard.

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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(Bapan Adak)

Date:

Abstract

The present research study explores different approaches to improve gas barrier and weather resistance performance of thermoplastic polyurethane (TPU) films by incorporating different nanomaterials such as organoclays, functionalized graphene, UV shielding nanopowder and organic UV additives. The process route, process conditions and concentration of different nanofillers and additives were optimized to get the best properties. Different polyurethane nanocomposite (PUNC) films with optimized compositions were used in various combinations to produce nylon fabric based laminates and their performance was analyzed.

TPU/clay nanocomposite (PUCN) based helium gas barrier films were produced by two different process routes (direct melt-mixing and master-batch mixing) and using two different organoclays (montmorillonite and bentonite based) at a concentration range of 1-5wt% (w.r.t weight of TPU), followed by compression molding of nanocomposite extrudates. Using the novel master-batch mixing route, the nanocomposites were prepared in two steps – (i) preparation of master-batch by solution mixing of organoclay and TPU, (ii) subsequent melt-mixing of master-batch and neat TPU. In comparison to direct melt-mixing route, the master-batch mixing route resulted in a better dispersion of clay-layers in the TPU matrix. As a consequence, superior mechanical and gas barrier properties were obtained by the master-batch based mixing route. The presence of hydroxyl groups in the clay-modifier of montmorillonite clay was attributed to its nearly exfoliated structure up to 3 wt% concentration due to improved interaction of ether groups or urethane linkages of TPU with nanoclay through hydrogen bonding. Whereas, organo-modified bentonite showed partially intercalated and flocculated morphology, due to the absence of any polar group in the clay-modifier. As a consequence, TPU/montmorillonite clay based nanocomposite films showed much better mechanical and gas barrier properties in comparison to TPU/bentonite clay based nanocomposite films. Moreover, a significant reduction in helium gas permeability and improvement in mechanical (tensile and tear) properties were observed for PUCN films produced with both organoclays in comparison to neat TPU. The helium gas permeability reduced by about 40 and 32% in case of TPU/montmorillonite and TPU/bentonite nanocomposite, respectively, prepared by the master-batch mixing route. At a lower volume fraction of organoclays, a good correlation was

obtained between gas permeability values determined experimentally and as predicted by different mathematical models. In the presence of organic additives with optimum concentration (3 wt%) of organoclays, the gas barrier property of PUCN films slightly deteriorated as they show a plasticizing effect. However, after 200 h exposure under accelerated weathering, the organic UV additive based PUCN films showed slightly better gas barrier property due to less photooxidative degradation of TPU.

In another approach, TPU/functionalized-graphene nanocomposite (PGN) films were produced by master-batch based melt mixing, followed by compression molding. The concentration of graphene was varied in the 0-3 wt% range, when a good dispersion and partial exfoliation of graphene-sheets in TPU matrix was obtained. The helium gas barrier property of nanocomposite films improved gradually with increasing graphene concentration, showing about 30% reduction in gas-permeability at 3 wt% graphene loading. The tensile strength and Young's modulus of PGN films improved significantly with increasing concentration of graphene, with marginal reduction in breaking extension. The prepared PGN films were exposed to accelerated artificial weathering conditions for up to 300 h. Due to excellent UV absorption capability of graphene, the weather resistance property of nanocomposite films improved significantly, resulting in lower photooxidative index and carbonyl index as analyzed by FTIR. Best weather resistance in term of retention of tensile and gas barrier properties was obtained with 2-3 wt% graphene content. When an optimized composition of UV additives was used in combination of 2 wt% graphene, slight deterioration in gas barrier was observed compared to the PGN films without organic UV additives. However, after 200 h exposure, the UV additive based PGN films showed better weather resistance in comparison to the PGN film without organic UV additives, resulting in less reduction in tensile properties and lower percentage increase in permeability values.

In another part of this work, the synergistic effect of ZnO nanoparticles with two different crystal phases (anatase and rutile) of TiO₂ nanoparticles on improving weather resistance property of TPU film has also been studied. The UV Shielding nanopowder containing TiO₂ and ZnO nanoparticles was calcinated at varying conditions and the process was optimized to obtain the desired crystal structure. The as-received as well as calcinated UV shielding nanopowders (1-5 wt%) were incorporated in TPU matrix by melt mixing in a twin-screw extruder and the extrudate nanocomposites were used to produce films. The neat TPU and

nanocomposite films were exposed to accelerated artificial weathering for 300 h and analyzed after each 100 h interval. The UV protection factor (UPF) of both types of TPU nanocomposite films increased with increased loading of nanoparticles, although the UPF values were slightly lower for calcinated UV shielding nanopowder based TPU nanocomposite films. The calcinated UV shielding nanopowder showed good potential in improving weather resistance of TPU nanocomposite films in term of - (i) less change in surface morphology and surface chemistry and (ii) better retention in tensile properties after exposure to accelerated artificial weathering. The synergistic effect of ZnO nanoparticle and rutile phase enriched TiO₂ nanoparticles in calcinated UV shielding nanopowder enhanced the weather resistance of TPU films significantly. A suitable combination of organic UV additives (UV absorber, antioxidant and HALS) was also determined by varying their concentration in different combinations and exposing the films under artificial weathering. The optimized composition of organic UV additives showed good potential in improving the weather resistance properties of TPU films. Moreover, the optimized composition of organic UV additives in combination with 3 wt% of calcinated UV shielding nanopowder resulted in 94 and 86% retention in tensile strength and breaking extension, respectively, hence showing much better potential in improving weather resistance of TPU films.

The optimized formulations of PUNC films with best gas barrier and weather resistance properties were used to prepare six sets of nylon fabric based laminates and their performance were analyzed after exposure under accelerated artificial weathering. An optimized TPU based adhesive formulation containing organic UV additives and cross-linker was used to join TPU based films and nylon fabric. With addition of UV additive in additive formulation, the weather resistance property of the TPU based adhesive increased significantly, showing good retention in peel strength even after 300 h exposure. In comparison to control sample, all other laminated sample performed well in terms of helium gas barrier and weather resistance property. Among five-layered laminates, the laminated sample containing nanoclay in barrier layer and a combination of calcinated UV shielding nanopowder with organic UV additive in protective outer layer showed the best property. Among seven-layered laminates, the laminated samples containing nanoclay and graphene in barrier layer, and nanoclay and calcinated UV shielding nanopowder with organic UV additive in protective outer layer showed the best property. After 300 h exposure under artificial weathering, the optimized laminated structures (both the five-

layered and seven-layered laminates) showed more than 95% retention in all properties (tensile, tear, peel strength and gas barrier). Thus, these optimized laminated fabrics with excellent gas barrier and weather resistance properties have a good potential for aerostat envelope applications.

सार

वर्तमान शोध अध्ययन विभिन्न नैनोमटेरियल्स जैसे ऑर्गेनोक्लेज़, फंक्शनलाइज़्ड ग्राफीन, यूवी परिरक्षण नैनोपाउडर और कार्बनिक योज्य एडिटिव्स को शामिल करके थर्मोप्लास्टिक पॉल्यूरेथन (टीपीयू) के गैस अवरोध और मौसम प्रतिरोध प्रदर्शन में सुधार के लिए विभिन्न दृष्टिकोणों की अन्वेषण करता है। नैनोफिलर और एडिटिव्स की प्रक्रिया मार्ग, प्रक्रिया की स्थिति और एकाग्रता को मध्यनज़र रखते हुए पॉल्यूरेथन का सर्वोत्तम गुण की निर्णय की गयी हैं। विभिन्न पॉल्यूरेथन नैनोकम्पोजिट(पीयूएनसी) फिल्मों की अनुकूलित रचनाओं को लेते हुए नायलॉन कपड़ा आधारित लैमिनेटेड कपड़े पर विश्लेषण की गयी हैं।

टीपीयू / क्ले नैनोकम्पोजिट (पीयूएनसी) आधारित हीलियम गैस बैरियर फिल्मों दो अलग-अलग प्रक्रिया मार्गों (प्रत्यक्ष पिघल-मिश्रण और मास्टर-बैच मिश्रण) द्वारा निर्मित की गईं और टीपीयू का वजन आधारित १ से ५ प्रतिशत की एकाग्रता सीमा पर दो अलग-अलग ऑर्गेनोक्लेज़ (मॉटमोरोलाइट और बेंटोनाइट आधारित) का उपयोग किया गया है और तदुपरांत एक्सट्रूडर में डालके नैनो कम्पोजिट एक्सट्रूडेड निर्माण किया गया। एक नया मास्टर-बैच मिश्रण मार्ग का उपयोग करते हुए, नैनोकम्पोजिट्स दो चरणों में तैयार किए गए थे - (अ) ऑर्गेनोक्ले और टीपीयू के समाधान मिश्रण द्वारा मास्टर-बैच की तैयारी, (ब) मास्टर-बैच और नीट टीपीयू के पिघल-मिश्रण द्वारा निर्माण। प्रत्यक्ष पिघल-मिक्सिंग मार्ग की तुलना में, मास्टर-बैच मिक्सिंग मार्ग के परिणामस्वरूप टीपीयू मैट्रिक्स में मिट्टी-परतों का बेहतर फैलाव होता है। परिणामस्वरूप, मास्टर-बैच आधारित मिश्रण मार्ग द्वारा बेहतर यांत्रिक और गैस बाधा गुण प्राप्त किए गए। मॉटमोरिलोनाइट क्ले के क्ले-संशोधक में हाइड्रॉक्सिल समूहों की उपस्थिति में एक लगभग एक्सफोलिएटेड संरचना पाया गया तीन दशमिक शुन्य वजन प्रतिशत एकाग्रता तक हैं और जिसका श्रेय हाइड्रोजन बॉन्डिंग संचालित नैनोकले एवं टीपीयू के यूरेथन सम्पर्कों और ईथर समूहों के बीच बेहतर सम्पर्कों को ठहराया गया। जबकि, मिट्टी-संशोधक में किसी भी ध्रुवीय समूह की अनुपस्थिति के कारण ऑर्गेनो-संशोधित बेंटोनाइट ने आंशिक रूप से अंतःसंबंधित और एग्लोमेरेटेड पार्टिकल विज्ञान दिखाया। परिणामस्वरूप, टीपीयू/मोटोर्मिलोनाइट क्ले आधारित नैनोकॉम्पोसाइट फिल्मों ने टीपीयू/बेंटोनाइट क्ले आधारित नैनोकम्पोजिट फिल्मों की तुलना में बहुत बेहतर मैकेनिकल और गैस बैरियर गुण दिखाए। इसके अलावा, हीलियम गैस पारगम्यता में उल्लेखनीय मैकेनिकल(टेंसाइल एवं टियर) गुणों में सुधार दोनों ऑर्गेनोक्लेज़ के साथ निर्मित पीयूसीएन फिल्मों के लिए देखा गया, जो कि साफ टीपीयू की तुलना में बेहतर हैं। मास्टर-बैच मिक्सिंग मार्ग द्वारा तैयार क्रमशः टीपीयू / मॉटमोरिलोनाइट और टीपीयू /

बेंटोनाइट नैनोकम्पोजिट के मामले में हीलियम गैस की परमियाबिलिटी लगभग ४० और ३२ प्रतिशत कम हो गई है। ऑर्गेनोक्लेज़ के कम वॉल्यूम अंश पर, प्रयोगात्मक रूप से निर्धारित गैस पारगम्यता मूल्यों और विभिन्न गणितीय मॉडल द्वारा भविष्यवाणी के बीच एक अच्छा सहसंबंध प्राप्त किया गया था। ऑर्गेनोक्लेज़ के इष्टतम एकाग्रता (३ वजन प्रतिशत) के साथ कार्बनिक योजक की उपस्थिति में, पीयूएनसी फिल्मों की गैस बाधा गुण थोड़ी खराब हो जाती है क्योंकि वे प्लास्टिसाइजेशन प्रभाव दिखाते हैं। हालांकि, एक्सेलरेटेड वेदरिंग के तहत २०० घंटे अनावरणके बाद, ऑर्गेनिक यूवी एडिटिव आधारित पीयूएन फिल्मों ने टीपीयू के कम फोटोऑक्सीडेटिव गिरावट के कारण गैस अवरोधक संपत्ति को थोड़ा बेहतर दिखाया।

एक अन्य दृष्टिकोण में, टीपीयू/ फंक्शनल-ग्राफीन नैनोकम्पोजिट (पीजीएन) फिल्मों का निर्माण मास्टर-बैच आधारित पिघल मिश्रण द्वारा किया गया था, इसके बाद कम्प्रेसन मोल्डिंग किया गया। ०-३ वजन प्रतिशत श्रेणी में ग्राफीन की सांद्रता भिन्न थी, जब टीपीयू मैट्रिक्स में ग्राफीन-शीट्स का अच्छा फैलाव और आंशिक एक्सफोलिएशन प्राप्त हुई थी। नैनोकम्पोजिट फिल्मों की हीलियम गैस बैरियर गुण में धीरे-धीरे ग्राफीन की सघनता बढ़ने के साथ धीरे-धीरे सुधार हुआ, जिससे गैस-पारगम्यता में ३ वजन प्रतिशत ग्राफीन लोडिंग में लगभग ३० प्रतिशत की कमी देखी गई। पीजीएन फिल्मों की टेंसाइल और यंग मॉडुलास के मापांक ने ग्राफीन की बढ़ती एकाग्रता के साथ, ब्रेकिंग एक्सटेंशन में मामूली कमी के साथ काफी सुधार किया। तैयार पीजीएन फिल्मों को ३०० घंटे तक की कृत्रिम परिस्थितियों के लिए उजागर किया गया था। ग्राफीन की उत्कृष्ट यूवी अवशोषण क्षमता के कारण, नैनोकंपोजिट फिल्मों की मौसम प्रतिरोध गुण में काफी सुधार हुआ, जिसके परिणामस्वरूप एफटीआईआर द्वारा बिश्लेषित कम फोटोऑक्सीडेटिव इंडेक्स और कार्बोनिल सूचकांक देखा गया था। टेंसाइल और गैस अवरोधक गुणों के प्रतिधारण की अवधि में सर्वश्रेष्ठ मौसम प्रतिरोध २-३ वजन प्रतिशत ग्राफीन सामग्री के साथ प्राप्त किया गया था। जब यूवी एडिटिव्स की एक अनुकूलित रचना का उपयोग २ वजन प्रतिशत ग्राफीन के संयोजन में किया गया था, तो कार्बनिक यूवी एडिटिव्स के बिना पी जी एन फिल्मों की तुलना में गैस बाधा में मामूली गिरावट देखी गई थी। हालांकि, २०० घंटे उजागर के बाद, यूवी एडिटिव आधारित पीजीएन फिल्मों ने ऑर्गेनिक यूवी एडिटिव्स के बिना पीजीएन फिल्म की तुलना में बेहतर मौसम प्रतिरोध दिखाया, जिससे टेंसाइल प्रॉपर्टीज में कम कमी और परमीअबिलिटी मूल्यों में कम प्रतिशत वृद्धि हुई।

इस काम के एक अन्य हिस्से में, टीपीयू फिल्म की मौसम प्रतिरोधक प्रॉपर्टी में सुधार पर टाइटेनियम ऑक्साइड नैनोपार्टिकल्स के दो अलग-अलग क्रिस्टल चरणों (एनाटेज और रूटाइल) के साथ जिंक आक्साइड नैनोकणों के सहक्रियात्मक प्रभाव का भी अध्ययन किया गया है। टाइटेनियम ऑक्साइड और जिंक आक्साइड नैनोकणों वाले यूवी परिरक्षण नैनोपार्ट को अलग-अलग स्थितियों में शांत किया गया और वांछित क्रिस्टल संरचना प्राप्त करने के लिए प्रक्रिया को अनुकूलित किया गया। अच्छी तरह से प्राप्त कैल्सिनेटेड यूवी परिरक्षण नैनो पाउडर (१-५ वजन प्रतिशत) को टीपीयू मैट्रिक्स में एक जुड़वाँ पेंच में पिघलाकर मिलाया गया था और फिल्मों का उत्पादन करने के लिए इस्तेमाल किया गया था। साफ-सुथरी टीपीयू और नैनोकोम्पोसाइट फिल्मों को ३०० घंटे के लिए त्वरित कृत्रिम अपक्षय के लिए उजागर किया गया और प्रत्येक १०० घंटे के अंतराल के बाद विश्लेषण किया गया। दोनों प्रकार के टीपीयू नैनोकोम्पोजिट फिल्मों के यूवी प्रोटेक्शन फैक्टर (यूपीएफ) में नैनोपार्टिकल्स की बढ़ती लोडिंग के साथ वृद्धि हुई है, हालांकि यूपीएफ का मान कैल्सिनेटेड यूवी परिरक्षण नैनो पाउडर आधारित टीपीयू नैनोकोम्पोजिट फिल्मों के लिए थोड़ा कम था। कैल्सिनेटेड यूवी परिरक्षण नैनोपाउडर ने टीपीयू नैनोकोम्पोसिट फिल्मों के मौसम प्रतिरोध में सुधार करने में अच्छी क्षमता दिखाई – (अ) सतह आकारिकी और सतह रसायन विज्ञान में कम परिवर्तन और (ब) त्वरित कृत्रिम अपक्षय के संपर्क में आने के बाद तन्य गुणों में बेहतर प्रतिधारण। जिंक आक्साइड नैनोपार्टिकल और रूटाइल चरण के सहक्रियात्मक प्रभाव ने कैल्सिनेटेड यूवी परिरक्षण नैनोपार्टिकल्स में टाइटेनियम ऑक्साइड नैनोकणों को समृद्ध किया, जिससे टीपीयू फिल्मों के मौसम प्रतिरोध में काफी वृद्धि हुई। कार्बनिक यूवी एडिटिव्स (यूवी अवशोषक, एंटीऑक्सिडेंट और एचएएलएस) का एक उपयुक्त संयोजन भी विभिन्न संयोजनों में उनकी एकाग्रता को अलग करके और आर्टिफीसियल वैथेरिंग के तहत फिल्मों को उजागर करने के द्वारा निर्धारित किया गया। कार्बनिक यूवी एडिटिव्स की अनुकूलित रचना ने टीपीयू फिल्मों के मौसम प्रतिरोध गुणों को बेहतर बनाने में अच्छी क्षमता दिखाई। इसके अलावा, कैल्सिनेटेड यूवी शील्डिंग नैनोपेडर के ३ वजन प्रतिशत के साथ कार्बनिक यूवी एडिटिव्स की अनुकूलित रचना क्रमशः तन्य शक्ति और ब्रेकिंग एक्सटेंशन में ९४ और ८६ प्रतिशत प्रतिधारण के परिणामस्वरूप, इसलिए टीपीयू फिल्मों के मौसम प्रतिरोध में सुधार करने में बहुत बेहतर क्षमता दिखाती है।

सबसे अच्छा गैस बाधा और मौसम प्रतिरोध गुणों के साथ पीयूएनसी फिल्मों के अनुकूलित योगों का उपयोग नायलॉन कपड़े आधारित लैमिनेट के छह सेट तैयार करने के लिए किया गया और अक्सेलरतातेड आर्टिफीसियल वैथेरिंग के तहत प्रदर्शन के बाद उनके प्रदर्शन का विश्लेषण किया गया

। टीपीयू आधारित फिल्मों और नायलॉन कपड़े में शामिल होने के लिए कार्बनिक यूवी एडिटिक्स और क्रॉस-लिंकर युक्त एक अनुकूलित टीपीयू आधारित चिपकने वाला सूत्रीकरण का उपयोग किया गया था। एडिटिक्स सूत्रीकरण में यूवी एडिटिव के साथ, टीपीयू आधारित गोंद की मौसम प्रतिरोध गुण में काफी इजाफा हुआ, जिससे ३०० घंटे एक्सपोजर के बाद भी पील स्ट्रेंथ में अच्छी बढ़त दिखाई दे रही है। नमूने को नियंत्रित करने की तुलना में, अन्य सभी लेमिनेट्स नमूने ने हीलियम गैस बाधा और मौसम प्रतिरोध संपत्ति के मामले में अच्छा प्रदर्शन किया। पांच- परत वाले लैमिनेट्स के बीच, बाधा परत में नैनो क्ले युक्त लैमिनेट्स नमूने और सुरक्षात्मक बाहरी परत में कार्बनिक यूवी एडिटिव के साथ कैल्सिनेटेड यूवी परिरक्षण नैनोपाउडर के संयोजन ने सबसे अच्छी प्रॉपर्टी दिखाई। सात- परत लैमिनेट्स के बीच, बाधा परत में नैनो क्ले और ग्राफीन युक्त लैमिनेटेड नमूने, और सुरक्षात्मक बाहरी परत में कार्बनिक यूवी एडिटिव के साथ नैनो क्ले और कैल्सिनेटेड यूवी परिरक्षण नैनो पाउडर सबसे अच्छी प्रदर्शन दिखाया। कृत्रिम अपक्षय के तहत ३०० घंटे के जोखिम के बाद, अनुकूलित लैमिनेट्स में संरचनाएं (पांच-स्तरित और सात-स्तरित लैमिनेट दोनों) ने सभी गुणों (टेंसाइल, टीयर, पील स्ट्रेंथ और गैस अवरोध) में ९५ प्रतिशत से अधिक प्रतिधारण दिखाया। इस प्रकार, उत्कृष्ट गैस बैरियर और मौसम प्रतिरोध गुणों के साथ ये अनुकूलित लैमिनेट्स में कपड़े एयरोस्टेट आवरण अनुप्रयोगों के लिए एक अच्छी संभावना है।

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List of Symbols

c	Permeant concentration
Δc	Concentration difference across the film or membrane
D	Diffusion constant
D_0	Diffusivity of the pure polymer matrix
J	Permeant (gas or vapor) flux
l	Film or membrane thickness
l'	The distance that gas has to travel across the polymer nanocomposite
L	Length of the nanoplatelets (dispersed in a polymer matrix)
N	Number of nanoplatelets
p	Permeant pressure
Δp	Pressure difference across the film or membrane
P	Permeability
Q	Permeance
S	Solubility or sorption coefficient
S_0	Solubility of gas in pure polymer matrix
T_g	Glass Transition Temperature
w	Width of the nanoplatelets (dispersed in a polymer matrix)
φ	Volume fraction of fillers
τ	Tortuosity
α	Aspect ratio of the nanoplatelets
μ	A geometric factor
θ	Angle between the direction of preferred orientation and the sheet normal unit vector
$\%X_c$	Crystallinity percentage

List of Abbreviations

AFM	Atomic Force Microscopy
Al ₂ O ₃	Aluminum oxide
ATR	Attenuated total reflection
BoPET	Biaxially oriented polyester
CA	Claytone APA
C30B	Closite 30B
C ₁₆ -MMT	Hexadecylamine montmorillonite
CeO ₂	Cerium oxide
CI	Carbonyl Index
CNT	Carbon nanotube
CRG	Chemically reduced graphene
CTAB	Cetyltrimethylammonium bromide
DTA-MMT	Dodecyltrimethylammonium montmorillonite
DLS	Dynamic light scattering
DMF	Dimethyl formamide
DSC	Differential scanning calorimeter
EDX	Energy dispersive X-ray
EVOH	Ethylene vinyl alcohol copolymer
FEP	Fluorinated ethylene-propylene copolymer
f-Graphene	Functionalized graphene
FTIR	Fourier transmission infrared spectroscopy
GO	Graphene oxide
GTR	Gas transmission rate
h-BN	Hexagonal boron nitride
HALS	Hindered amine light stabilizer
HDI	Hexamethylene diisocyanate
HD-GNRs	Hexadecyl-functionalized low-defect graphene nanoribbons
H12MDI	4,4'-diisocyanate dicyclohexylmethane

IDT	Initial degradation temperature
IFR-PU	Intumescent flame retardant polyurethane
iGO	Isocyanate treated graphene oxide
LDPE	Low density polyethylene
LTA	Lighter than air
MDI	4,4'-diphenylmethane diisocyanate
MMT	Montmorillonite
MMT-Fe	Na ⁺ Montmorillonite modified by iron (III)
MMT-Cu	Na ⁺ Montmorillonite modified by copper (II)
NF	Nylon 6,6 fabric
NMP	N-Methyl-2-Pyrrolidone
NP	Neat polymer
OBMAC	Octadecyl bis (hydroxyethyl)methylammonium chloride
OMMT	Organically modified montmorillonite
PDMS	Poly(dimethylsiloxane)
PGN	Polyurethane/graphene nanocomposite
PI	Photooxidative index
POSS	Polyhedral oligomeric silsesquioxane
PPG	Polypropylene glycol
PTFE	Polytetrafluoroethylene
PU	Polyurethane
PUCN	Polyurethane/clay nanocomposite
PUNC	Polyurethane nanocomposite
PUU	Polyurethane urea
PVDC	Polyvinylidene chloride
PVDF	Polyvinylidene fluoride
PVF	Polyvinyl fluoride
rGO	Reduced graphene oxide
SAED	Selected area electron diffraction
SDD	Silicon drift detector
SEM	Scanning electron microscope

SiO ₂	Silicon dioxide
TDI	Toluene diisocyanate
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TiO ₂	Titanium dioxide
TPU	Thermoplastic polyurethane
TRG	Thermally reduced graphene
TZA	As received UV shielding nanopowder
TZC	Calcinated UV shielding nanopowder
UV	Ultraviolet
UPF	Ultraviolet protection factor
VMT	Vermiculite
WVP	Water vapor permeability
XRD	X-ray diffraction
ZnO	Zinc oxide