

## Photostabilization Efficiency of polymer nanocomposite: Functionalized Additives

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### Abstract:

Multiwalled carbon nanotubes (MWCNTs) were effectively coated with a hindered amine light stabilizer (HALS). A study was conducted to examine how light-stabilizing MWCNTs affected the photo-oxidation behaviour of polyethylene (PE). MWCNTs were mixed in a solution to create the nanocomposites, which were then melted and compounded with polyethylene (PE). Polymer nanocomposites films were photo irradiated at 60°C for varying durations of time, with accelerated weathering conditions ( $\lambda > 290\text{nm}$ ) applied. Transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FTIR) were used to characterize the photo degradation. The homogeneous dispersion of the HALS functionalized polymer nanocomposite into a polymer matrix. Pure MWCNTs and HALS-f-MWCNTs/PE were contrasted. It was noted that during rapid weathering, the degree of photo degradation of HALS-f-MWCNTs was decreased. To achieve longer performances in outdoor conditions, functionalization of HALS onto the polymer backbone is often achieved.

**Keywords:** Polyethylene, hindered amine light stabilizer, multiwalled carbon nanotubes, photodegradation, photostabilization.

### Introduction:

Researchers are paying close attention to the possibility of creating fresh and new hybrid carbon-based materials and their polymer composite. In the field of polymer nanocomposites, we are currently at a similar turning point where robust, long-lasting, and multipurpose materials with little nano-filler content are possible. The creation and deployment of sophisticated super-performing composites for various advanced applications may be facilitated by the utilization of nano-engineered multifunctional materials in the future (1-6).

The polymer nanocomposite's aspect ratio, dispersion state, loading size, and nanotube alignment all affect its mechanical, electrical, flammability, and rheological properties (7). CNTs are perfect for use as reinforcing material in polymers and many other engineering applications due to their aspect ratio, thermo-electric conductivity, and mechanical strength (8–11). When creating lightweight, highly durable materials for cutting-edge applications, polymer composites are an appealing option. However, it has been firmly believed that real-world attributes like robustness in particular outdoor performance situations are necessary before such nanocomposite materials can find feasible uses. Few studies have examined how carbon nanotubes affect the photo degradation of polymers in MWCNT-based polymer nanocomposites, and they have shown that nanotubes can function as weak antioxidants (12–16). Long-term outdoor durability still requires stabilization, and there are currently no reports that provide comprehensive photo stabilization investigations on these materials.

Light stabilizers, such as hindered amine light stabilizers (HALS), are frequently added to polymeric materials as light-protective additives to prolong their life and manage the photo-oxidation process (17–19). To achieve long-term stability, the additives must have a high retention rate. Therefore, to achieve prolonged outside application, covalent functionalization of HALS onto the polymer backbone is frequently used (20). Chemical functionalization of the nanotubes is one of the best ways to achieve their uniform dispersion in a polymer matrix (21).

The covalent method used in this study to secure the active HALS attachment onto MWCNTs (MWCNTs-f-HALS) is described. The homogeneous dispersion of nanotubes into the polymer matrix has been guided and the compatibilizer effectuated by the HALS has been utilized. The grafting was verified.

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was used to validate the grafting. The TEM morphological study was used to characterize the dispersion of MWCNTs into the polymer matrix. Melt extrusion was used to create the MWCNTs/PE nanocomposites after solution mixing. Using FTIR spectroscopy, the photo stabilizing of MWCNTs-f-HALS was evaluated during accelerated UV weathering.

## Literature Review:

In order to address polymer nanocomposites' vulnerability to photodegradation, this literature review investigates the usage of functionalized additives in enhancing the photostabilization efficiency of such materials. The review emphasizes the significance of surface modification techniques and antioxidants, as well as the requirement for biodegradability in environmentally friendly substitutes.

A method has been devised by a study to coat 3D-printed polyurethane scaffolds with graphene and PDA to increase their mechanical qualities and UV stability. The PDA coating promotes the bonding of graphene and PU, which raises the material's Young's modulus and compressive strength. Additionally, the composites exhibit improved UV durability, indicating possible synergistic benefits between graphene and PDA. This method provides an economical and sustainable option for applications using 3D printing.

[Burhan S.](#) et al (2023) study has developed a method to improve UV stability and mechanical properties of 3D-printed PU scaffolds by coating them with PDA and graphene, offering a cost-effective, environmentally friendly solution. The study also explores the use of titanium dioxide-based photo catalysts in wastewater treatment.

Chemical vapor deposition was used to make a MWCNT/Zeolite composite(12-16), which underwent up to 98% discolouration in 210 minutes under sunshine irradiation and revealed increased structural flaws ([J. Enrique Samaniego-Benítez et al 2023](#)).

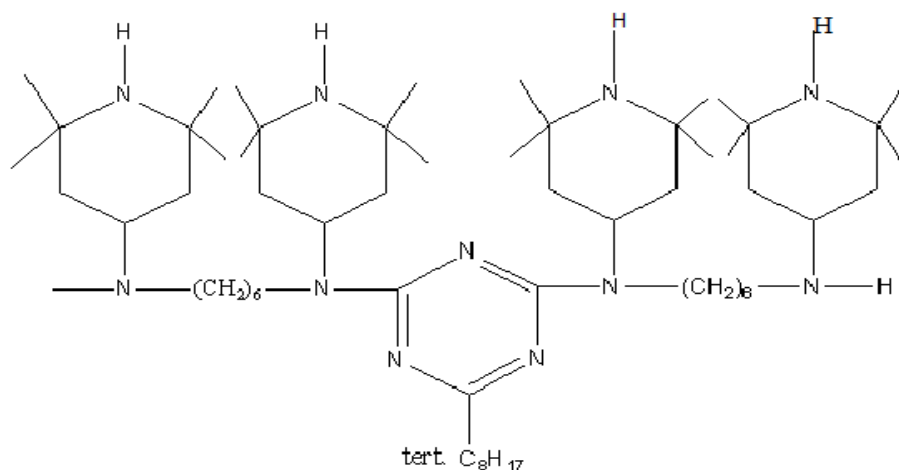
Effective PVC photostabilizers (Arraq, R. R. et al 2023), tin-cephalexin complexes 1-3 minimize photodegradation caused by UV light, polarized C–Cl bonds, and free radical breakdown. They deactivate dangerous species and release the cephalixin ligand. Higher aromatic substituent additives work better. Subsequent investigations ought to focus on the potentially harmful consequences and possible environmental metal leakage.

## Experimental:

### Materials:

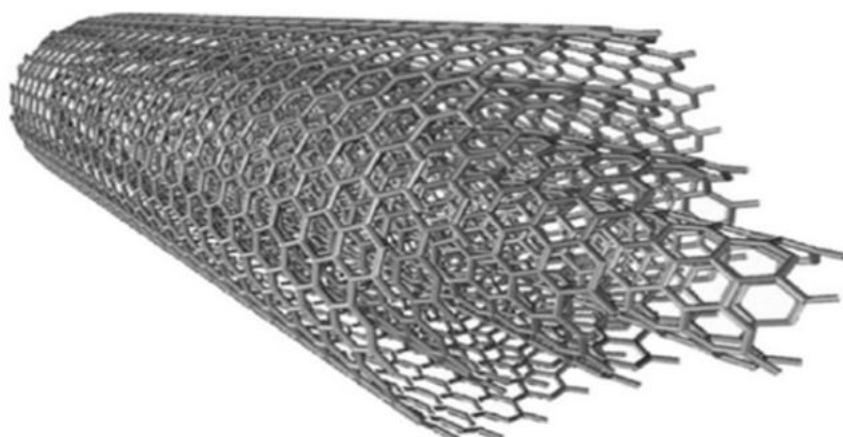
Chimassorb 944, a commercial stabilizer, and polyethylene [(PE), HMA 035] [poly{6-[tetramethylbutyl]-1,1,3,3-amino]2,4-diyl-1,3,5-triazine}]-[tetramethyl-4-piperidiny]-imino-2,2,6,6}. In this study, one nanoparticle of multiwalled carbon nanotubes (MWCNTs) obtained from M/s. Ciba-Geigy, Switzerland, DCC (dicyclohexylcarbodiimide) and THF (tetrahydrofuran) from Merck, and cysteamine from Sigma-Aldrich were utilized. -1,6-hexanediyl[(2,2,6,6-tetramethyl-4-piperidiny)-imino], white powder, M.P.:115-125 °C,  $M_n \approx 3000$ ].

### Structures of additives:



a) Chimaasorb944 (22)

## b) Multiwalled carbon nanotubes (23)



### Synthesis:

#### Chemical oxidation of MWCNTs

Chimassorb 944, a commercial stabilizer, and polyethylene [(PE), HMA 035] [poly{6-[tetramethyl-butyl)-1,1,3,3-amino]2,4-diyl-1,3,5-triazine}]-[tetramethyl-4-piperidinyl]-imino-2,2,6,6] In this study, one nanoparticle of multiwalled carbon nanotubes (MWCNTs) obtained from M/s. Ciba-Geigy, Switzerland, DCC (dicyclohexylcarbodiimide) and THF (tetrahydrofuran) from Merck, and cysteamine from Sigma-Aldrich were utilized. -1,6-hexanediyl[(2,2,6,6-tetramethyl-4-piperidinyl)-imino], white powder, M.P.:115-125 °C, Mn ≈ 3000].

#### Synthesis of MWCNTs functionalized to additive

The thiol functionalized MWCNTs with HALS under reflux in THF (Tetrahydrofuran) solvent at 60°C for 48h under a nitrogen atmosphere to give MWCNTs functionalized HALS. Then they washed well with methanol and dried under vacuum at room temperature (25).

#### Preparation of the MWCNTs-f-HALS/PE nanocomposites

A designated amount of MWCNTs-f-HALS was dissolved in toluene and mixed with fixed proportion of PE. These mixtures were subjected to ultra-sonication and subsequent solvent evaporated at room temperature. The resulting MWCNTs-f-HALS coated polymer composite was

further dried in hot air oven at 60°C. These polymer nanocomposites were further subjected to melt extrusion using a DMS microcompounder (5cc) at 180°C temperature, 100rpm pressure for 4 min to get polymer nanocomposites pellets.

The polymer nanocomposite pellets were compression moulded in between two metal plates at a temperature of 170°C and pressure ~100kg/cm<sup>2</sup> for 1 min, using pre-heated Carver Press (Model PF-M15 Technosearch instrument) to form thin films (~100µm thickness).

### **Photoirradiation**

Polymer composite sheets were exposed to radiation using an accelerated weathering chamber (SEPAP 12/24; M/s). Material Physico Chimique, Neuilly Marne/France) at 60°C with four mercury vapour lamps (400 W) delivering polychromatic irradiation ( $\lambda \geq 290\text{nm}$ ) at the varied time intervals (26).

### **Characterization**

#### **FT-IR Spectroscopy**

Polymer nanocomposite film photodegradation was examined using the Nicolet i35 FT-IR instrument's ATR (attenuated total reflectance) mode. The polymer nanocomposite films were scanned with the 32 scan at a resolution of 4 cm<sup>-1</sup>. The primary goal of the FT-IR-ATR spectroscopy was to concentrate on the alterations in the carbonyl and hydroxyl regions.

#### **Transmission electron microscopy (TEM)**

Though it utilizes electronics in place of light, the TEM functions according to the same general principles as a light microscope. The HALS functionalized MWCNTs' nanoscale architectures were observed through the use of a TEM 2000EX-II operating at a 100kV accelerating voltage to produce TEM pictures.

## Result and Discussion:

### FT-IR Spectroscopy

#### Evaluation of carboxylic group in MWCNTs by FTIR:

Four prominent peaks can be seen in the FT-IR spectra of oxidized MWCNTs: 3491, 2348, 1618, and 1542  $\text{cm}^{-1}$ . The O-H stretch from carboxyl groups (O=C-OH and C-OH) can be attributed to the peak at 3491  $\text{cm}^{-1}$ , whereas the O-H stretch from highly hydrogen-bonded -COOH can be linked to the peak at 2348  $\text{cm}^{-1}$ . The carboxylate anion stretch mode is connected to the peak at 1542  $\text{cm}^{-1}$ . It is assumed that these commercial MWCNTs include carboxylic groups. The carbon nanotube backbone's stretching can be linked to the peak at 1642  $\text{cm}^{-1}$ .

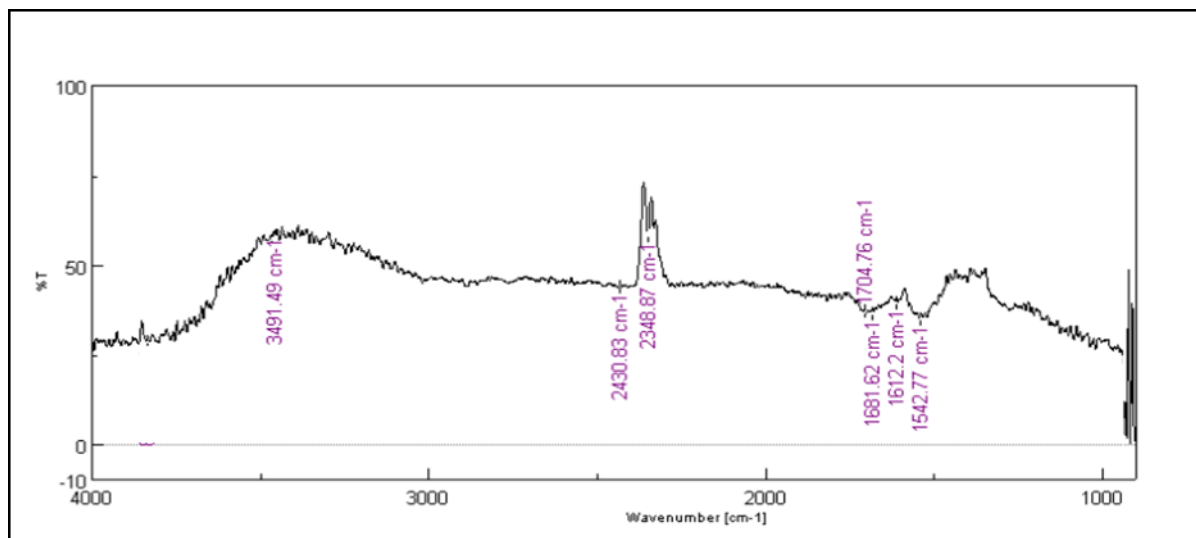


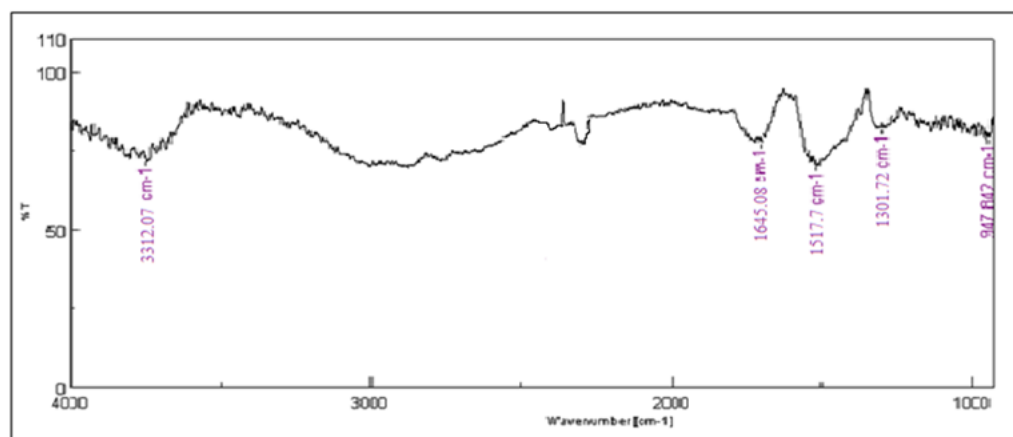
Fig. 1 Evaluation of carboxylic group in MWCNTs by FTIR

#### Evaluation thiol functionalized MWCNTs by FTIR:

The amide group produced during the thiolation process of carboxyl ended carbon nanotubes with cysteamine, and this amide group functionalized on MWCNTs, as determined by FTIR. FTIR spectra show the optimum peak for the amide group at 3312.07  $\text{cm}^{-1}$ . The stretching of the carbonyl group in the presence of amide is indicated by the peak at 1645.08  $\text{cm}^{-1}$ . In the FTIR spectra, the stretching of the N-H bond is seen as a peak at 1517.7  $\text{cm}^{-1}$ . In FTIR spectra, the C-N stretching bond peak was found at 1301.72  $\text{cm}^{-1}$ . The carboxyl terminated carbon nanotubes' thiolization

process with cysteamine functionalized the amide group on MWCNTs. Following this functionalization, an additive reaction occurs.

**Fig. 2 Evaluation of thiol functionalized MWCNTs by FTIR**



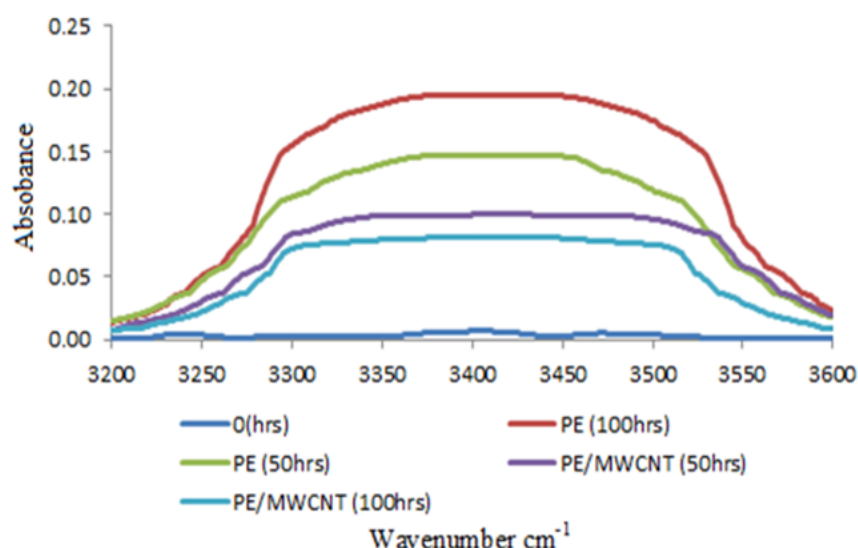
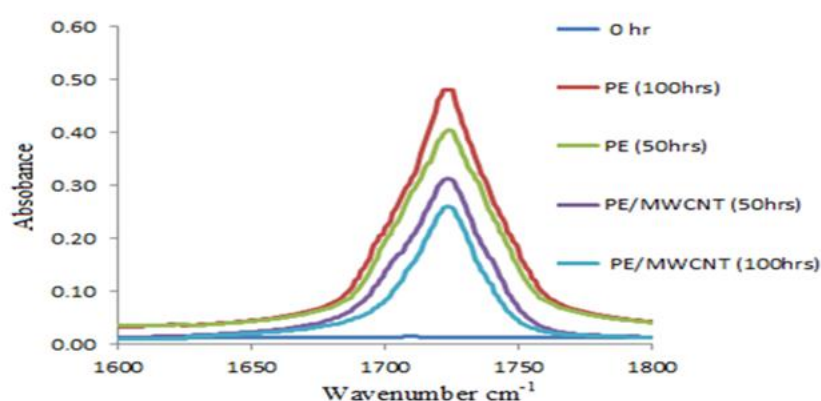
### **Evaluation of Carbonyl and Hydroxyl group of MWCNTs-f-HALS/polymer nanocomposite samples by FT-IR**

The current effort is expected to produce the needed extra durable polymer nanocomposites for outdoor applications through the grafting of HALS onto carbon nanotubes via chemical fixing, followed by the mixing of MWCNT-f-HALS. Stabilizers are typically introduced while polymeric materials are being prepared and processed, primarily for the purpose of creating polymer nanocomposites. The photostability efficiency of HALS grafted on carbon nanotubes was tested in an accelerated weathering environment using polymer composites including MWCNTs. The FTIR spectra of the PE/MWCNT hybrids were used to assess their photodegradation behavior. The creation of hydroperoxide is the primary result of UV light and oxygen working together. The PET and PE/HALS-MWCNTs were exposed to radiation for 50 and 100 hours, respectively, in an irradiation chamber. At 100 hours, the tidy PE exhibits more photodegradation. Compared to plain PE, the PE/HALS-MWCNTs exhibit greater stability at 100 hours. The polymer's nanoparticle aids in lessening outdoor use deterioration. In FTIR spectra, the primary concentrated carbonyl area can be seen at 1721 cm-1. In FTIR spectra, the hydroxyl area is visible around 3412cm-1. The physical, thermal, electrical, and optical properties of polymers are typically enhanced by additions based on



nanoparticles. Therefore, excellent retention of the nano additions in the polymer matrix is extremely desirable to achieve long term stability of materials. To achieve longer performances in outdoor conditions, covalent functionalization of HALS onto the polymer backbone is therefore often achieved.

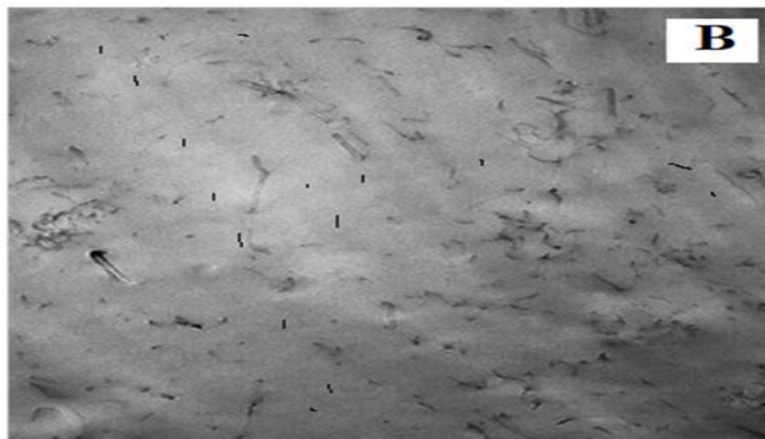
**Fig.3 Evaluation of carbonyl region during at 50hrs and 100hrs UV irradiation of PE/MWCNT-f HALS**



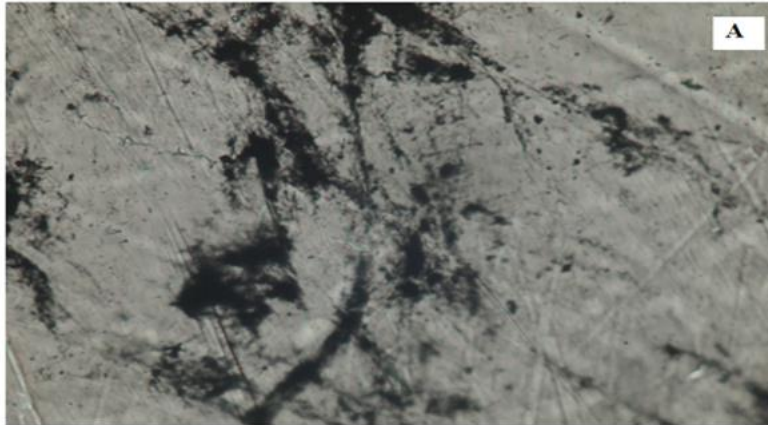
**Fig.4 Evaluation of hydroxyl region during at 50hrs and 100hrs UV irradiation of PE/MWCNT-f HALS**

### Transmission electron microscopy (TEM)

The degree of functionalized MWCNT dispersion in MWCNTs/PE nanocomposites, as measured by TEM, is an interesting topic to research. Each sample's MWCNTs/PE nanocomposites had a nanotube content of 0.5 weight percent. The pure MWCNTs are not evenly distributed throughout the polymer matrix, as Fig. 5.23 illustrates. A portion of the carbon nanotubes is distributed singly, and the remaining portion is distributed in the form of various-sized agglomerates. In contrast, as Fig. 5.24 illustrates, the MWCNTs-f-HALS nanocomposites have superior homogeneity and comparatively good dispersion in the polymer matrix, maybe because functionalized MWCNTs are very compatible with the polymer matrix. Rather than being extracted, the functionalized nanotubes were incorporated into the PE matrix and linked to networks. This implies that MWCNTs-f-HALS is firmly bonded to the polymer matrix, indicating a robust connection between functionalized nanotubes and the PE matrix.



**Fig. 5 TEM micrographs of PE/MWCNT, (200 nm)**



**Fig. 6 TEM micrographs of PE/ HALS-MWCNTs, (200 nm)**

## **Conclusion**

MWCNTs functionalized with light stabilizers have been developed for this investigation. The covalent binding of HALS to the nanotube surface is demonstrated by the spectroscopic and microscopic characterization. When used outside, the polymer's nanoparticle aids to lessen deterioration. Comparing functionalized MWCNTs to pure MWCNTs, the TEM micrographs demonstrate that the former have a better dispersion in the PE matrix. Studies on accelerate UV aging have indicated that the resultant nanocomposite exhibits a superior photo stabilization effect when the MWCNTs-f-HALS is used. A high retention rate of the nano-additives in the polymer matrix is very desirable for materials to achieve long-term stability. For this reason, covalent functionalization of HALS onto the polymer backbone is often achieved in order to provide extended performances in outdoor settings.

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## References

1. Arraq, R. R., Hadi, A. G., Ahmed, D. S., El-Hiti, G. A., Kariuki, B. M., Husain, A. A., Bufaroosha, M., et al. (2023). Enhancement of Photostabilization of Poly(Vinyl Chloride) in the Presence of Tin–Cephalexin Complexes. *Polymers*, 15(3), 550. MDPI AG. Retrieved from <http://dx.doi.org/10.3390/polym15030550D>. Pomogailo, Russ. Chem. Rev., 2000, 69, 53-80.
2. D. A. Tomalia, *Polymer J.* 17.1, 1985, 117-132.
3. D. Cai and M. Song, *J. Mater. Chem.*, 2010, 20, 7906-7915.
4. E. P. Giannelis, *Adv. Mater.*, 1996, 8, 29-35.
5. F. Beguin and P. Ehrburger, *Carbon*, 2002, 40, 1619.
6. F. Gugumus, *Polym. Degrad. Stab.* 1989, 24, 289-301.
7. F. Jonas and L. Schrader. *Synthetic Metals*, 1991, 41, 831-836.
8. Fowler, W. David. *Cement and Concrete Compo*, 1999, 21, 449-452.
9. H. Althues, J. Henle and S. Kaskel, *Chem. Soc. Rev.*, 2007, 36, 1454-1465.
10. J. Enrique Samaniego-Benítez, Alejandra García-García, S. Ivette Rivera-Manrique, Jeannete Ramírez-Aparicio(2023), Multiwalled carbon nanotubes/zeolite composite for dye degradation under sunlight, *Materials Today Communications*, Volume 35, 2023, 106046, ISSN 2352-4928, <https://doi.org/10.1016/j.mtcomm.2023.106046>.
11. K. Schwetlick and W. D. Habicher, *Polym. Degrad. Stab.* 2002, 78, 35-40.
12. L. Guadagno, C. Naddeo, M. Raimondo, G. Gorrasi and V. Vittoria, *Polym. Degrad. Stab.* 2010, 95, 1614-1626.
13. M. Auer, R. Nicolas, A. Vesterinen, H. Luttikhedde and C. E. Wilen, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, 42, 1350-1355.
14. M. J. Comstock. *ACS Symp. Series*, No. 172, Am. Chem. Soc., 1981, Chapter 1.
15. M. Kaci, G. Hebal, N. Touati, A. Rabouchi, L. Zaidi and H. Djidjelli, *Macromol. Mater. Eng.*, 2004, 289, 681-687.
16. M. Naffakh, M. Remskar, C. Marco, M. A. Gomez-Fatou and I. Jimenez, *J. Mater. Chem.*, 2011, 21, 3574-3578.
17. Md. Burhan Kabir Suhan, Md. Rashid Al-Mamun, Nawshin Farzana, Sirazam Munira Aishee, Md. Shahinoor Islam, Hadi M. Marwani, Md. Munjur Hasan, Abdullah M. Asiri, Mohammed M. Rahman, Aminul Islam, Md. Rabiul Awual, Sustainable pollutant removal and wastewater remediation using TiO<sub>2</sub>-based nanocomposites: A critical review, *Nano-Structures & Nano-Objects*, Volume 36, 2023, 101050, ISSN 2352-507X, <https://doi.org/10.1016/j.nanoso.2023.101050>.
18. N. G. Sahoo., S. Rana, J.W. Cho, L. Li and S. H. Chan, *Prog. Polym. Sci.*, 2010, 35, 837-867.
19. P. C. P. Watts, P. K. Fearon, W. K. Hsu, N. C. Billingham, H. W. Kroto and D. R. M. Waiton, *J. Mater. Chem.*, 2003, 13, 491-495.
20. P. M. Miladinova, T. N. Konstantinova *J. of chem. Techn. And metallurgy*, 2015, 50, 229-239.
21. S. Bocchini, A.-D. Blasio and A. Frache, *Macromol, Symp.*, 2011, 301, 16-22.
22. S. Morlat-Therias, E. Fanton, J.-L. Gardatte, S. Peeterbroek, M. Alexandre and Ph. Dubois, *Polym. Degrad. Stab.* 2007, 92, 1873-1882.

23. S. P. Lonkar, O. S. Kushwaha, A. Leuteritz, G. Heinrich and R. P. Singh, *Rsc Adv.*, 2012, 2, 12255-12262.
24. S. Subramoney, *Adv. Mater.*, 1998, 10, 1157-1173.
25. Tung, C.-C., Lin, Y.-H., Chen, Y.-W., & Wang, F.-M. (2023). Enhancing the Mechanical Properties and Aging Resistance of 3D-Printed Polyurethane through Polydopamine and Graphene Coating. *Polymers*, 15(18), 3744. MDPI AG. Retrieved from <http://dx.doi.org/10.3390/polym15183744>
26. Weiss, A. Emily, G. K. Kaufman, J. K. Kriebel, Z. Li, R. Schalek, and G. M. Whitesides. *Langmuir* 23, 2007, 9686-9694.
27. X. Shi, B. Jiang, J. Wang and Y. Yang, *Carbon*, 2012, 50, 1005-1013.
28. Y. Lin, M. J. Meziani and Y. P. Sun, *J. Mater. Chem.*, 2007, 17, 1143-1148.
29. Y. Lin, M. J. Meziani and Y.-P. Sun, *J. Mater. Chem.*, 2007, 17, 1143-1148.