

# Thermoplastic polyurethane coating for defense inflatables: Influence of polyurethane chemistry and UV additives on weathering performances

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This paper aims to investigate the weathering degradation of thermoplastic polyurethane (TPU) coatings particularly targeting the protective layer of inflatable systems used for defense applications. The study provides a comprehensive evaluation of the degradation characteristics of two thermoplastic polyurethanes (TPUs) with distinct chemical backbones, aliphatic ether-based and aromatic ester-based, when exposed to accelerated artificial weathering. Additionally, the influence of commercially available UV-stabilizing additives on the degradation extent was systematically investigated. It has been found from the study, both qualitatively and quantitatively, that the amount of degradation is much lower in case of aliphatic ether based TPU than the aromatic ester one. Incorporation of only 1wt% UV protective additive shows a further delay indegradation. The extent of the changes in the weathering degradation has been found to correlate well with the variations in the ultimate performance properties of the coatings.

**Keywords:** Accelerated weathering, Degradation, Defense inflatables, TPU coatings, UV protective additives

## 1 Introduction

Coated inflatable structures used in lighter-than-air (LTA) systems have garnered significant attention for aerial monitoring applications. Owing to their promising utility in advanced technological fields, numerous research organizations worldwide are actively engaged in developing and engineering unmanned aerial platforms such as free-floating balloons, aerostats, and high-altitude airships.<sup>1-6</sup> These technologically advanced inflatable systems are typically constructed from coated textile materials shaped to resemble aircraft. Helium gas is commonly employed to keep them airborne, often for extended periods in harsh environmental conditions. The envelope of such inflatables generally comprises two main components: a strength-bearing layer, usually a woven textile providing mechanical flexibility and robustness, and a protective coating that serves as a gas barrier to sustain inflation. Prolonged exposure to environmental stresses, particularly ultraviolet radiation and temperature variation, leads to the deterioration of the barrier layer, compromising the functionality and reducing the operational lifespan of the structure. Consequently, the durability of the

inflatable largely depends on the shielding effectiveness of the polymer coating.

Designing a better weather resistant inflatable coated structure requires knowledge of the conventional materials and also their degradation trends. Unfortunately, very few works on this have been documented till date.<sup>3,7-8</sup> PUs are well known resins to be used as a protective coating owing to their ease of process-ability, good mechanical properties and chemical resistance. But like any other organic polymer, the properties of PU also deteriorate in harsh atmospheric weather due to prolonged exposure to factors such as UV radiation, temperature, humidity, rain etc. Since PU is a very versatile polymer in respect to its chemistry, use of suitable chemical composition (grade) is also an important criterion in selecting the suitable protective layer. Based on the type of hard segment (diisocyanate) and soft segment (diol) of a PU, the property may vary significantly.<sup>9-11</sup> One of the key limitations observed in existing literature on polyurethane (PU) weathering degradation lies in the variability of PU chemistries investigated across studies.<sup>12-16</sup> Additionally, notable inconsistencies exist in the form and characteristics of samples used—ranging from films to coated metal panels and fabrics, each differing in thickness and processing methods. The experimental conditions for weathering, such as

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UV exposure levels and ambient temperature, also vary significantly. As a result, previous research has not enabled a comprehensive understanding of PU degradation behavior or its long-term performance. In light of this, a focused and systematic investigation of a specific PU formulation, especially one relevant for inflatable structural applications, would be of significant value.

This study presents a detailed investigation into the degradation behavior of two thermoplastic polyurethanes (TPUs) with distinct chemistries, one based on aliphatic ether and the other on aromatic ester. The focus is on their application in coated fabrics designed to offer superior weather durability and effective gas barrier performance for use in inflatable systems. As in case of ultimate coated fabric, coating material is bonded and impregnated into the fabric such that a composite structure is created and it is very difficult to find out degradation of the coating only on weathering exposure of composite. Keeping this in mind, uniform thin (100  $\mu\text{m}$ ) films out of two different grades of TPU (aliphatic ether and aromatic ester) have been prepared via solution cast method and thereafter, their degradation behavior has been studied against artificial accelerated weathering. To enhance the resistance of polymers against weather-induced degradation, a range of commercial UV stabilizers are commonly employed. In this work, the influence of selected commercially available UV protective additives on the weathering performance of the selected TPUs has been thoroughly examined. Finally, to study the ultimate performance properties, a series of TPU coated high strength polyester (PET) fabric samples have been prepared in a continuous solution coating machine. Single side coating (solid content 100  $\text{g}/\text{m}^2$  of fabric, average thickness 100  $\mu\text{m}$ ) have been done on the fabric using some selected TPU formulations, and the ultimate performances of the coated fabrics have been evaluated against artificial accelerated weathering.

## 2 Materials and Methods

### 2.1 Materials

Two grades of TPU pellets, based on aromatic diisocyanates polyester polyol (Desmopan KU 2-8080, specific gravity 1.19) and aliphatic diisocyanate polyether polyol (Texin SUN-3006, specific gravity 1.01), have been procured from Bayer Material Science, USA. The solvent, laboratory

grade Dimethyl formamide (DMF) was supplied by Merck, India. Three types of UV protective additives; UV absorber (UVA), hindered amine light stabilizer (HALS) and a synergistic liquid mixture of UVA, HALS and anti-oxidant (AO); have been purchased from BASF, India. Details of the same are given in Table 1. Plain woven PET fabric (500 denier, 180  $\text{g}/\text{m}^2$ ) supplied by Kusumgar Corporate, India has been used as the coating substrate. The fabric used in the study had an average thickness of approximately 0.35 mm.

### 2.2 Preparation of TPU Solution

Initially, TPU pellets were vacuum-dried at 85  $^{\circ}\text{C}$  for 3 h to eliminate residual moisture. Following this, they were immersed in DMF solvent and left to swell overnight. The swollen mixture was subsequently heated slowly to 50  $^{\circ}\text{C}$  in a water bath for 3 h and then subjected to magnetic stirring for an additional 3 h, resulting in a clear 10 wt% TPU solution. Separately, additives (1 wt%) were dissolved in DMF first and then added to the final TPU solution to prepare the formulations. A total 10 different formulations were made with two neat TPUs, TPUs with 1 wt% UVA (Tinuvin 326), TPUs with 1 wt% HALS (Tinuvin 770), TPUs with 1 wt% UVA and HALS (in 1:1 ratio) and TPUs with 1 wt% synergistic liquid mixture of UVA, HALS and AO (Tinuvin B 75). The preparation of solutions for both aliphatic and aromatic TPUs follows the same procedure.

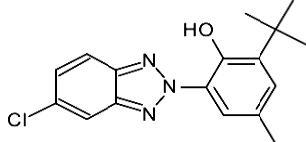
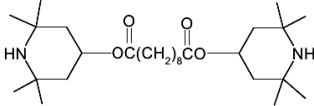
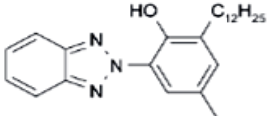
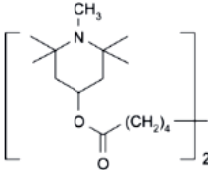
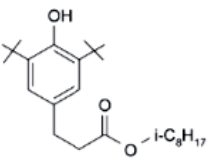
### 2.3 Preparation of Solution Cast Film

Around 100  $\mu\text{m}$  thin films are produced out of the TPU formulations by solution cast method. Uniform films have been casted on a smooth horizontal glass tray following ASTM D823-95 Practice E and then dried in the air oven at 40  $^{\circ}\text{C}$  for 2 h followed by in vacuum oven at 80  $^{\circ}\text{C}$  for 4 h to evaporate the solvent fully.

### 2.4 Preparation of Solution Coated Fabric

TPU solutions were applied onto a polyester (PET) base fabric using a continuous coating unit (Mathis, Switzerland; Model: KTF-S) equipped with a knife-over-roll mechanism. During the process, solvent removal was carried out in the machine's drying chamber by circulating hot air at 140  $^{\circ}\text{C}$  and a fan speed of 2000 rpm. The coating was performed in multiple passes, with each pass contributing approximately 10  $\text{g}/\text{m}^2$  of solid content post drying. The total solid deposition on one side of the fabric

Table 1 — Details of additives

Type	Commercial Name	Basic Chemistry
UV Absorber (UVA)	Tinuvin 326	 Phenol, 2-(5-chloro-2H-benzotriazole-2-yl)-6-(1,1-dimethylethyl)-4-methyl-
Hindered Amine Light Stabiliser (HALS)	Tinuvin 770	 Bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate
Liquid Mixture (40% UVA+ 40% HALS+ 20% Anti Oxidant)	Tinuvin B 75	 Phenol, 2-(2H-benzotriazol-2-yl)-6-dodecyl-4-methyl-, branched and linear
		 Bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate
		 Benzenepropanoic acid, 3,5-bis(1,1-dimethyl-ethyl)-4-hydroxy-C7-C9 branched alkyl esters

was controlled to reach around 100 g/m<sup>2</sup>. A slow web speed of 0.3 mt/min was maintained throughout to ensure efficient and complete solvent evaporation.

### 2.5 Artificial Accelerated Weathering

All samples, including films and coated fabrics, were artificially weathered up to 300 h in Xenotest Weatherometer (Model: Xenotest Beta+, ATLAS). ISO 4892 method was used to simulate weathering. The details of the test program have been given in Table 2. The samples were taken out after each 100 h of exposure for evaluating the degradation. A sample of PET base fabric i.e., the substrate material was also been exposed simultaneously as a reference material. Three replicates of each sample were made.

### 2.6 Characterizations

Gel permeation chromatography (GPC) was performed (Perkin Elmer, Model: Turbo matrix-40) to

determine the molecular weight of both the TPUs. Viscosity of TPU-DMF solutions was determined using Brookfield Viscometer following ASTM D 2393.

The change in the surface morphological characteristics of the polymer films with weathering were analyzed by using optical microscopy (Nikon, Model: SMZ-1500) and scanning electron microscopy (Zeiss, Model: EVO50) techniques. As a measure of degradation, yellowness index of the irradiated films was determined using Gretag Macbeth Color Eye spectrophotometer following ASTM E-313 method. High-resolution solid-state <sup>13</sup>C NMR spectra of the TPU films were obtained using a multinuclear FT-NMR spectrometer (Jeol ECX400 model). FT-IR analysis was carried out using a Perkin Elmer Spectrum BX spectrometer (USA) in attenuated total reflectance (ATR) mode,

scanning from 400 to 4000  $\text{cm}^{-1}$  at an interval of 4  $\text{cm}^{-1}$ . To assess the influence of weathering on mechanical performance, uniaxial tensile testing was performed in accordance with ASTM D2370-98 using an Instron 3365 Universal Testing Machine, with the crosshead moving at a constant speed of 50 mm/min. The tensile strength of coated fabrics was further measured using a Tinius Olsen H5KS system (USA), operated via QMat 5.14 S series software, following the ISO 7016 standard. Helium gas permeability through the coated samples was evaluated with a gas permeability tester<sup>17</sup>, adhering to ASTM D1434-82. The test was performed at 25 °C under an initial pressure of a 20 cm water column, and the gas transmission rate was determined based on manometer displacement recorded over a 24-hour period.

### 3 Results and Discussion

#### 3.1 Characterization of Neat TPUs

Molecular weight of the TPUs has been determined from GPC. The weight average molecular weight

Table 2 — Details of artificial accelerated weathering test program (ISO 4892)

Parameters	Specifications
Type of lamp	Xenon arc
Type of filters	Inner filter glass – Type ‘S’ Borosilicate/ CIRA
	Outer filter glass – Type ‘S’ Borosilicate
Total irradiance	60 $\text{watt/m}^2$ (300-400nm)
Dry cycle	Exposure for 1 hour 42 minutes in simulated radiation
Wet cycle	Exposure for 18 minutes in simulated radiation with water spray
Relative humidity	50 ± 5% (for dry cycle)

( $M_w$ ) of the aliphatic ether based TPU was found as 2,11,313 which is almost three times higher than that of aromatic ester based TPU ( $M_w = 45,790$ ).

The viscosity TPU-DMF solution was measured at two different spindle rpms in Brookfield Viscometer. The temperature was kept constant (about 25 °C) throughout the experiment.

It can be seen from Table 3 that at 10 wt %, aromatic ester based TPU showed a very low viscosity in comparison with 10 wt% aliphatic ether based TPU. As polymer solutions having viscosity around 2000-2500 cPs are desirable for making solution cast film or for solution coating process, the wt % of aromatic ester TPU was increased to match the viscosity of 10 wt % of aliphatic ether based TPU. It can be seen from the results that 30 wt % aromatic ester based TPU solution can achieve viscosity similar to that of 10 wt% aliphatic ether based TPU solution. For all the cases, with increase in spindle rpm, the viscosity decreased. Higher spindle rpm results in higher shear rates and decrease in viscosity at higher shear rates shows shear thinning behavior of the fluid which is considered to be good for coating solution. As shearing force increases, the component chains start to align themselves along the axis and parallel to flow direction, resulting in shear thinning.

Figure 1 displays the FT-IR spectra of both unmodified TPU films. In the spectral region between

Table 3 — Viscosity Evaluation of TPU Dissolved in DMF

Spindle Speed (rpm)	Viscosity (cPs) at 25 °C of TPU solution in DMF		
	Aliphatic ether (10 wt %)	Aromatic ester (10 wt %)	Aromatic ester (30 wt %)
10	2570	80	2300
20	2550	75	2260

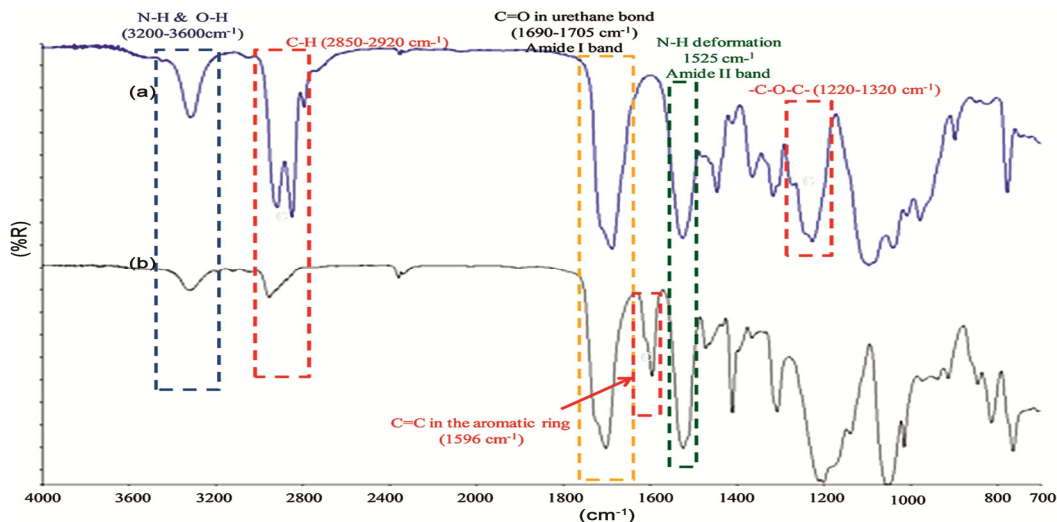


Fig. 1 — FT-IR spectra of TPU films: (a) Aliphatic ether-based, and (b) Aromatic ester-based

3200-3600  $\text{cm}^{-1}$ , characteristic absorption bands for N-H and O-H stretching vibrations are observed, indicating the urethane linkage. This is further supported by the C=O stretching band (amide I) appearing around 1690-1705  $\text{cm}^{-1}$ . A peak at approximately 1525  $\text{cm}^{-1}$  corresponds to N-H bending vibrations, commonly referred to as the amide II band. The C-O stretching associated with the urethane group is evident in the 1220-1320  $\text{cm}^{-1}$  range. A broad reflection band between 2850 and 2920  $\text{cm}^{-1}$  corresponds to C-H stretching vibrations, which are more intense in the aliphatic TPU. In contrast, a peak near 1597  $\text{cm}^{-1}$  found in the aromatic TPU spectrum is attributed to the C=C skeletal vibration of the aromatic ring.

Figure 2 shows the tensile behaviour of the neat TPU films. It can be clearly concluded from the stress-strain curves that the aliphatic ether TPU has superior tensile properties than the aromatic ester one. Aromatic ester TPU shows lower breaking strength as well as lower elongation at break than the aliphatic ether TPU. Initial modulus is significantly higher in case of aromatic ester TPU which indicates higher stiffness than the aliphatic ether based TPU.

### 3.2 Weathering of Films

#### 3.2.1 Surface Morphology

Figure 3 (a-c) presents the surface morphological features of both TPU films prior to and following

xenon arc exposure. It was observed visually that the neat film prepared from aromatic ester grade TPU, turned yellowish and stiffer after only 100 h of xenon arc exposure whereas no such change was observed in case of aliphatic ether based TPU film even after 300 h (Fig.3(a)). When the films were observed under optical microscope (Fig.3(b)), severe cracks were found in the exposed samples of aromatic ester TPU. Figure 3(c) displays SEM images of the TPU film surfaces captured before and after 300 hours of xenon

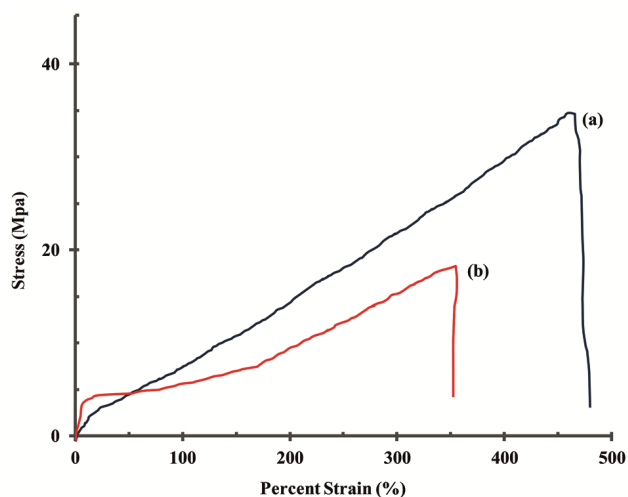


Fig. 2 — Tensile response of TPU films: (a) Aliphatic ether-based and (b) Aromatic ester-based

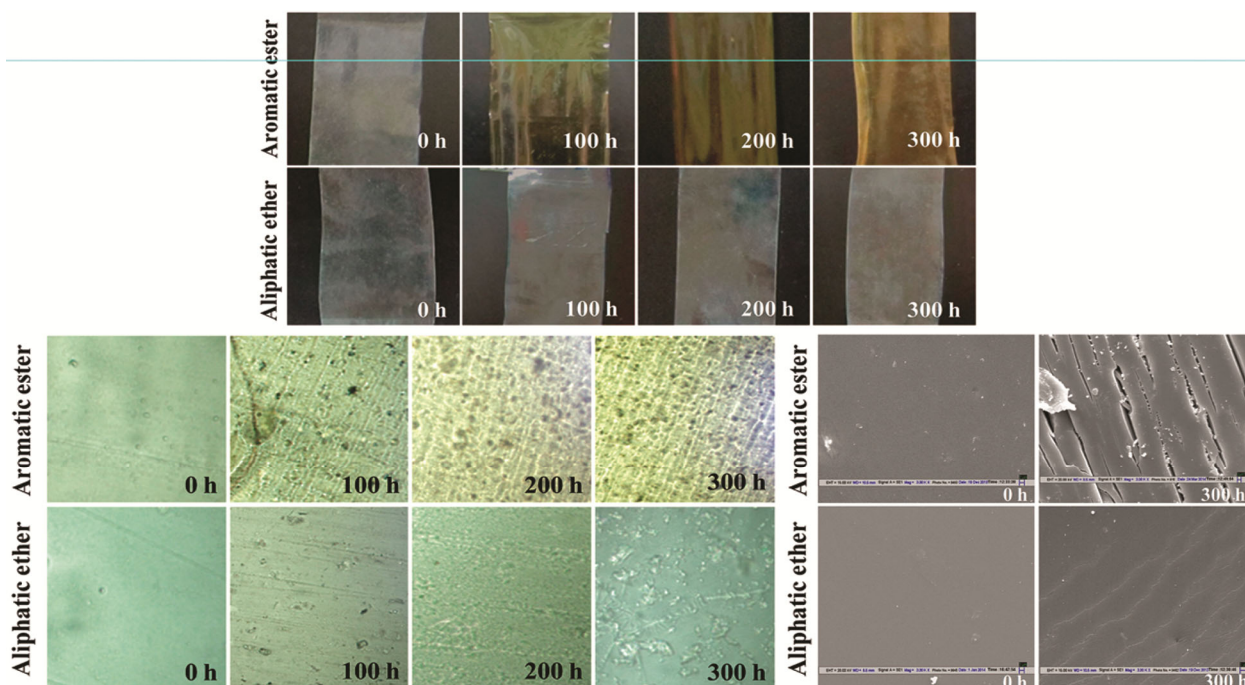


Fig. 3 — Surface morphological changes in tpu films due to weathering (a) Visual image, (b) Under optical microscope (200 X), and (c) Under scanning electron microscope (3000 X)

arc exposure. Under SEM, cracks can be seen very clearly for aromatic ester TPU; however, aliphatic ether TPU also seems to have some surface defects.

### 3.2.2 Yellowness Index

As a measure of degradation, yellowness index (YI) of the films has been measured. The average yellowness index value of the aromatic ester TPU increased up to 46.1 at 300 h, however, aliphatic ether based TPU showed a value as low as 0.28 after 300 h which can be considered as negligible. Figure 4 illustrates the variation in YI of the aromatic ester-based TPU with respect to irradiation duration. The photodegradation of aromatic polyurethane systems is generally attributed to a quinonoid degradation pathway. The urethane bridge oxidizes to the quinone-imide structure, which being a chromophore, results in the yellowing of the TPU. As can be seen from the graph, mixture of UVA, HALS as well as the mixture of UVA, HALS and AO significantly inhibited the development of yellowing even after 300 h of irradiation. For both the cases, the YI value reached around 23 after 300 h of exposure. However UVA or HALS alone are unable to produce satisfactory result.

The synergism comes from the effective diffusion of HALS (quenches free radicals) from the polymer bulk, which is protected by the UVA (absorbs UV radiation), towards the surface layer where photo-oxidation proceeds.

### 3.2.3 NMR Spectra

The NMR spectra of the neat films and the irradiated films at 300 h were recorded to analyze the degradation behaviour. Figure 5 illustrate the

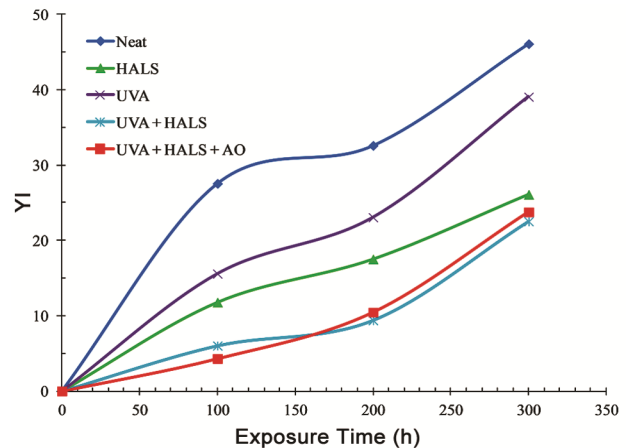


Fig. 4 — Variation in yellowness index of aromatic polyester tpu with irradiation duration

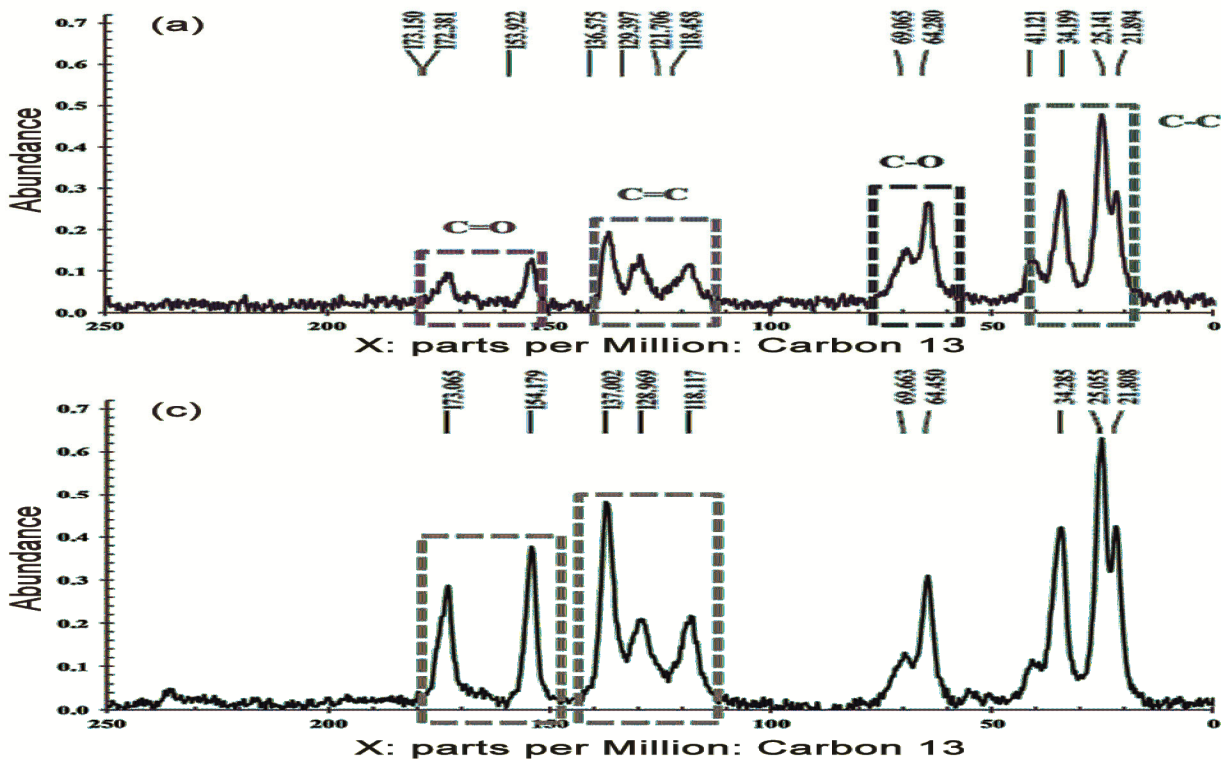


Fig.5 —  $^{13}\text{C}$  NMR spectra profile of aromatic ester based TPU (a & b) and aliphatic ether TPU (c & d)

comparative NMR spectra of both the TPUs, aromatic ester and aliphatic ether, before and after 300 h of weathering.

In case of the unexposed aromatic ester TPU (Fig. 5 (a)), peaks can be seen for C-C which can be attributed to  $\text{CH}_3\text{CO-}$ ,  $\text{R}_2\text{CH}_2$  or  $\text{RCH}_2\text{NH}_2$  structures. C-O peak has also been found which corresponds to  $\text{RCH}_2\text{O-}$  structure. Peak for C=C indicates the presence of aromatic structures and peak for C=O refers to the presence of ester group of the TPU structure.

After 300 h of weathering (Fig.5 (b)), the intensity of C=C peaks was found to increase significantly which may be attributed to the chain scission and increase in number of end groups. Significant increase in the peak C=O can also be seen due to the formation of new C=O group indicating degradation of the TPU structure

In case of aliphatic ether based TPU, peaks were found for C-C, C-O and C=O as well (Fig. 5(c)) and the intensity of the peaks seems to decrease a bit after 300 h of weathering (Fig.5(d)). The changes may refer to the degradation of the TPU to some extent and formation of small chains which may have been lost physically with weathering. Except this, no change has been noticed in the NMR spectra for aliphatic ether based TPU.

### 3.2.4 FT-IR Spectra

FT-IR spectra of both the TPUs with and without weathering have been analyzed in detail. The changes in the FT-IR spectra of the irradiated aromatic ester films as a function of exposure time are illustrated in Fig.6 (a).

The broadening of NH-OH peak at  $3200\text{-}3600\text{ cm}^{-1}$  can be attributed to hydroperoxidation. The change in the intensity of the peak at  $1525\text{ cm}^{-1}$  that corresponds to N-H deformation (amide II band) can be related to scission of urethane group. The progressive broadening of carbonyl peak at  $1690\text{-}1705\text{ cm}^{-1}$  can be related to formation of new C=O group due to quinone-imide formation which imparts yellow colour to the films. However, much improvement is seen in the aromatic ester TPU when the synergistic mixture of UVA, HALS and AO is incorporated.

An acceptable agreement between the change in YI and the FT-IR data was found for the irradiated aromatic polyester TPU samples. As has been discussed in section 3.4.2.2., in aromatic based TPU, the urethane bridge is photo-oxidized to form

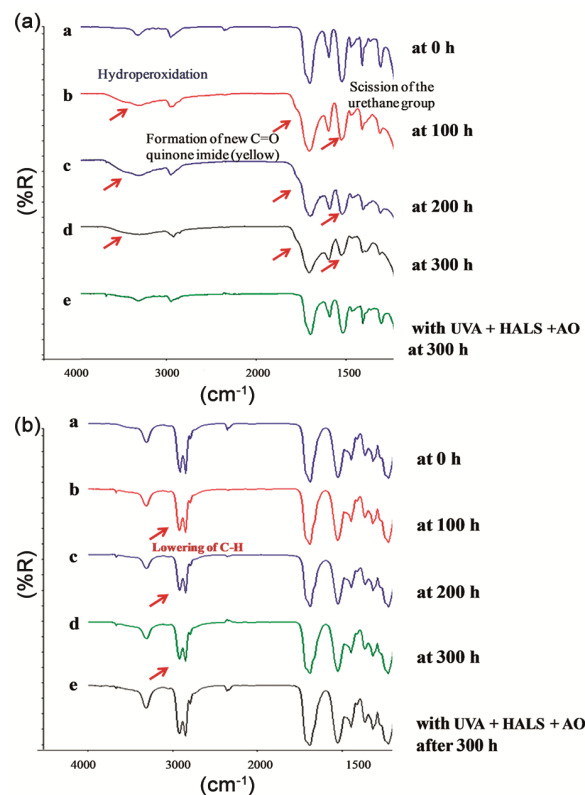


Fig. 6 — FTIR spectra of aromatic ester TPU (a) Aliphatic ether TPU, and (b) Against weathering

monoquinone-imide, a strong yellow coloured chromophore, which gets further oxidized to form diquinone-imide, producing brown colour.

Unlike aromatic ester, hardly any significant change has been ascertained for aliphatic ether based TPU upon weathering (Fig. 6 (b)). Lowering in the intensity of peaks attributed to C-H group between  $2850\text{ and }2920\text{ cm}^{-1}$  is observed which seems to be retarded when a mixture of UVA, HALS and AO is used.

### 3.2.5 Tensile Behavior

The tensile behavior of the neat TPU films upon weathering is illustrated in Fig. 7. As can be seen for aliphatic ether TPU (Fig. 7(a)), elongation decreased considerably with a slight change in the modulus. However, for aromatic ester based TPU (Fig. 7(b)), change in the modulus has been found to be significantly higher after 300 h exposure, following a steep break. To elaborate this further, in Fig. 7(a), due to the UV radiation exposure, the cross-linking in the polymer system may occur which may actuate the formation of additional chemical bonds between polymer chains. These bonds may act as reinforcing

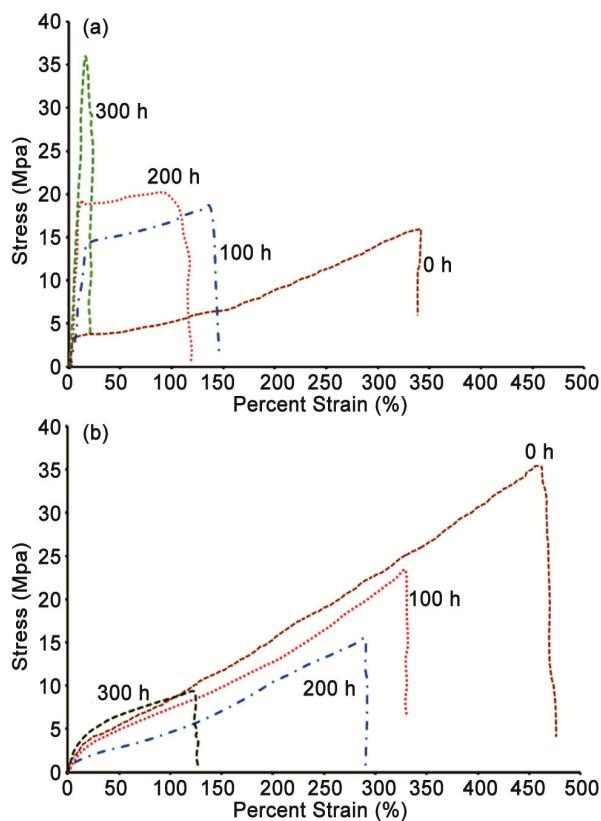


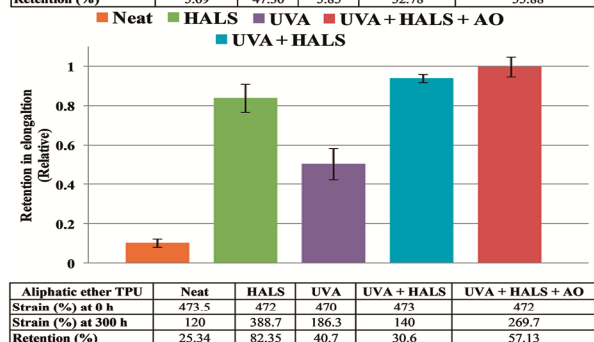
Fig. 7 — Tensile behaviour of aromatic ester TPU films (a) Aliphatic ether TPU films, and (b) With weathering time (without additives)

links, limiting the material's ability to deform and significantly enhancing its stiffness.<sup>12,14</sup> On the other hand, in Figure 7 b, chain scission involves the cleavage of existing bonds within the polymer chains, resulting in a decrease in both elongation and strength.<sup>12-16</sup>

To analyze the influence of the additives on the tensile behaviour of the TPU films upon weathering, the relative retention in elongation of the TPU films after 300 h of exposure has been plotted in Fig. 8 (a-b).

For aromatic ester based TPU (Fig. 8 (a)), the neat one shows the minimum retention value of 5.69% only, whereas, the value is 55.88% when incorporated with the mixture of UVA, HALS and AO. However, for aliphatic ether TPU, 25.34% retention is found for the neat film and 82.35% retention when incorporated with the mixture of UVA, HALS and AO. When compared with the aliphatic ether TPU (Fig. 8(b)), it is clear that no additive has performed to the satisfactory level to retain the elongation for the aromatic ester one (Fig. 8(a)).

Aromatic ester TPU	Neat	HALS	UVA	UVA + HALS	UVA + HALS + AO
Strain (%) at 0 h	341.7	341	340.5	341	340
Strain (%) at 300 h	18.76	161.5	19.9	180	190
Retention (%)	5.69	47.36	5.85	52.78	55.88



Aliphatic ether TPU	Neat	HALS	UVA	UVA + HALS	UVA + HALS + AO
Strain (%) at 0 h	473.5	472	470	473	472
Strain (%) at 300 h	120	388.7	186.3	140	269.7
Retention (%)	25.34	82.35	40.7	30.6	57.13

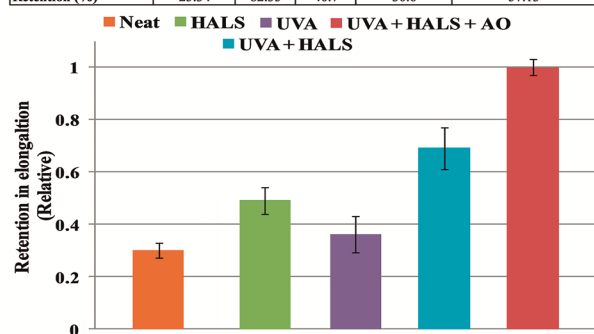


Fig. 8 — Effect of UV additives on elongation retention of TPU films after 300 h weathering: (a) aromatic ester based TPU films post 300 hours of weathering exposure, and (b) aliphatic ether based TPU films after 300 h of weathering exposure

### 3.3 Weathering Response of Coated Fabrics

#### 3.3.1 Tensile Behaviour

The base fabric exhibited an average breaking strength of 1323 N. Upon coating with aliphatic ether-based TPU, a strength reduction of approximately 19.1% was recorded, whereas the loss increased to around 33.2% for the aromatic ester-coated variant. This decrease could be attributed to diminished thread cohesion caused by the coating layer. Notably, the uncoated PET fabric showed a significant drop in tensile strength after weathering exposure. As depicted in Fig. 9, the breaking strength of both coated and uncoated fabrics declined with increased weathering duration. The uncoated fabric alone experienced a substantial reduction of about 48.9% in strength after 300 h of exposure.

Figure 10 presents the strength reduction observed in the weathered fabrics coated with aliphatic ether and aromatic ester based TPU, with and without stabilization with incorporation of UVA, HALS and AO. It can be observed that the mixture of UVA, HALS and AO was able to reduce the loss significantly, up to 200 h exposure for aliphatic ether TPU. After that, the loss increases at a higher rate which indicates the physical loss of additives.

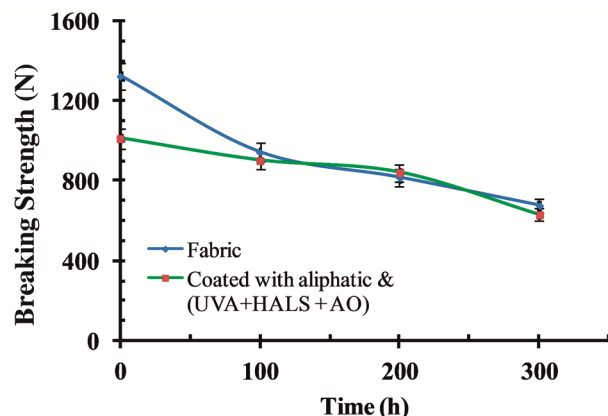


Fig. 9—Breaking strength of base fabric and aliphatic ether TPU-coated fabric containing UVA, HALS, and AO additives

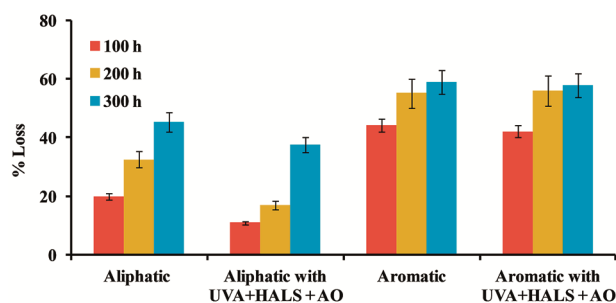


Fig. 10—Reduction in breaking strength of weathered fabrics coated with various TPU formulations

However, for aromatic ester TPU which is more prone to degradation, no significant effect on retaining the breaking strength was observed, even with incorporation of combination of UVA, HALS and AO. This might be associated with excessive stiffening effect, potentially arising from the crosslinking of polymeric chains under UV exposure.

### 3.3.2 Helium Gas Permeability

Table 4 shows the average helium gas permeability values in  $L/m^2$  per day for the samples exposed to different durations. For aliphatic ether based TPU coated samples, the permeability value increased from 2.17 to 3.02  $L/m^2$  per day for unexposed sample to sample exposed to 300 h respectively. However, incorporation of UVA, HALS, AO into the aliphatic ether based TPU coating did not provide much protection in terms of retaining He gas permeability (2.06 to 2.99  $L/m^2$  per day).

Unlike other cases, much lower permeability (1.40  $L/m^2$  per day) was observed in case of aromatic ester based TPU coating. Due to its lower molecular weight, aromatic ester TPU may be able to penetrate the small interstices and gaps between the yarns/fibres of

Table 4— Helium gas permeability rates ( $L/m^2$  per day) of coated fabrics with weathering exposure

Coating formulation	Gas permeability (in $L/m^2$ per day) after			
	0 h	100 h	200 h	300 h
Aliphatic ether based TPU	2.17	2.79	2.91	3.02
Aliphatic ether based TPU Formulation Containing (UVA +HALS +AO)	2.16	2.61	2.82	2.99
Aromatic ester based TPU	1.40	2.36	2.54	6.77
Aromatic ester based TPU formulation containing (UVA+ HALS +AO)	1.40	2.34	2.54	7.00

the PET fabric and thus block the pores of the fabrics more effectively than the aliphatic ether based TPU. However, upon weathering, the gas permeability increases drastically. After 300 h exposure, the fabric with aromatic ester coating even failed to sustain the helium gas for 24 h. The value (6.77  $L/m^2$  per day) has been calculated by measuring the He gas loss for one hour and converting it to 24 h. Almost similar observation was made for the aromatic ester based TPU coating stabilized with additives. It can be inferred that the UV stabilizers do not improve the gas barrier property significantly of both aromatic ester and aliphatic ether based TPU coated PET fabric when exposed to artificial weathering. UV protective effect of the additives on performance properties deteriorates with weathering time significantly which indicates the physical loss of this kind of organic additives in coatings.

## 4 Conclusion

The degradation behavior of aliphatic ether based TPU and aromatic ester based TPU films and coatings have been studied in detail in this article, specifically targeting coated fabrics for inflatable applications. Aliphatic ether based TPU have shown much better performance than the aromatic polyester one. While the Aliphatic ether based TPU exhibits higher UV resistance and oxidation stability, aromatic ester based TPU is more prone towards photooxidation. Urethane bridge of the adjacent aromatic ring in aromatic ester based TPU is photo-oxidized and in turn produces strong chromophoric groups producing yellow colour. To achieve satisfactory performance of the TPU, the synergistic mixture of different types of stabilizers was used. The combined use of UVA, HALS and AO exhibits a significant synergistic effect, delivering superior stabilization compared to their individual applications. This enhanced performance arises from the simultaneous activation

of their distinct photo-stabilization mechanisms. UVA acts by absorbing ultraviolet radiation and safely dissipating the energy without triggering oxidative degradation in the polymer. Antioxidants (AO) serve to further suppress oxidation processes, while HALS participate in multiple reactions that effectively interrupt the polymer's photooxidative degradation pathways. In this study, Tinuvin B75 (UVA + HALS + AO) has been found to improve the property for both types of TPUs. However, the effect of Tinuvin B75 seems to deteriorate with weathering time which indicates the physical loss of Tinuvin due to migration, blooming, leaching etc. Unlike other cases, aromatic ester based TPU was found to be more effective in reducing the He gas permeability value before weathering due to its low molecular weight which allows it to block pores in the fabric more effectively. However, the property deteriorated drastically upon weathering. However, in this regard, it should also be noted that there could be several factors that may influence the degradation behavior of a TPU. The morphology of the solid-state polymer as well as the long-term stability of the final coating are influenced by several factors, including the chemical structure and composition of the soft and hard segments, their respective lengths and molecular weights, the sequence distribution of segments, and the presence of irregular linkages such as branching or crosslinking.<sup>10, 12, 18, 19</sup> The research scope exists in this context. The effect of Tinuvin B75 on aromatic TPU, which is more prone to degradation, has not been found to be significant enough. Although the study of yellowness index and FTIR seem to give better results, no significant improvement has been found on tensile and gas barrier properties. This may be attributed to high stiffness of and poor retention of elongation of the aromatic TPU upon weathering.

The study provides valuable insights into the degradation behavior of coated fabrics for 300 hours, laying the groundwork for predicting long-term performance under actual service conditions. Future research will focus on developing a robust statistical model to estimate the service life of coated materials, enabling their effective use in extended deployment scenarios.

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