EFFECTS OF HALSS AND NANO-ZnO WORKED AS UV STABILIZERS OF POLYPROPYLENE

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Thesis Prepared for the Degree of

MASTER OF SCIENCE

UNIVERSITY OF NORTH TEXAS

December 2017

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Lu, Xinyao. *Effects of HALSs and Nano-ZnO Worked as UV Stabilizers of Polypropylene*. Master of Science (Materials Science and Engineering), December 2017, 42 pp., 5 tables, 23 figures, 31 numbered references.

This work reports the outdoor weathering performance of ultraviolet (UV)-stabilized polypropylene (PP) products (using PP resins from Encore Wire). Different hindered amine light stabilizers (HALSs) and nano-ZnO were used to stabilize PP-film-based formulations that were exposed under UV light for 6 weeks simulating for in harsh outdoor weather of Dallas, Texas, USA in 2016. Characterization of the exposed PP film products was done in terms of mechanical and friction spectroscopic properties. The PP film formulations were divided into 15 categories based on the type of HALS and nano-ZnO incorporated. This was done to derive meaningful comparison of the various film formulations. Following exposure under UV light, the lifetimes of certain formulations were determined. On the basis of the mechanical and friction properties, it was determined that generally, the HALS or nano-ZnO stabilized PP film give better properties and if those two kinds of UV stabilizers can work together.

ACKNOWLEDGEMENTS

I would like to sincerely thank to my academic adviser, Dr. Witold Brostow, who provides me such a precious opportunity to work in LAPOM. Dr. Witold Brostow is the best guider I have ever met. He is a wise man who not only imparts knowledge regarding polymers to me, but also teaches me some philosophies through his life experience. I would also like to thank to my committee members including Dr. Jincheng Du and Dr. Zhenhai Xia, who gave me useful advices to make my thesis more completed.

I would like to thank to all my laboratory mates who have ever helped me to do variety experiments.

I appreciate what my beloved family members have done for me. I would not have a Master’s degree without their support.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Page

CHAPTER 1

INTRODUCTION

1.1 Introduction of Polypropylene and Current Situation

Polypropylene (PP), is a thermoplastic polymer used in a wide variety of applications including packaging, labeling, and wire industry, textiles (e.g. ropes, thermal underwear and carpets), stationery, plastic parts and reusable containers of various types, laboratory equipment, loudspeakers, automotive components, transvaginal mesh[1] and polymer banknotes. An addition polymer made from the monomer propylene, it is rugged and unusually resistant to many chemical solvents, bases and acids. Polypropylene has a relatively slippery "low energy surface" that means that many common glues will not form adequate joints. Joining of polypropylene is often done using welding processes. In 2013, the global market for polypropylene was about 55 million tonnes.[2] Polypropylene is the world's second-most widely produced synthetic plastic, after polyethylene.

The density of PP is between 0.895 and 0.92 g/cm^3. Therefore, PP is the commodity plastic with the lowest density. With lower density, moldings parts with lower weight and more parts of a certain mass of plastic can be produced. Unlike polyethylene, crystalline and amorphous regions differ only slightly in their density. However, the density of polyethylene can significantly change with fillers.[3] The Young's modulus of PP is between 1300 and 1800 N/mm^2. Polypropylene is normally tough and flexible, especially when copolymerized with ethylene. This allows polypropylene to be used as an engineering plastic, competing with materials such as acrylonitrile butadiene styrene (ABS). Polypropylene is reasonably economical. Polypropylene has good resistance to fatigue.[4] The melting point of polypropylene occurs at a range, so a melting point is determined by finding the highest temperature of a differential scanning calorimetry chart. Perfectly isotactic PP has a melting point of 171 °C (340 °F). Commercial isotactic PP has a melting point that ranges from 160 to 166 °C (320 to 331 °F), depending on atactic material and crystallinity. Syndiotactic PP with a crystallinity of 30% has a melting point of 130 °C (266 °F).[4] Below 0 °C, PP becomes brittle. The thermal expansion of polypropylene is very large, but somewhat less than that of polyethylene.[5]

1.2 Problems Now PP Products Face and Approach of Inhibiting Plasticizer Light Decomposition

Light stabilization of plastics has been a challenge for the industry for long time.[6] Polymers, in general and especially polypropylene, are highly sensitive to degradation processes when exposed to oxidant atmospheres and Ultraviolet (UV) light.[7-8] Hence, industrial formulations require the addition of antioxidants and light stabilizers to preserve their physical and mechanical properties for long periods.

The polymeric materials exposed to sunlight undergo degradation which decreases the usage value and shortens their service life, mainly by photo oxidation. The inherent characteristic materials may be weakened as a result of photo degradation.[9-11] Hence, polymeric auxiliaries are being studied and analyzed.

1.2.1 Hindered Amine Light Stabilizers (HALSs)

Hindered amine light stabilizers (HALSs) are one of the most important thermal/light stabilizing agents of polymeric materials. They are widely available with low toxicity and low cost, and they have excellent compatibilities with a broad range of commercially significant polymeric materials. HALSs have a good photo stabilizing effect on organic materials, which may be 2–4 times higher than that of traditional ultraviolet stabilizers.[12-13] The theory of HALSs stabilizers working on protecting PP is not acting by absorbing UV radiation, but by inhibiting degradation of the polymer, which has started the formation of free radicals. They function by scavenging radicals. HALS has low volatility and high extraction resistance.[14] Another advantage is that it provides a significant level of stabilization at relatively low concentration.[15] HALSs have high molecular weight undergoes thermal degradation at elevated temperatures and are colorless, highly efficient at very low concentrations.[16-17] Those properties make HALSs very famous on PP processing industry.

Chemical scavenging of alkyl and peroxy macroradicals is considered to be the most important process in the mechanism of polymer stabilization by HALSs.[18] It is commonly accepted that during polymer exposure, both amine and aminoether derivatives of HALSs yield nitroxides which function as interceptors of alkyl radicals to yield aminoethers. These aminoethers in turn react with peroxy radicals to regenerate nitroxides.[19-20] Therefore the inter conversions of HALSs of various structures operate in a cyclic pathway. In polymer media this reaction is probably controlled by molecular diffusion. This cyclic pathway is shown in fig. 3.7.

1.2.2 Nano-ZnO

Another ultraviolet stabilizer is nano-ZnO. Nano-ZnO is widely used as an additive in numerous materials and products including rubbers, plastics, ceramics, glass, cement and lubricants.[21] ZnO is a wide-bandgap semiconductor of the II-VI semiconductor group. The native doping of the semiconductor due to oxygen vacancies or zinc interstitials is n-type.[22]

Micronized and nano-scale zinc oxide and titanium dioxide provide strong protection against ultraviolet radiation, and are used in suntan lotion,[23] and also in UV-blocking sunglasses for use in space and for protection when welding, following research by scientists at Jet Propulsion Laboratory (JPL).[23] Theory of nano-ZnO used as UV stabilizer is stopping the formation of cracks in the polymer, comparing with to nano-TiO_2, nano-ZnO is more effective in diminishing the tendency of the polymers to yellowing.[24-25] Nano-ZnO has the quantum size effect, which may cause blue-shifted phenomenon to some specific wave length light; and has wide phenomenon to absorption band of all length of wave light. When the particle size of nano-ZnO is smaller than 100nm, the forbidden band gap would increase to 4.5eV (equals to the most of energy of UV radiation), which causes the absorption ability of nano-ZnO to UV light.

1.3 Objectives

Given the situation described above, I chose HALS1, HALS2 and nano-ZnO as UV stabilizers of PP films to find which kind of UV stabilizer, what combination and what concentration of UV stabilizers give the best effects on thermal and mechanical properties to PP films in order to find which gives the best UV resistance under different periods of UV exposure.

CHAPTER 2

EXPERIMENTAL PROCEDURES

2.1 Material

In this research, samples are composed of different materials, including PP resin, three kinds of UV plasticizers. All of the components we used are commercially available materials.

2.1.1 Polypropylene

(EP315J), offered by Lyondellbasell, wire and cable grade, melt flow rate 2.6 g/10min and density 0.9g/cc, tensile strength 3,200 psi, elongation at break 600%, flexural Modulus, 1% secant 150,000 psi, and low temperature brittleness is -30℃.

2.1.2 HALS1

[Bis(2,2,6,6-tetramethyl-4-piperidyl)] sebacate, offered by Sigma-Aldrich, CAS number: 52829-07-9. White color powder, melting temperature 82-85℃ and degradation temperature 350℃. The chemical structure of HALS1 is shown in fig. 2.2(1).

2.1.3 HALS2

[Poly[[6-[(1,1,3,3-tetramethylbutyl)amino]-*s*-triazine-2,4-diyl]-[(2,2,6,6-tetramethyl-4-piperidyl)imino]-hexamethylene-[(2,2,6,6-tetramethyl-4-piperidyl)imino] offered by Sigma-Aldrich, CAS number: 70624-18-9. White color powder, melting temperature 136-140℃ and degradation temperature 300℃. The chemical structure of HALS1 is shown in fig. 2.2(2).

2.1.4 Nano-ZnO

Offered by Sigma-Aldrich, CAS number: 1314-13-2. White color powder, particle size 50nm, surface area 10.8m^2/g, Refractive index 2.0041, degradation temperature 1975℃.

2.2 Sample Preparation: Mixing Procedures

Table 2.1 shows the comparison of mechanical properties and concentrations for PP samples blended with different UV stabilizers. According to Table 2.1, Young's modulus of all samples will increase as concentration of UV stabilizers increase. However, there are no obvious changes of elongation at break as the concentrations of UV stabilizers increase. In general, elongation at break of HALSs samples is higher than nano-ZnO samples. For toughness, when loading level of UV stabilizers is over 1wt.%, toughness of PP films seems higher than PP films whose loading level of UV stabilizers is lower than 1wt.%.

Table 2.1. Comparison of mechanical properties for samples with different concentrations of UV stabilizers.

Concentration	Mechanical Properties	HALS1	HALS2	Nano-ZnO
0.5wt.%	Young's Modulus (MPa)	374±31	364±64	429±65
	Elongation at break(mm)	288±47	290±36	279±13
	Tensile toughness (N*m)	9±1	13±2	10±3
0.75wt.%	Young's Modulus (MPa)	379±20	317±57	414±39
	Elongation at break(mm)	295±50	310±64	289±32
	Tensile toughness (N*m)	11±2	14±3	11±2
1wt.%	Young's Modulus (MPa)	382±54	419±23	402±44
	Elongation at break(mm)	321±31	312±28	270±38
	Tensile toughness (N*m)	13±1	12±2	12±2
1.25wt.%	Young's Modulus (MPa)	404±82	444±30	466±70
	Elongation at break(mm)	286±31	276±18	299±50
	Tensile toughness (N*m)	12±2	14±1	12±3

Table 2.2 shows individual formulae for each kind of sample. Control sample was prepared without a UV stabilizer, while Samples I, II and III, etc., contained different UV stabilizers such as HALS1, HALS2 and Nano-ZnO, respectively.

Table 2.2. Formulae of samples.

	Samples						
Components	Control	I	Ⅱ	Ⅲ	Ⅳ	Ⅴ	Ⅵ
PP	40phr	40phr	40phr	40phr	40phr	40phr	40phr
HALS1	N/A	0.50%	N/A	N/A	0.75%	N/A	N/A
HALS2	N/A	N/A	0.50%	N/A	N/A	0.75%	N/A
Nano-ZnO	N/A	N/A	N/A	0.50%	N/A	N/A	0.75%
	Samples						
	Control	Ⅶ	Ⅷ	Ⅸ	Ⅹ	Ⅺ	Ⅻ
PP	40phr	40phr	40phr	40phr	40phr	40phr	40phr
HALS1	N/A	1%	N/A	N/A	1.25%	N/A	N/A
HALS2	N/A	N/A	1%	N/A	N/A	1.25%	N/A
Nano-ZnO	N/A	N/A	N/A	1%	N/A	N/A	1.25%

In order to prepare homogeneous PVC mixtures, several steps are needed:

First, Brabender, (C.W. Brabender Instruments. Inc. 105800): 0.5%, 0.75%, 1% and 1.25% wt. of HALS1, HALS2 and nano-ZnO UV stabilizers were mixed with PP respectively in the Brabender at 190℃ for 6 min and cool the mixture. Second, put cooled stabilized PP products into pelletizer (Greiffenberger Antriebstechnik 4EK90SBX-2) respectively and get smashed particles. Last, pour the particles into extruder （Encore Wire Corporation, 1329 Millwood Road McKinney, TX 75069）respectively and get films wanted. The temperature gradients are 355°F, 355°F, 365°F, 375°F and 385°F from the entrance to exit respectively. Then we got the PP films we want. The last step is cut the PP film into dog-bone-shape samples we want for the following testing. The procedure is shown in figs. 2.1 and 2.2.

Fig. 2.1. Procedure of samples making

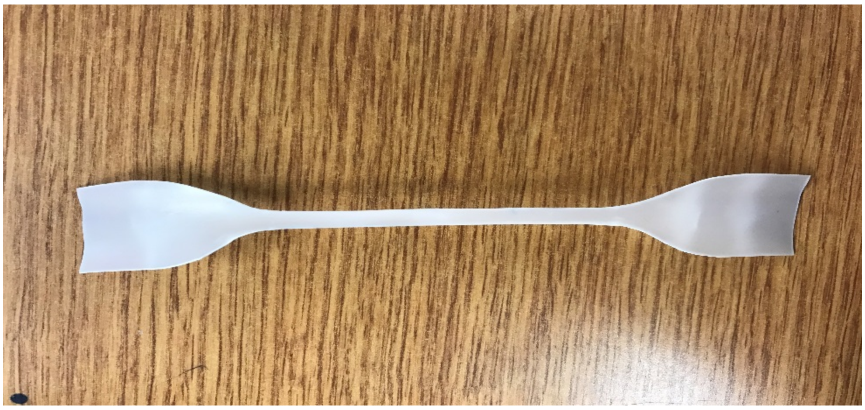


Fig. 2.2. Picture of dog-bone-shape sample

2.3 Film Characterization

In order to characterize and to evaluate the efficiency of the plasticizers in stretch PVC films for packaging the following methods were employed: physical mechanical properties, infrared spectroscopy and light transmission. The tests were conducted at 23℃ ± 2℃ and 50% ± 5% relative humidity after conditioning the samples in these same conditions for at least 48 hours.

2.4 UV Treatment

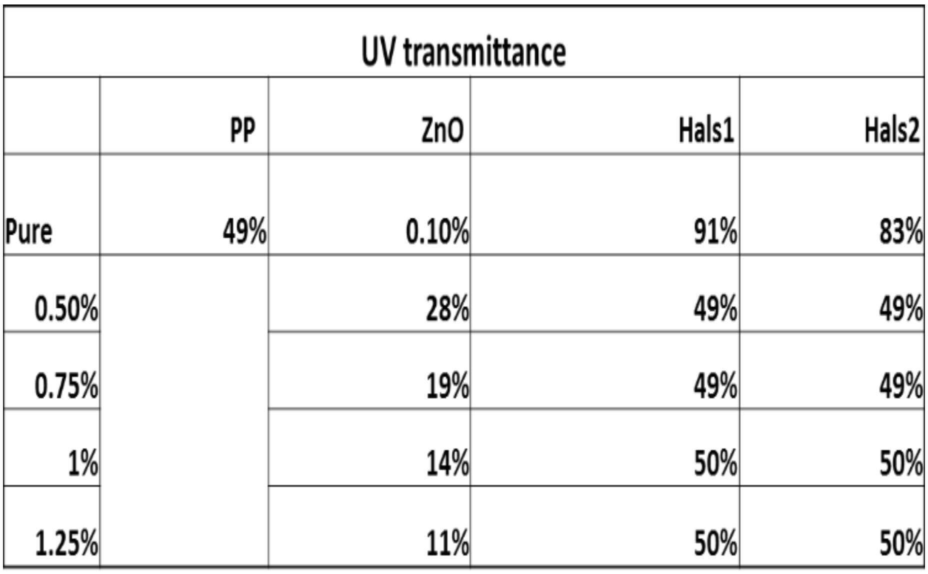
As mentioned before, UV radiation is a critical factor affecting the migration rate. So our study is based on researching the thermal and mechanical properties of PP films with or without UV stabilizers after different periods of UV exposure. Samples were placed under an UV light (BlakRay B-100A High intensity UV Lamp/365nm/intensity: 16.9 mW/cm^2).

UV dose is measured in milli joules seconds per cm^2(mJ/cm^2). It is calculated using the following parameters: UV intensity (**I**), measured in milli watts per cm^2 (mW/cm^2); UV transmittance (**UVT**) (%) (shown in table 2.3) and exposure time (under UV lamp) (**t**) (seconds). The relationship between these parameters can be described by the following simplified equation:

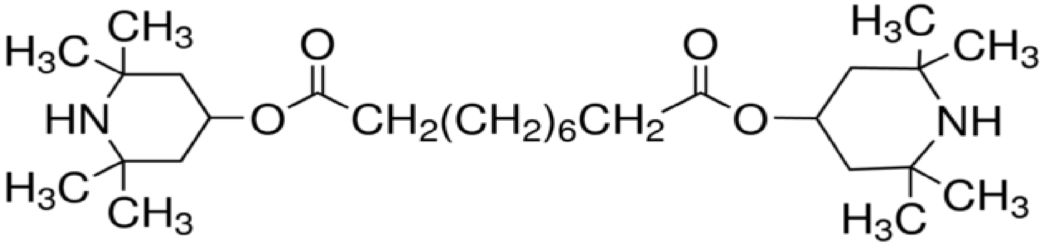
$$\textbf{UV Dose} = \mathbf{(I/UVT) \times t}^{[26]} \qquad (1)$$

The UV dose we get in lab is 121 times higher than sun light in Texas. Different UV transmittances are shown in table 2.31. The average UV intensity of Texas in 2016 is: 0.14 mW/cm^2.[27]

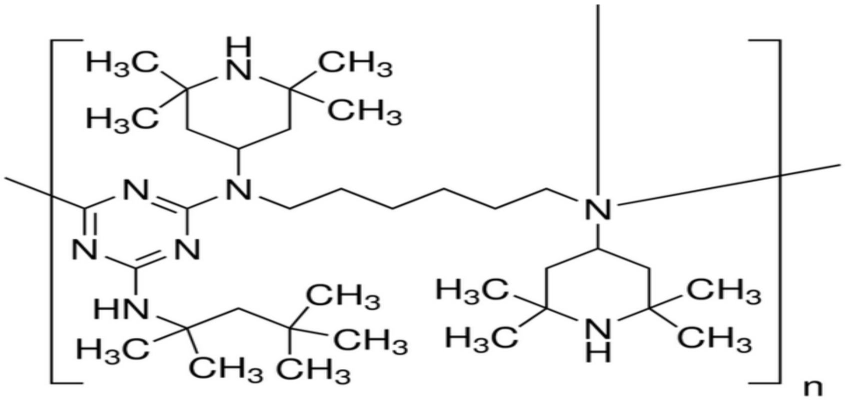
Table 2.3. UV transmittance of all components



UV transmittance				
	PP	ZnO	Hals1	Hals2
Pure	49%	0.10%	91%	83%
0.50%		28%	49%	49%
0.75%		19%	49%	49%
1%		14%	50%	50%
1.25%		11%	50%	50%



(1)

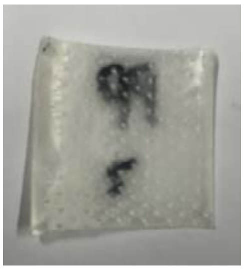
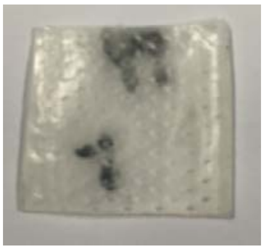
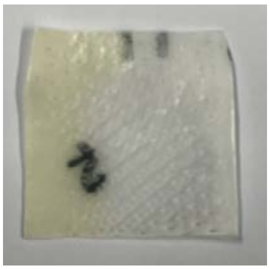
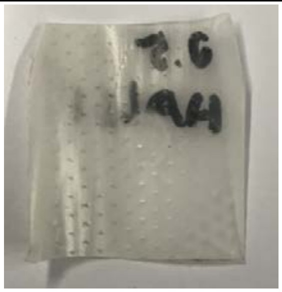


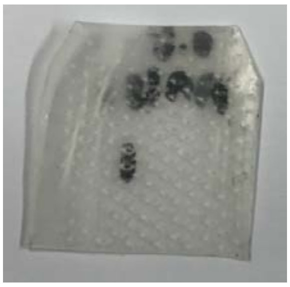
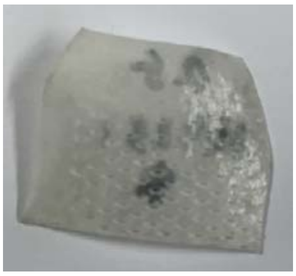
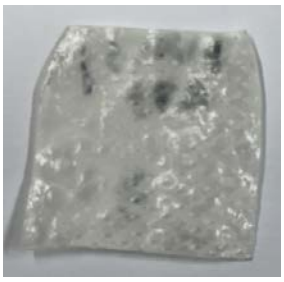
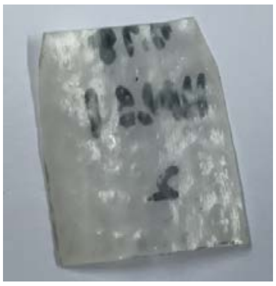
(2)

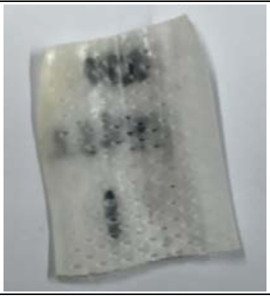
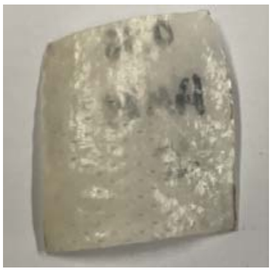
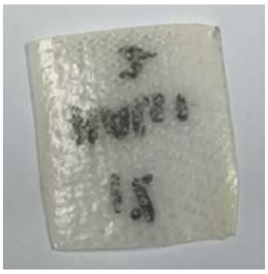
Fig. 2.3. Structure of HALS1(1) and HALS2(2)

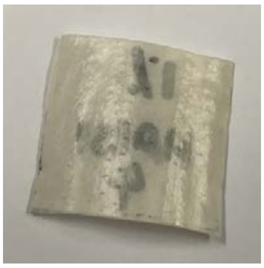
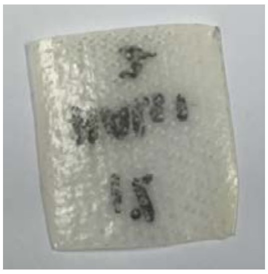
Table 2.5 shows the sample surface of all PP components. According to the table, pure PP films turned yellow on the surface when the UV exposure date increases and it became brittle and even fractured on the left corner after 6weeks' UV exposure; For HALS1 samples the yellowish was turned on 3 weeks' and 6 weeks' UV exposure, this phenomenon matches the mechanical properties of PP films with HALS1 UV stabilizers and the degree of yellowish did not change with loading level; For HALS2 samples the yellowish showed on 3 weeks', 4.5 weeks' and 6 weeks' UV exposure just like pure PP films but did not turn brittle; For nano-ZnO samples, all loading level of samples did not show obvious yellowish during all UV exposure periods. We can see that nano-ZnO can not only gives UV resistance of PP films but can improves appearance stable of them.

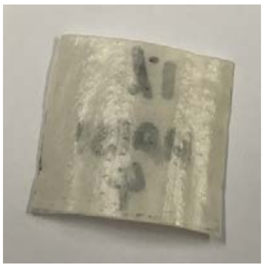
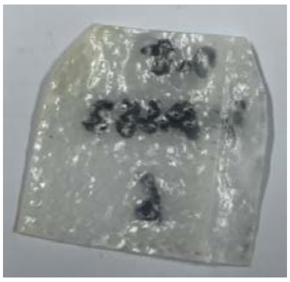
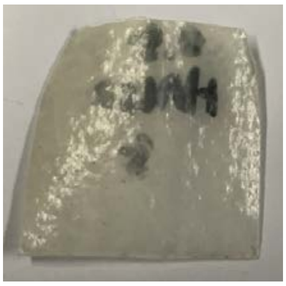
Table 2.4. Samples and images of surfaces.

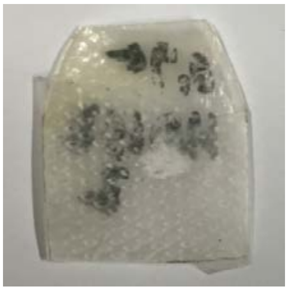
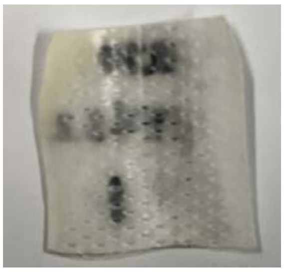
Sample	Type of UV Stabilizer	UV Treatment	Surface
Non UV Control	N/A	N/A	
1.5weeks control	N/A	UV exposure 1.5weeks	
3weeks control	N/A	UV exposure 3weeks	
4.5weeks control	N/A	UV exposure 4.5weeks	
6weeks control	N/A	UV exposure 6weeks	
Non UV 0.5%HALS1	HALS1	N/A	

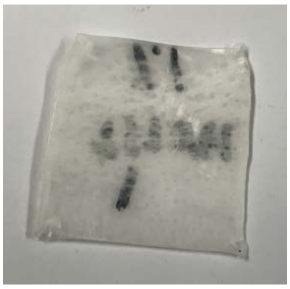
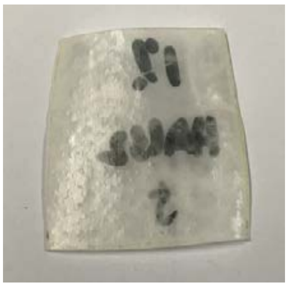
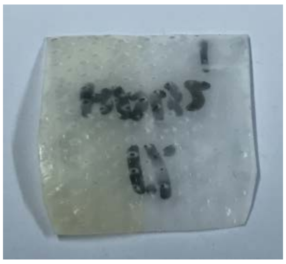
Sample	Type of UV Stabilizer	UV Treatment	Surface
1.5weeks 0.5% HALS1	HALS1	UV exposure 1.5weeks	
3weeks 0.5%HALS1	HALS1	UV exposure 3weeks	
4.5weeks 0.5%HALS1	HALS1	UV exposure 4.5weeks	
6weeks 0.5%HALS1	HALS1	UV exposure 6weeks	
Non UV 0.75%HALS1	HALS1	N/A	
1.5weeks 0.75% HALS1	HALS1	UV exposure 1.5weeks	

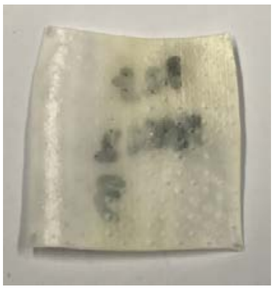
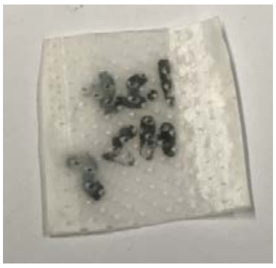
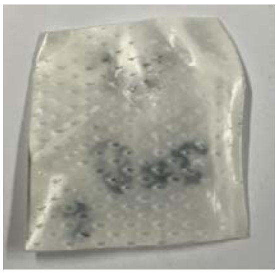
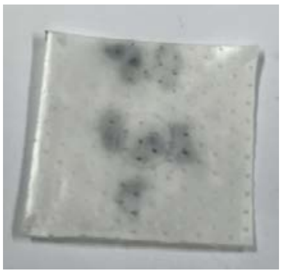
Sample	Type of UV Stabilizer	UV Treatment	Surface
3weeks 0.75%HALS1	HALS1	UV exposure 3weeks	
4.5weeks 0.75%HALS1	HALS1	UV exposure 4.5weeks	
6weeks 0.75%HALS1	HALS1	UV exposure 6weeks	
Non UV 1%HALS1	HALS1	N/A	
1.5weeks 1% HALS1	HALS1	UV exposure 1.5weeks	
3weeks 1%HALS1	HALS1	UV exposure 3weeks	

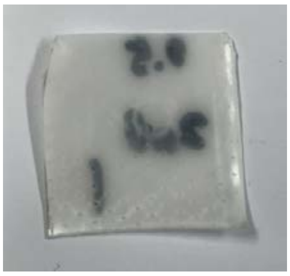
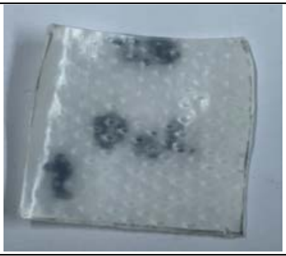
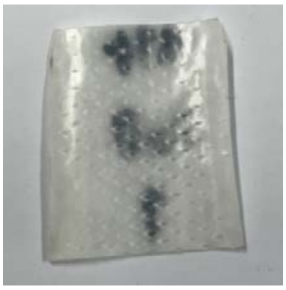
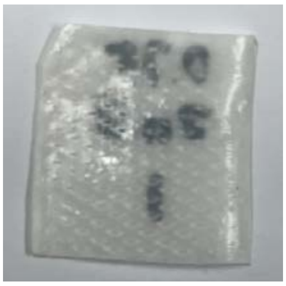
Sample	Type of UV Stabilizer	UV Treatment	Surface
4.5weeks 1%HALS1	HALS1	UV exposure 4.5weeks	
6weeks 1%HALS1	HALS1	UV exposure 6weeks	
Non UV 1.25%HALS1	HALS1	N/A	
1.5weeks 1.25% HALS1	HALS1	UV exposure 1.5weeks	
3weeks 1.25%HALS1	HALS1	UV exposure 3weeks	
4.5weeks 1.25%HALS1	HALS1	UV exposure 4.5weeks	

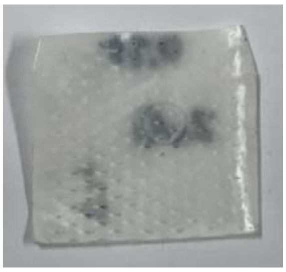
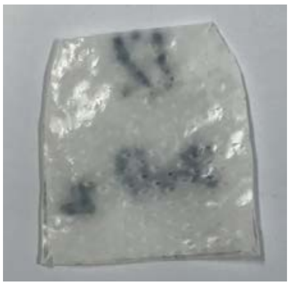
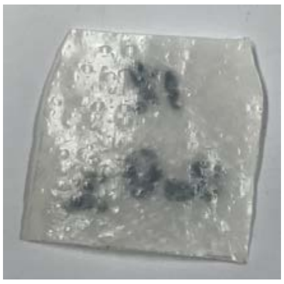
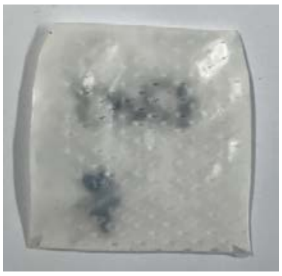
Sample	Type of UV Stabilizer	UV Treatment	Surface
6weeks 1.25%HALS1	HALS1	UV exposure 6weeks	
Non UV 0.5%HALS2	HALS2	N/A	
1.5weeks 0.5% HALS2	HALS2	UV exposure 1.5weeks	
3weeks 0.5%HALS2	HALS2	UV exposure 3weeks	
4.5weeks 0.5%HALS2	HALS2	UV exposure 4.5weeks	

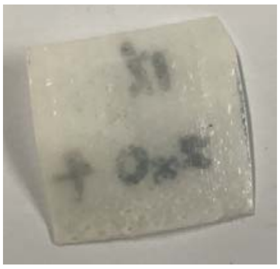
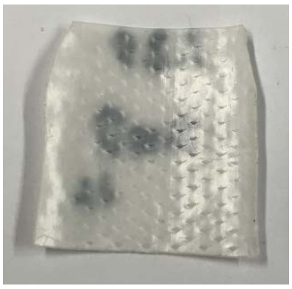
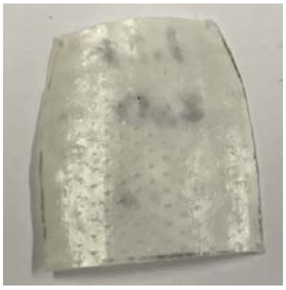
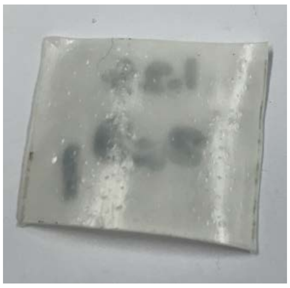
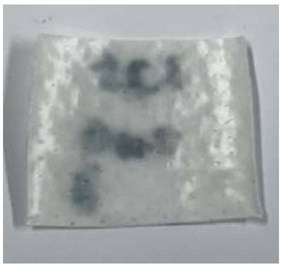
Sample	Type of UV Stabilizer	UV Treatment	Surface
6weeks 0.5%HALS2	HALS2	UV exposure 6weeks	
Non UV 0.75%HALS2	HALS2	N/A	
1.5weeks 0.75% HALS2	HALS2	UV exposure 1.5weeks	
3weeks 0.75%HALS2	HALS2	UV exposure 3weeks	
4.5weeks 0.75%HALS2	HALS2	UV exposure 4.5weeks	
6weeks 0.75%HALS2	HALS2	UV exposure 6weeks	

Sample	Type of UV Stabilizer	UV Treatment	Surface
Non UV 1%HALS2	HALS2	N/A	
1.5weeks 1% HALS2	HALS2	UV exposure 1.5weeks	
3weeks 1%HALS2	HALS2	UV exposure 3weeks	
4.5weeks 1%HALS2	HALS2	UV exposure 4.5weeks	
6weeks 1%HALS2	HALS2	UV exposure 6weeks	
Non UV 1.25%HALS2	HALS2	N/A	

Sample	Type of UV Stabilizer	UV Treatment	Surface
1.5weeks 1.25% HALS2	HALS2	UV exposure 1.5weeks	
3weeks 1.25%HALS2	HALS2	UV exposure 3weeks	
4.5weeks 1.25%HALS2	HALS2	UV exposure 4.5weeks	
6weeks 1.25%HALS2	HALS2	UV exposure 6weeks	
Non UV 0.5%Nano-ZnO	Nano-ZnO	N/A	
1.5weeks 0.5%Nano-ZnO	Nano-ZnO	UV exposure 1.5weeks	

Sample	Type of UV Stabilizer	UV Treatment	Surface
3weeks 0.5%Nano-ZnO	Nano-ZnO	UV exposure 3weeks	
4.5weeks 0.5%Nano-ZnO	Nano-ZnO	UV exposure 4.5weeks	
6weeks 0.5%Nano-ZnO	Nano-ZnO	UV exposure 6weeks	
Non UV 0.75%Nano-ZnO	Nano-ZnO	N/A	
1.5weeks 0.75%Nano-ZnO	Nano-ZnO	UV exposure 1.5weeks	
3weeks 0.75%Nano-ZnO	Nano-ZnO	UV exposure 3weeks	

Sample	Type of UV Stabilizer	UV Treatment	Surface
4.5weeks 0.75%Nano-ZnO	Nano-ZnO	UV exposure 4.5weeks	
6weeks 0.75%Nano-ZnO	Nano-ZnO	UV exposure 6weeks	
Non UV 1%Nano-ZnO	Nano-ZnO	N/A	
1.5weeks 1%Nano-ZnO	Nano-ZnO	UV exposure 1.5weeks	
3weeks 1%Nano-ZnO	Nano-ZnO	UV exposure 3weeks	
4.5weeks 1%Nano-ZnO	Nano-ZnO	UV exposure 4.5weeks	

Sample	Type of UV Stabilizer	UV Treatment	Surface
6weeks 1%Nano-ZnO	Nano-ZnO	UV exposure 6weeks	
Non UV 1.25%Nano-ZnO	Nano-ZnO	N/A	
1.5weeks 1.25%Nano-ZnO	Nano-ZnO	UV exposure 1.5weeks	
3weeks 1.25%Nano-ZnO	Nano-ZnO	UV exposure 3weeks	
4.5weeks 1.25%Nano-ZnO	Nano-ZnO	UV exposure 4.5weeks	
6weeks 1.25%Nano-ZnO	Nano-ZnO	UV exposure 6weeks	

2.5 Theories, Apparatus and Test Procedures

2.5.1 Tensile Tests

Mechanical properties tensile strength (TS), tensile elongation at break (E) and Young’s modulus (M) of the films were determined at room temperature using a Mariana Tensile (TestWorks@4, USA) according to ASTM D882[28]. Films were cut into dog bone shape strips 10*5*1mm (testing parts), and mounted between the corrugated tensile grips of the instrument. For PVC film samples, the initial grip spacing and cross-head speed were set at 50 mm and 0.1 cm/s, respectively. The tensile strength was expressed as the maximum force at break divided by the initial cross-sectional area of the film strip and the elongation at break.

The definition of Young’s modulus is the slope in stress-strain diagram within the region of elastic deformation and it is written as:

$$E = \sigma/\varepsilon \qquad (2)$$

where σ and ε represent elastic stress and elastic strain, respectively. Larger Young’s modulus means more external force is needed to elastically deform the sample. For strain at break, it refers to the degree of deformation at break and the expression is:

$$\varepsilon = \Delta L/L \qquad (3)$$

where ΔL and L represent the elongation at break and the initial length of sample, respectively. Obviously, the higher strain at break the sample has, the larger elongation takes place. Lastly, tensile toughness indicates how much energy is required to tear the sample and is represented by the area under the stress-strain curve.

2.5.2 Dynamic Friction Analysis

Tribology is a very broad area that includes the studies of friction, lubrication, wear, adhesion, scratch resistance and any interactions of multiple surfaces.[29-30] Dynamic friction is an important indicator and it is determined by using tribological tester produced by Nanovea Inc. The testing mode we chose was called “pin-on-disk” mode. As the name implies, a specimen is secured on a spinning disk and it is contacted with a stationary pin which is subjected to normally 5.0 N force while the machine is running. A SS302 stainless steel ball with 3.2 mm diameter is used as a pin in this work. During the testing, the total sliding distance is 75.36 m (6000 revolutions and a track with 2 mm radius) and the spinning speed is 200 revs/min.

2.5.3 Thermal Gravimetric Analysis (TGA)

TGA is an important method to study the effects of stabilizers worked on PP films. Thermal gravimetric analysis was carried out in a Micromeritics TGA (Micromeritics Instruments Corp., USA) in an N_2 atmosphere (50 mL/min) at a heating rate of 20℃/min. The samples were put into platinum pans and scanned from ambient temperature to 600 C. After temperature attaching 600℃, we keep temperature stable for 1min, and then cool down to room temperature.

2.5.4 Scanning Electron Microscope (SEM) Analysis

All kinds of samples under different temperatures were done SEM tests using TM3030 Plus Tabletop Microscope from Hitachi High-technologies Corporation 2014. Surface of all kinds of samples were scanned to see the influence of UV light on samples. The Everhart-Thornley detector is used—operated in the high vacuum mode with the electron accelerating voltage of 12.50 kV. We could not use higher voltage for higher resolution and magnification since PVC samples could not withstand the irradiation of such high-energy electron beam.

The major damages to polymers resulting from electron beams can be categorized into two types: heat and radiolysis. [26] For electron beam heating, the temperature of specimen raises due to the inelastic collisions of incident electrons and molecules in a specimen. The heating damage becomes worse for polymers since polymers generally have low thermal conductivity. Thus, heat dissipation is restricted and degradation or even melting may take place at elevated temperatures. For radiolysis damage, ionization decomposition is the mechanism. As the name ionization 14 indicates, the electrons in the molecules are excited to higher energy states but do not return to stable states. Consequently, the breakages of chemical bonds are generated and cause mass loss of light atoms such as hydrogen, nitrogen and oxygen.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Mechanical Properties

Stabilized PP (with HALSs, nano-ZnO and HALSs+nano ZnO combined UV stabilizers) films produced by extrusion showed a white and homogenous surface. Average thickness of plasticized PVC films is given in Table 3.1. The chemical modification of the stabilizer did not show a significant influence in film thickness compared to the unstabilized PP resins. After periods of time under exposure of UV lamp, HALSs stabilized and unstabilized PP components showed a little yellowish homogenous surface. However, nano-ZnO stabilized PP components' surface did not change.

Because pure PP films is very soft, so all components based on PP resins showed soft behavior with low Young's modulus and high elongation at break. Results of mechanical properties show (figs. 3.1 to 3.6) stabilized PP films gave wave like trend lines. Young's modulus of pure PP film first decrease as UV exposure time increasing, after exposed 4.5 weeks, pure PP film start to degradation and became brittle. Elongation at break showed pure PP film in general has been declining as UV exposure date increasing. Both Young's modulus and elongation at break trend lines of HALSs stabilized PP films showed wave like tendency because of the reaction cycle of HALSs as fig. 3.7 shows: HALS compound (1) is converted into the corresponding nitroxyl radical (2) as reactive species, which then traps a free radical under formation of an aminoether function (3). (3) interacts with a peroxide radical under formation of intermediate structures (4) which then decompose into harmless alcohols and ketones while the nitroxyl radical (2) is re-formed, this cycle help PP film to resist UV radiation for longer time than pure PP.

Slops of HALS1 and HALS2 samples changed before and after 1.5 weeks' UV exposure; Young's modulus of HALS1 and HALS2 samples showed crest after 3 weeks' UV exposure, which means HALS samples were experiencing step (2), (3) and (4) at 1.5, 3 and 4.5 weeks and would continue to obey the circulation. For pure PP samples, internal structure of them had been destroyed after 4.5 weeks' UV exposure but HALS UV stabilizers would prevent it by entrancing circulation in fig. 3.1. As loading level of HALS stabilizers increasing, mechanical properties of PP films turned more stable. However for nano-ZnO samples as shown in figs. 3.2 and 3.5, they did not change the pattern of pure PP samples much but just remit the influence of UV light on PP samples by reflecting it. So we can see as the loading level increasing the ability of reflecting UV light was stronger and 1.25wt.% of nano-ZnO was not high enough to influence the original tensile properties of PP films and this maximum needs further research. Figs. 3.8 to 3.11 show the stress and strain curves of different samples at 1.25wt.% after 6 weeks' UV exposure (including pure PP sample).

Table 3.1. Thickness of all components

Components	0.5wt.%HALS1	0.75wt.%HALS1	1wt.%HALS1	1.25wt.%HALS1
Thickness(mm)	0.5±0.01	0.4±0.03	0.4±0.05	0.5±0.02
Components	0.5wt.%HALS2	0.75wt.%HALS2	1wt.%HALS2	1.25wt.%HALS2
Thickness(mm)	0.5±0.03	0.5±0.04	0.5±0.05	0.5±0.01
Components	0.5wt.%ZnO	0.75wt.%ZnO	1wt.%ZnO	1.25wt.%ZnO
Thickness(mm)	0.5±0.03	0.5±0.01	0.4±0.03	0.4±0.02

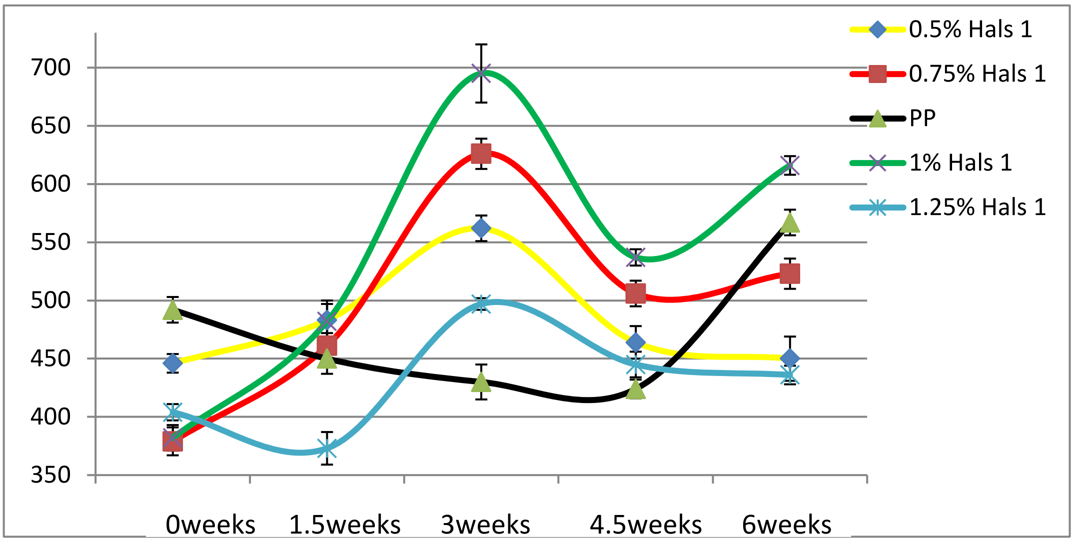


Fig. 3.1. Young's modulus (MPa) of HALS1 samples

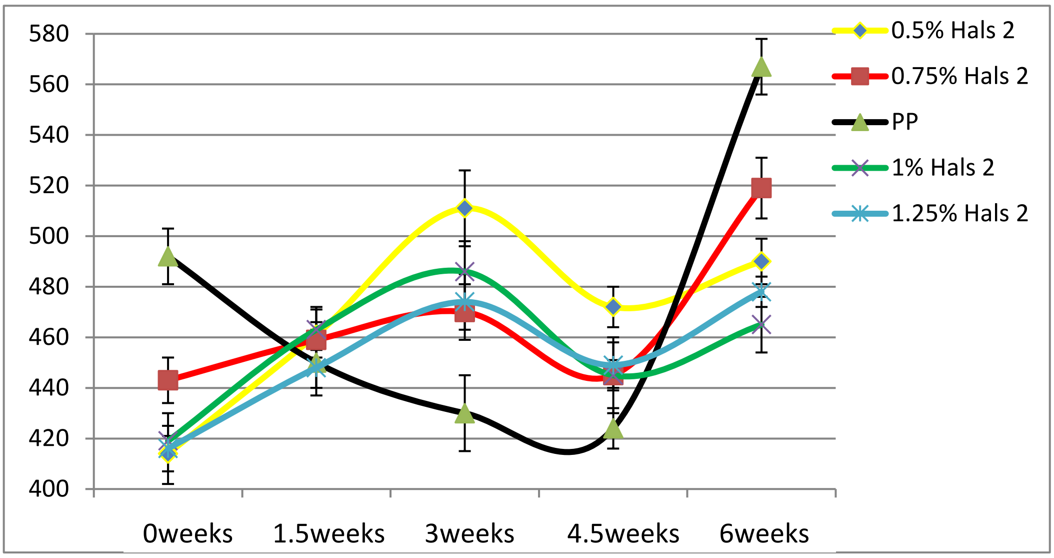


Fig. 3.2. Young's modulus (MPa) of HALS2 samples

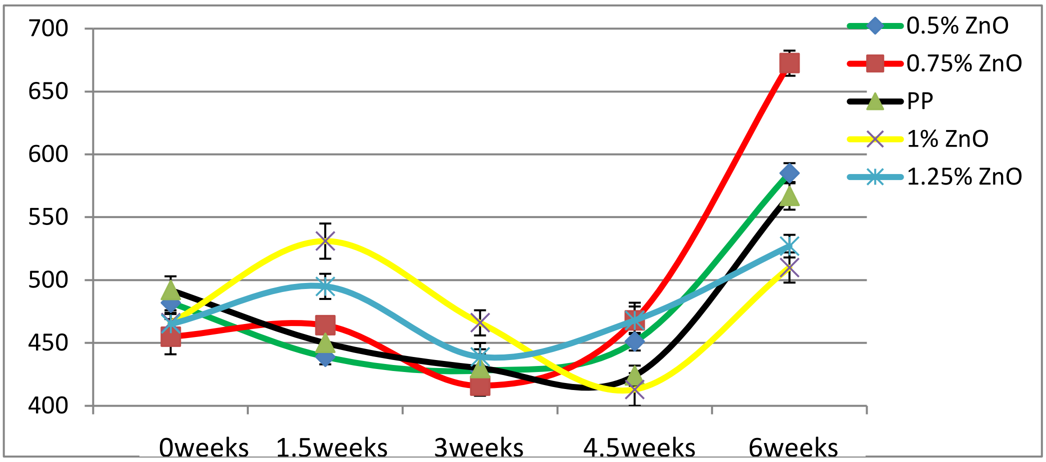


Fig. 3.3. Young's modulus (MPa) of nano-ZnO samples

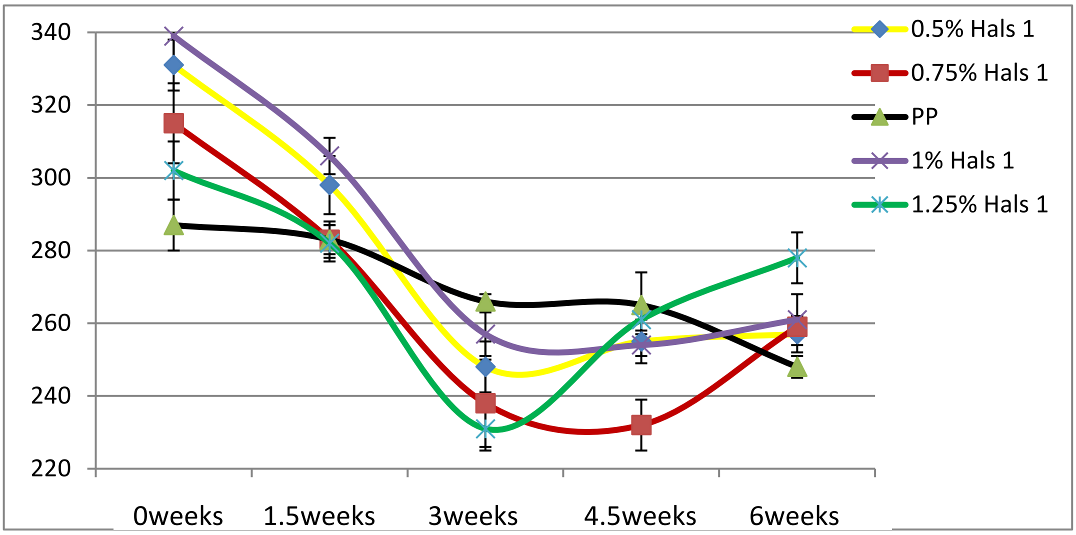


Fig. 3.4. Elongation at break (mm)of HALS2 samples

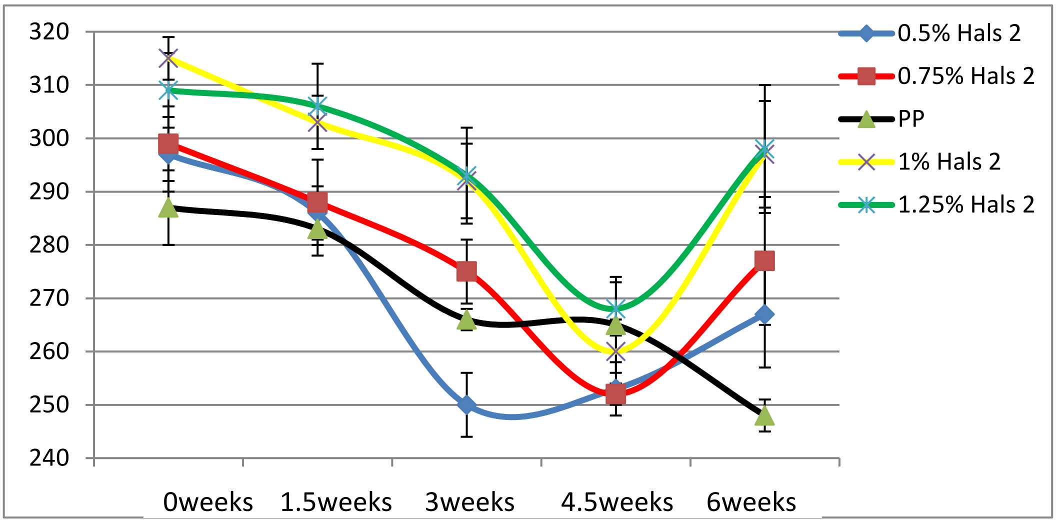


Fig. 3.5. Elongation at break (mm)of HALS2 samples

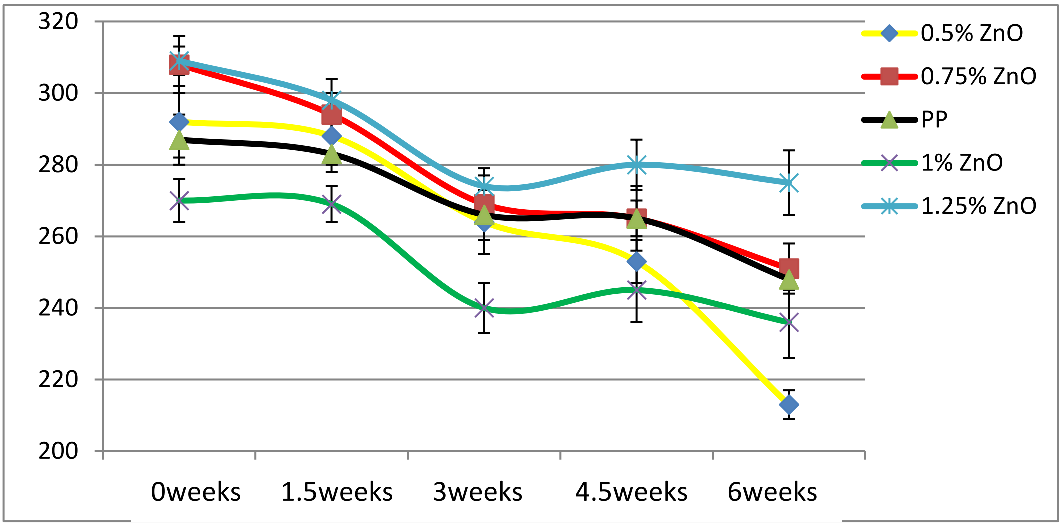


Fig. 3.6. Elongation at break(mm) of HALS2 samples

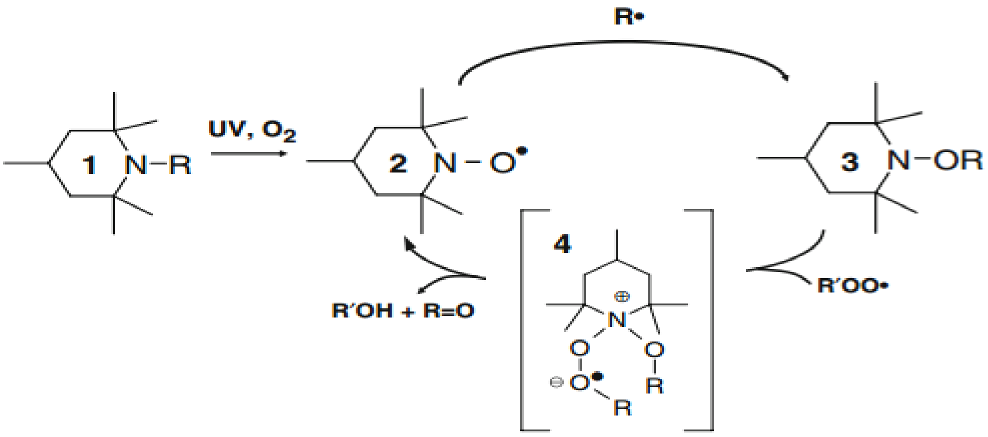


Fig. 3.7. Reaction cycle of HALSs stabilizers[31]

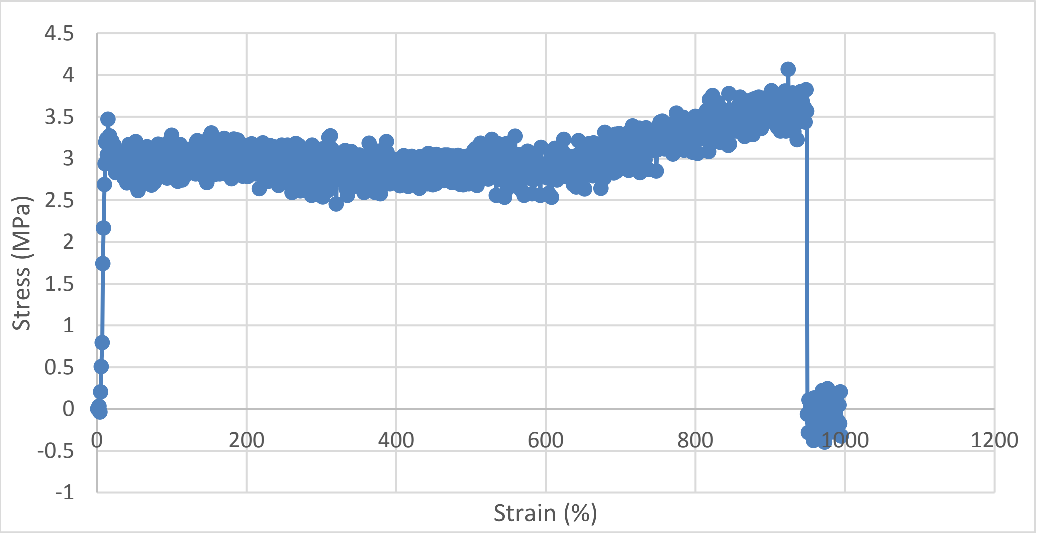


Fig. 3.8. Stress-strain curve of pure PP samples after 6 weeks' UV exposure

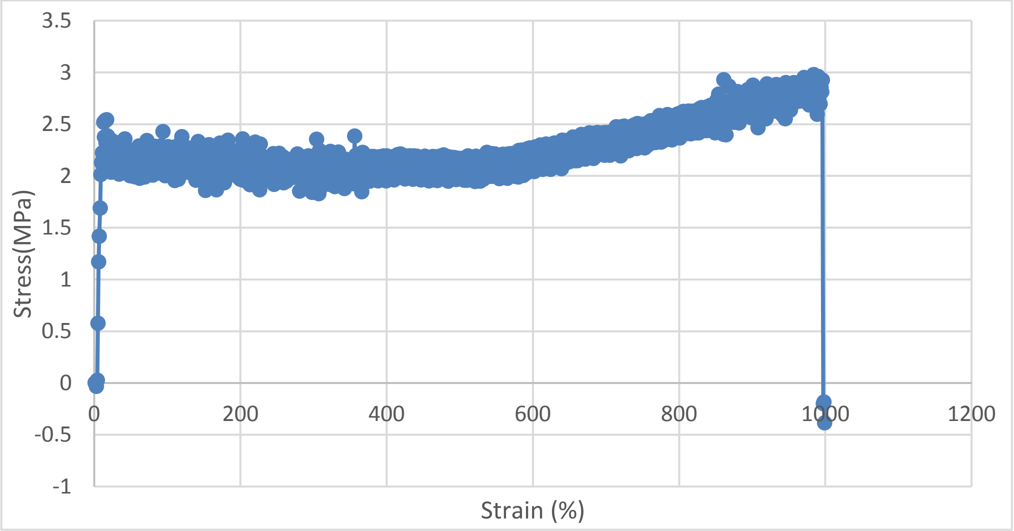


Fig. 3.9. Stress-strain curve of PP samples added HALS1 after 6 weeks' UV exposure

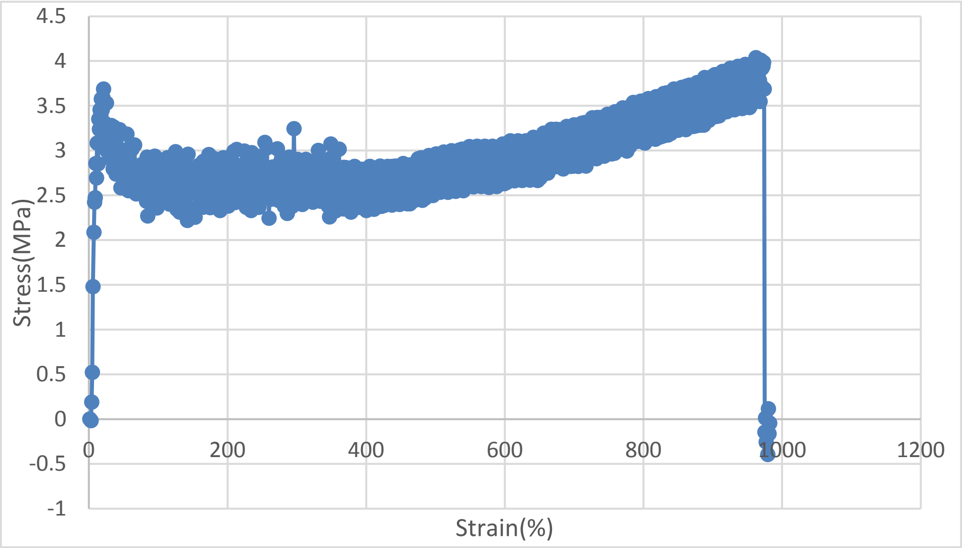


Fig. 3.10. Stress-strain curve of PP samples added HALS2 after 6 weeks' UV exposure

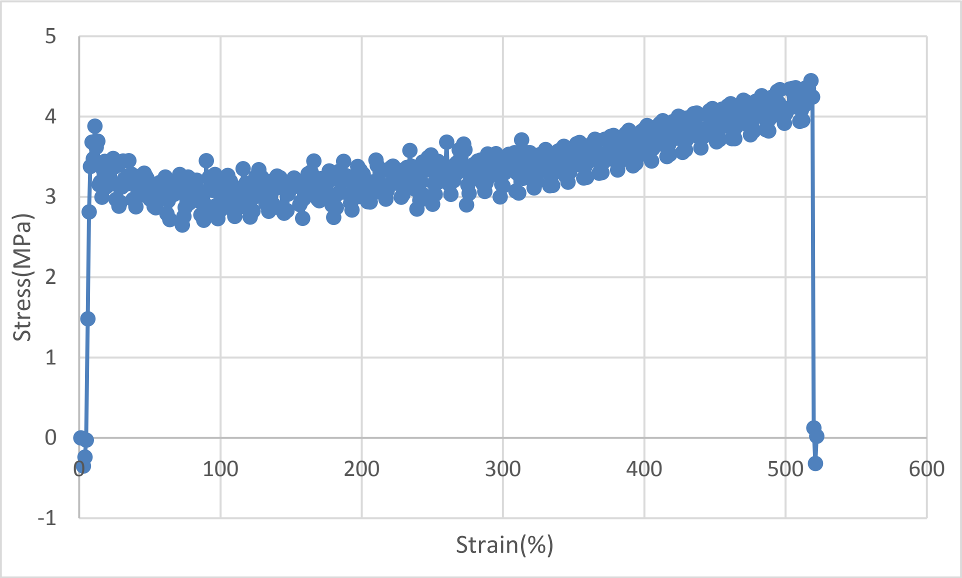


Fig. 3.11. Stress-strain curve of PP samples added nano-ZnO after 6 weeks' UV exposure

For researching if HALS and nano-ZnO has synergistic effects and influence each other, we also made 0.5wt.% nano-ZnO+0.5wt.% HALS1 and 0.5wt.% nano-ZnO+0.5wt.% HALS2 combined stabilizers added into pure PP films to see results. Young's modulus and elongation at break of combined UV stabilizers were shown in figs. 3.12 and 3.13 respecitvely. Adding nano-ZnO into HALS samples seemed make PP films harder but they still remained HALS'swave like patterns. Tensile properties of 0.5wt.% nano-ZnO+0.5wt.%

HALS2 samples seemed more stable than 0.5wt.% nano-ZnO+0.5wt.% HALS1 samples. This paper just studied 0.5wt.% nano-ZnO+0.5wt.% HALS situations, the influence of different concentration of nano-ZnO on different concentration of HALS needs further study.

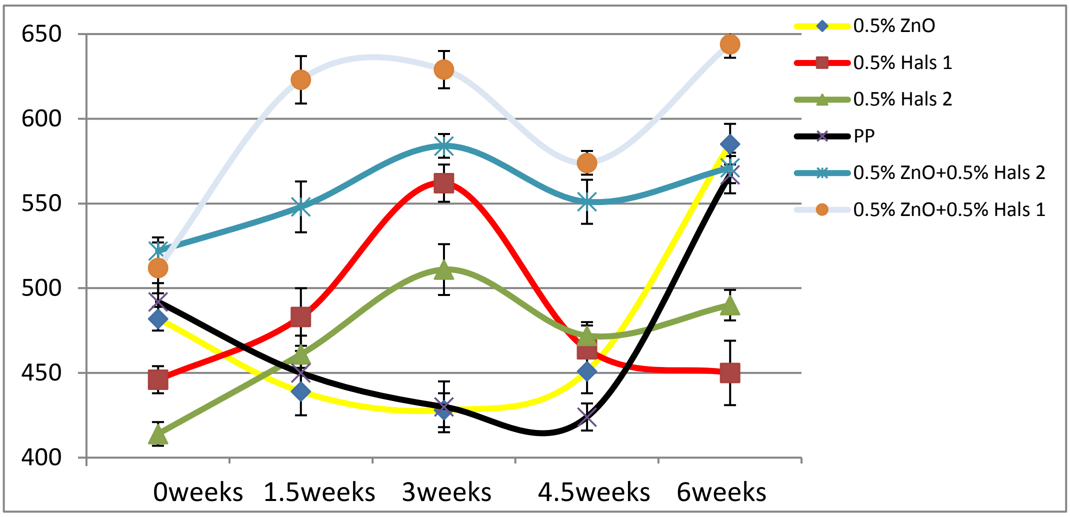


Fig. 3.12. Young’s modulus (MPa) of combined UV stabilizers

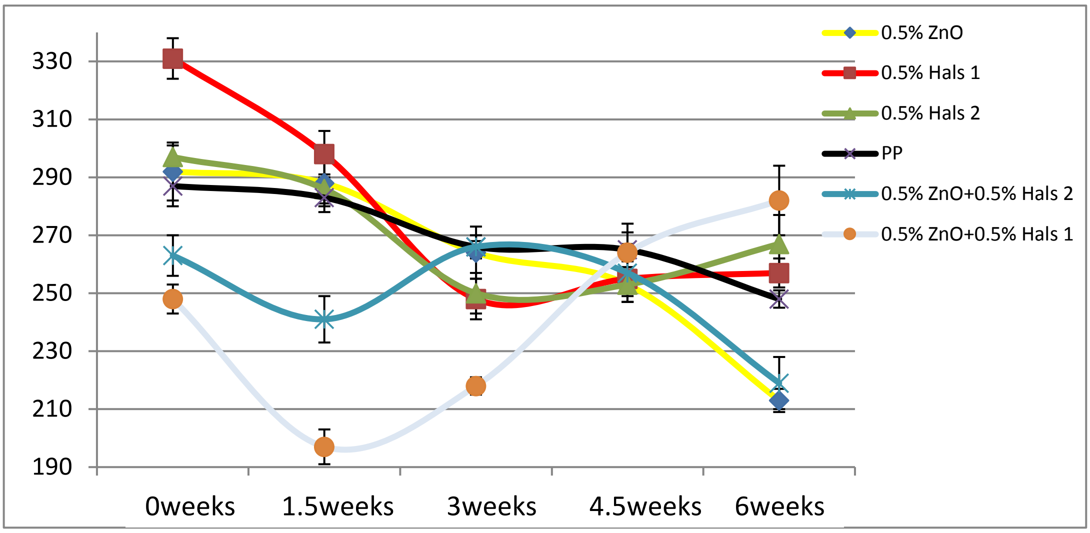


Fig. 3.13. Elongation at break(mm) of combined UV stabilizers

3.2 Dynamic Friction

As mentioned in Section 2.7, the friction is mainly affected by two factors: nature of the surface and type of the material. Figs. 3.14 to 3.16 showed dynamic friction fluctuation of PP films after different kinds of UV stabilizers adding into PP resin after different periods of

UV light exposure. Although the differences of dynamic friction of all samples were not too much, we can still observe some rules from the fluctuation. From fig. 3.14, we can see surfaces roughness of pure PP films would continue increasing which means under UV light, pure PP films' surfaces would become rough. Adding HALS1 stabilizers would make surfaces of PP films rough without UV exposure; after periods of UV exposure, the surfaces roughness would decrease; after 4.5 weeks' UV exposure, surfaces roughness of PP films added HALS1 stabilizers would recover but as the reaction circulation (talked above) exists, we assume the dynamic friction of HALS1 samples would decrease after 6 weeks' UV exposure. However, dynamic friction of pure PP films would keep increasing. From fig. 3.15 we can see dynamic friction of PP films with HALS2 UV stabilizers shared the same situation with HALS1 samples but when loading level of HALS2 stabilizer was o.5wt.%, it made PP films rougher than pure PP films when without UV exposure. From fig. 3.16 we can see adding nano-ZnO into PP films would make PP films rougher; after 3 weeks' UV exposure, dynamic friction of nano-ZnO added samples were lower than pure PP films; as dynamic friction of PP films would keep increasing after 6 weeks' UV exposure, we assume dynamic friction of nano-ZnO added samples would still lower than pure PP films.

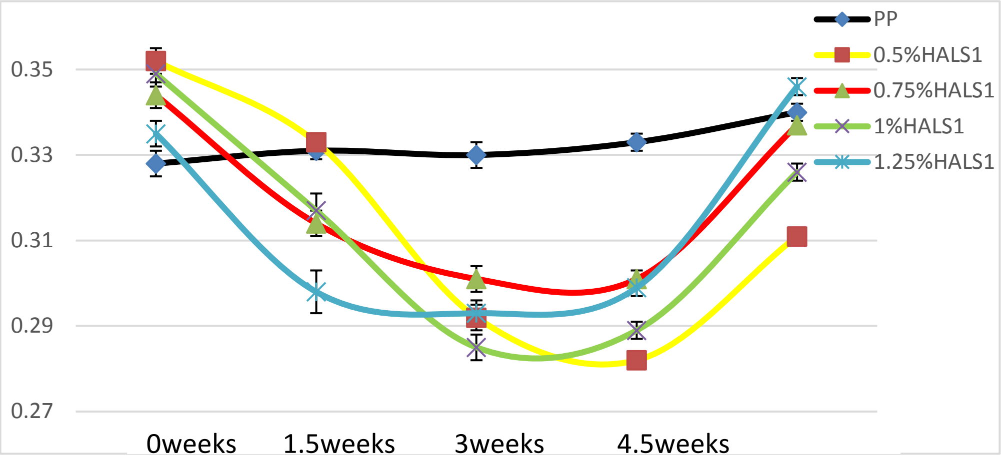


Fig. 3.14. Dynamic friction of pure PP and HALS1 samples

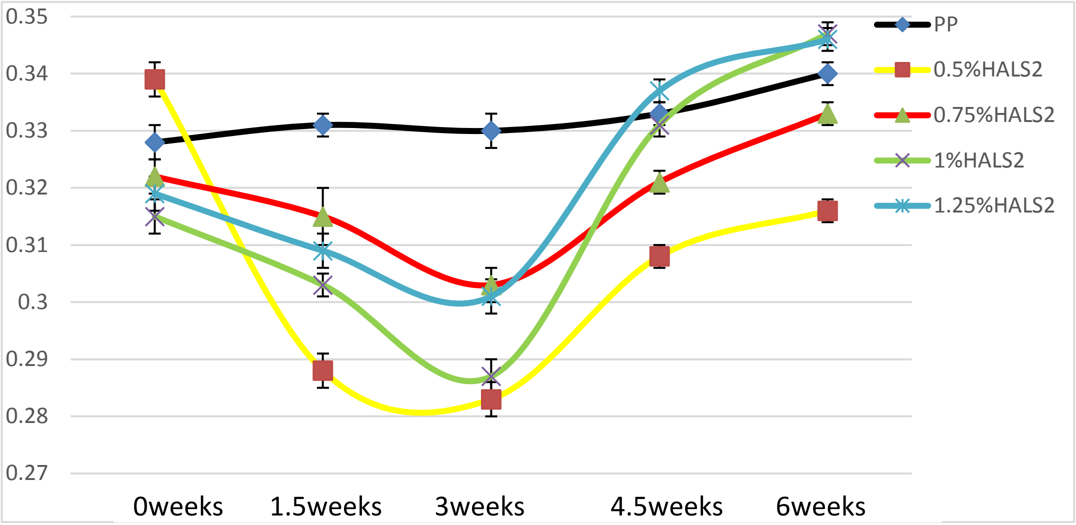


Fig. 3.15. Dynamic friction of pure PP and HALS2 samples

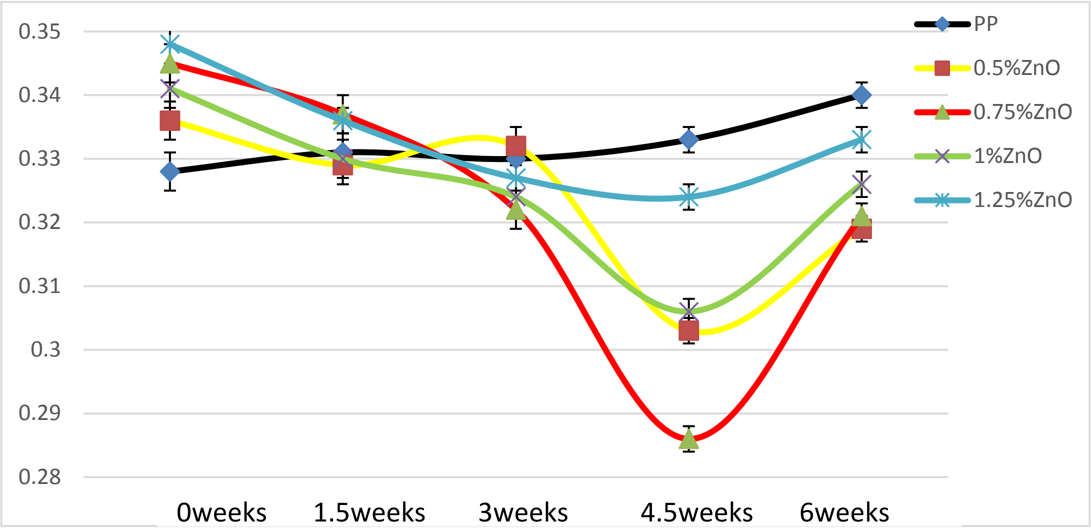


Fig. 3.16. Dynamic friction of pure PP and nano-ZnO samples

3.3 TGA Results

As shown in fig. 3.17 were the TGA curves of samples after 6 weeks' UV exposure. Because as loading level increases, mechanical properties of PP films seemed more stable for all UV stabilizers as we talked above, so we studied TGA curves of 1.25wt.% of HALS1, HALS2 and nano-ZnO. This study was aimed to see if UV stabilizer can help PP resin to remain thermal stability and keep thermal stability themselves after 6 weeks' UV exposure. From fig. 3.18, we can see although temperature of decompose peek of all samples did not have too much difference and they all around 447℃, after 6 weeks' UV exposure the 1.25wt.%HALS2 added PP films had the most thermal stabile property whose decompose peek was around 450℃.

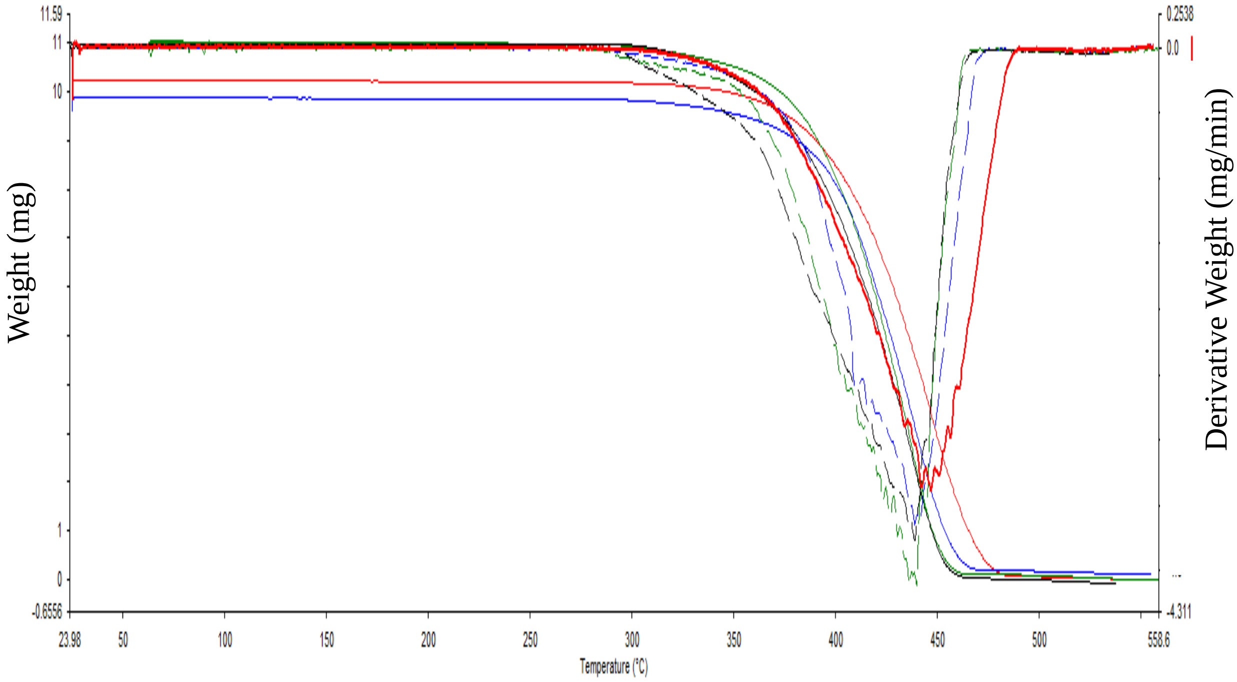


Fig. 3.17. TGA results of pure PP films (black), 1.25wt.%HALS1 added films (green), 1.25wt.%HALS2 added films (red) and 1.25wt.% nano-ZnO added films (blue)

3.4 SEM Results

SEM is a convenient method to understand how UV radiation and UV stabilizers change the structure of flexible PP; however, the limit of using high energy electron beam and high magnification is a disadvantage when polymers are concerned. We still can find some evidences of structure changes after different periods of UV exposure, although the UV stabilizers cannot be directly seen under a microscope. Figs. 3.18 to 3.20 show the SEM structure of fracture surface after tensile tests of pure PP, HALSs stabilized and nano-ZnO stabilized PP films respectively. For all figures, (1) represents films without UV exposure, (2) represents films after 3 weeks' UV exposure and (3) represents films under 6 weeks' UV exposure. From pure PP samples we can see, at first it showed compact fiber like structure and turned granular structure at 3 weeks, finally pure PP samples became brittle stone like micro structure which caused low tensile properties. HALS samples showed fiber like micro structure during all periods. Nano-ZnO showed granular structure at all periods.

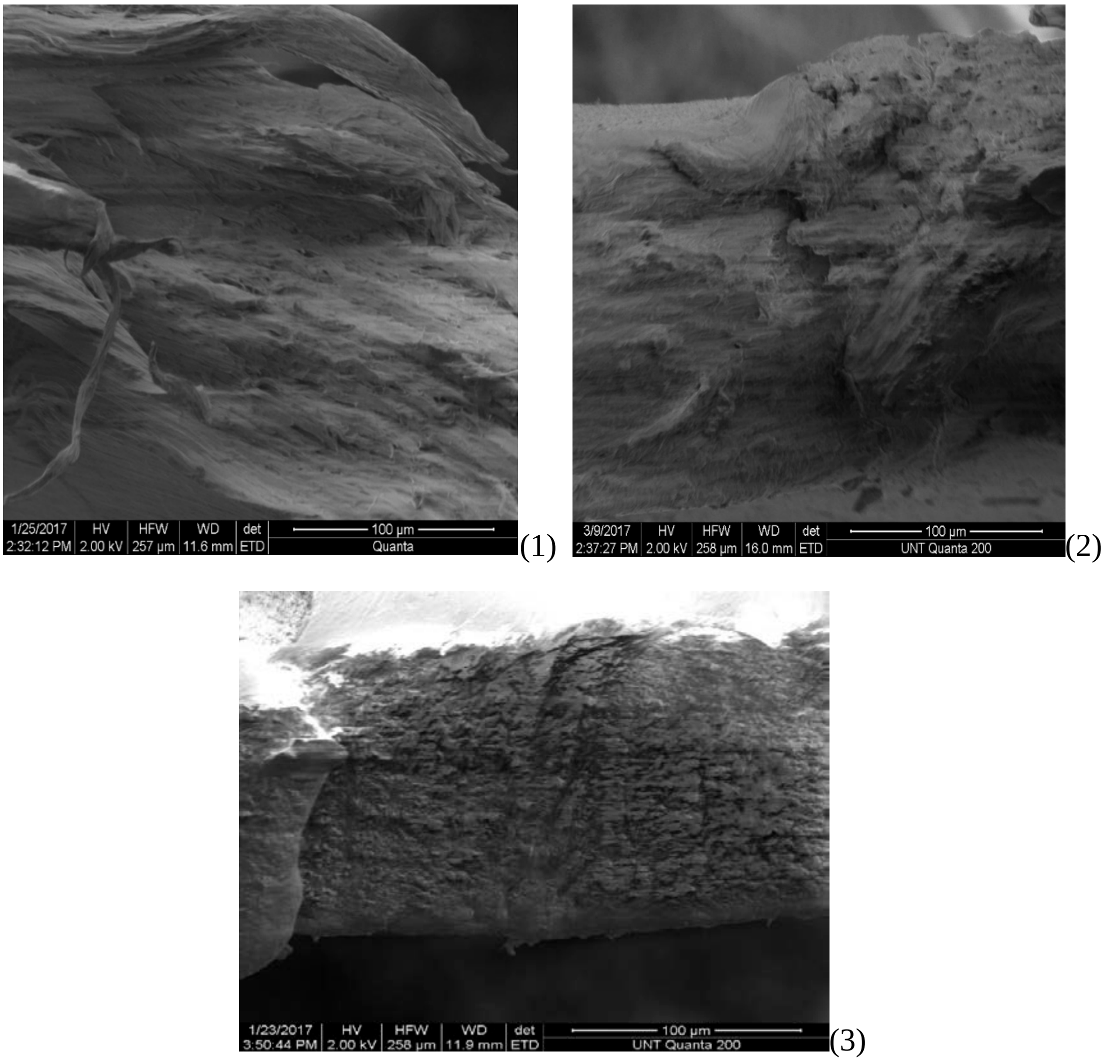


Fig. 3.18. SEM structure of pure PP films

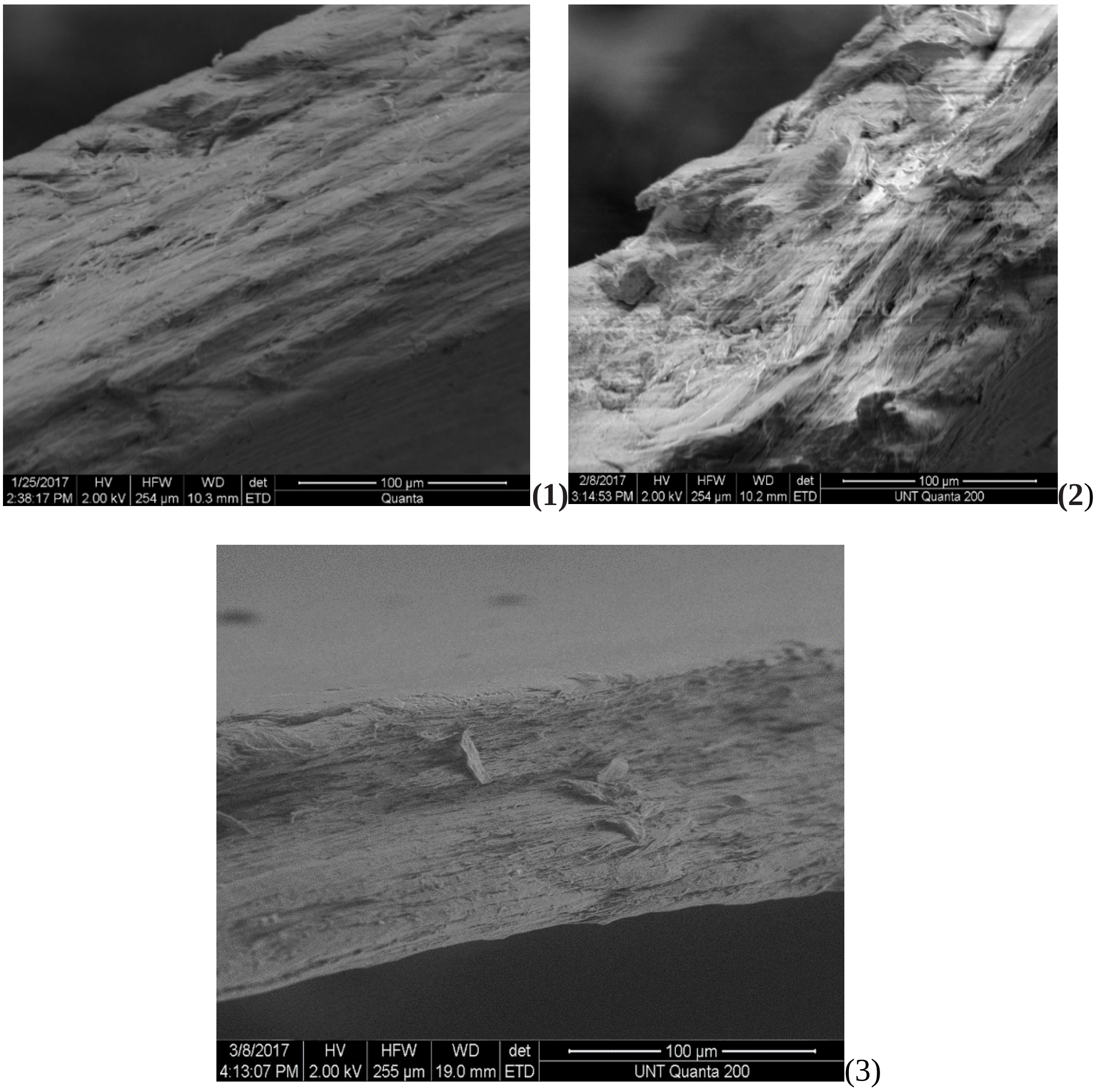


Fig. 3.19. SEM structures of PP films stabilized with 1.25wt.% of HALSs

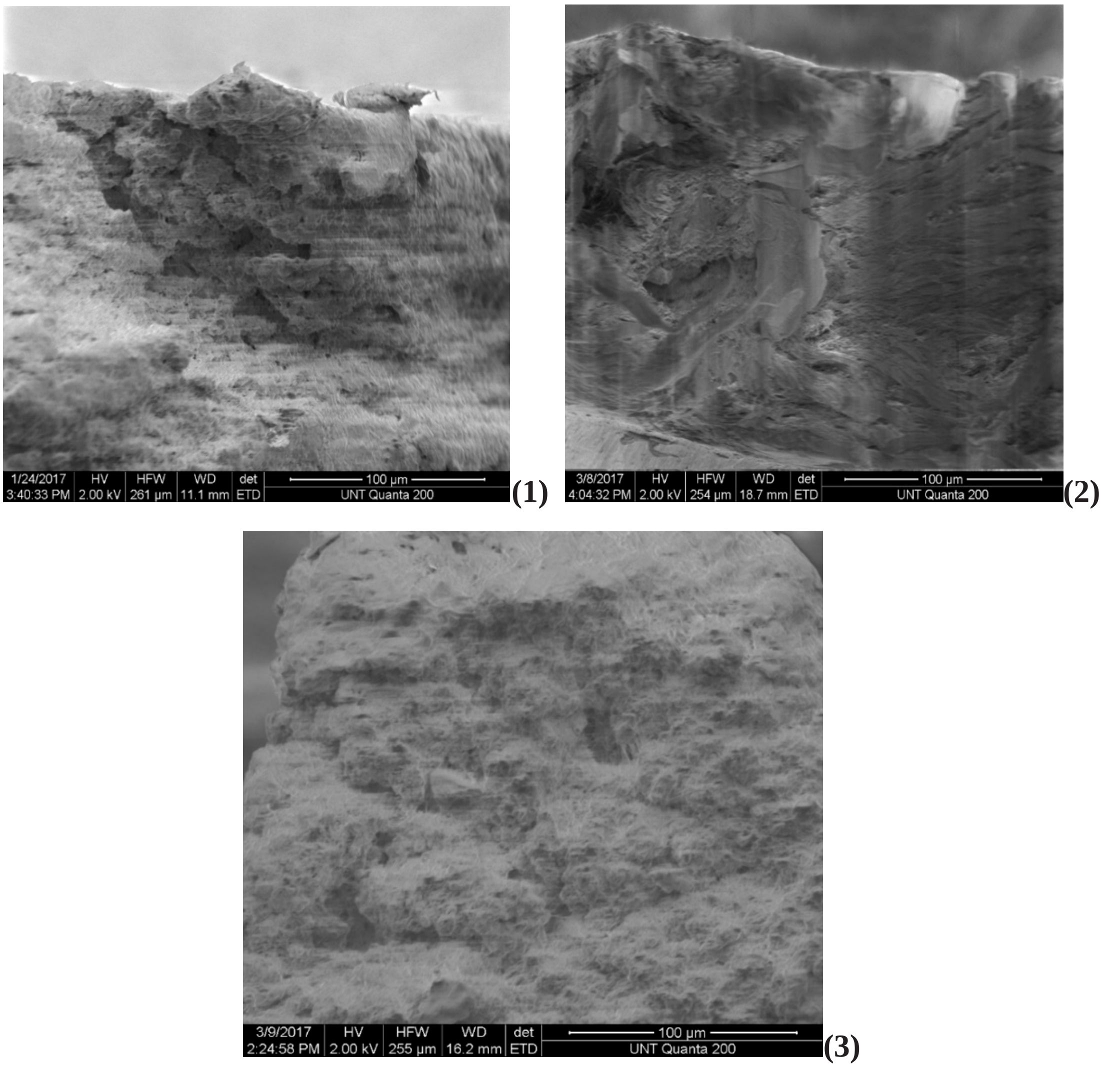


Fig. 3.20. SEM structures of PP films stabilized with 1.25wt.% of nano-ZnO

CHAPTER 4

CONCLUSIONS

Being one of the most popular plastics, PP is worth for scientists to do further researches and has gave us more convenient lives. However, until recent decades people started to aware of improving properties of PP under difference kinds of nature environment in order to keep human safe from danger and toxic of PP when they decomposed. In order to solve the problems, we must determine the most efficient fillers into PP products. In this study, three different kinds of UV stabilizers has chosen and blended with commercial PP. Our purpose is to achieve the most effective formula in order to improve the long-term performance of PP films.

According to the experimental results including mechanical properties, dynamic friction, TGA and SEM analysis, the effectiveness of UV stabilizers for different PP compositions was clearly presented. From the results we can generate several conclusions:

(1) Although nano-ZnO UV stabilizers can maintain appearance of PP films, the effects of UV resistance is no better than HALSs and as UV exposure time increasing, the effects would turn worse.

(2) HALS2 UV stabilizer can work better than HALS1 with PP resin resisting UV radiation in wire industry and has better thermal stability than HALS1and nano-ZnO stabilizers. HALS2 UV stabilizer is fit for PP processing like: wire industry. Nano-ZnO can hardly change or promote mechanical and thermal properties of PP, maybe when the loading level is more than 1.25wt.%, it will show obvious effects.

(3) Combination of HALSs and nano-ZnO stabilizers will make PP films harder which may fit in some plastic processing like wires and this needs further studies.

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