Preparation of PUV-3853 and Its Mechanical Properties in ABS Resin

Zhi-Xun LU¹, Shu Wang², Jie Chen¹, Qi Zhong Zhang¹, Wei Dong¹*

¹College of Materials Science and Engineering, Jilin Institute of Chemical Technology, Jilin 132022, People’s Republic of China
²China Huanqiu Engineering & Contracting Ltd. Co. Beijing Branch
Corresponding author: 546861954@qq.com

Abstract. This paper mainly studies the synthesis of polymeric hindered amine light stabilizers by copolymerization, UV3853 (2,2,6,6-tetramethyl-4-piperidine stearate) as monomer, styrene (St) as functional monomer, toluene is used as a solution, and the initiator is azobisisobutyronitrile (AIBN), and the hindered amine light stabilizer is synthesized by solution blending. The ABS composite is prepared by melt blending of the product and ABS pellets. The composite is tested for impact and tensile properties. The results show that when the addition amount of PUV-3853 is 0.1% (mass fraction), the mechanical properties of the composites are the best.

1. Introduction

Hindered amine light stabilizers (HALS) are currently the most widely used a class of light stabilizers with excellent light stability in polymer materials. In addition to its light stabilizing effect, HALS also has many functions such as anti-oxidation and absorption of ultraviolet rays[1-4]. UV-3853 uses a non-toxic, large molecular weight oleic acid group that retains photostability on the one hand and a double bond active group on the other hand can be bonded to the polymer backbone by chemical reaction to achieve a light stabilizer. The permanent "light stabilizing effect" can inhibit or slow down the degradation or aging of polymer materials due to photooxidation, while the relative molecular mass of PUV-3853 can improve the migration resistance, extraction resistance, precipitation resistance and resistance of light stabilizers. Heat and many other properties, reducing its loss due to physical effects[4].

Worldwide, hindered amine light stabilizers are the most widely used of all light stabilizers, with the highest sales being 44% of the total light stabilizer. Since the 1980s, new research products have been developed and applied in the research field of hindered amine light stabilizers [5]. According to statistics released in 1996, the annual consumption of the world's hindered amine light stabilizers accounted for 54% of the total light stabilizer consumption, and was still growing at an annual rate of 8% [6].

Since the 1980s, new products have been developed and applied in the research field of hindered amine light stabilizers [5], according to statistics released in 1996, the annual consumption of the world's hindered amine light stabilizers accounted for 54% of the total light stabilizer consumption, and is still growing at an annual rate of 8%, nowadays, hindered amine light stabilizers become the most widely used of all light stabilizers in the world.
2. Experimental part

2.1 Experimental materials and instruments

2.1.1 Experimental materials. 2,2,6,6-tetramethyl-4-piperidine stearate (analytical grade), molecular weight 423.7152, Wuhan Lanabai Pharmaceutical Chemical Co., Ltd.; azobisisobutyronitrile (AIBN) (analytical grade), Tianjin Damao Chemical Reagent Factory; styrene (analytical grade), Tianjin Yongda Chemical Reagent Co., Ltd.; toluene (analytical grade), Tianjin Kaixin Chemical Industry Co., Ltd.

2.1.2 Experimental equipment. 300OC electric blast drying oven, Shanghai Yiheng Scientific Instrument Co., Ltd.; HH-1 digital display constant temperature water bath, Jintan Huacheng Kaiyuan Experimental Instrument Factory; JC2000DM same-direction parallel twin-screw extruder, Shanghai Zhongchen Digital Equipment Co., Ltd. Company; SZ-SM1335 injection molding machine, Shenzhen Time Technology Development Co., Ltd.; WDW3010 micro control electronic universal testing machine, Changchun Kexin Experimental Instrument Co., Ltd.; Nicolet-6700 Fourier infrared spectrometer, American Nicolet; XJC-5D cantilever impact testing machine, Jinan Zhongluchang Testing Machine Co., Ltd.; Ubbelohde viscometer; GPC.

2.2 Experimental steps

2.2.1 Preparation of PUV-3853. 50 g UV-3853, 50 ml toluene, and a proportion of initiator were mixed in a 250 mL three-necked flask equipped with a motorized stirrer, reflux and thermometer. The compounds were heated under reflux with stirring, along with a certain amount of styrene was added dropwise in small portions. After the reaction was completed, the solvent toluene was distilled off under reduced pressure, the remaining solvent was cooled and crystallized at room temperature. The reaction equation is as follows:

\[
\text{PUV-3853} + \text{Styrene} \rightarrow \text{PUV-ABS}
\]

2.2.2 Preparation of ABS splines. PUV-3853 of 0.1%, 0.2%, 0.3%, 0.4% and 0.5%(mass fraction) were melt-blended with ABS pellets, and the ABS composite test strips were prepared by hot press forming. After standing at room temperature for 24 hours, the spline was subjected to impact and tensile experiments.
2.3 Test methods
Infrared spectrum analysis, gel permeation chromatography analysis, Ubbel viscometer analysis, tensile properties determination (measured according to GB/T 1040-2006), impact performance measurement (measured according to GB/T 1043.1-2008).

3. Results and discussion

3.1 PUV-3853 synthesis conditions

3.1.1 Determination of monomer ratio. The ABS resin is a terpolymer composed of acrylonitrile, butadiene and styrene. In order to make the product have a good compatibility with ABS, the functional monomer styrene was selected during the preparation of the product. Styrene/UV-3853 molar ratio selection: 0, 1/6, 1/5, 1/4, 1/3, 1/2, 1/1. The effluent time was determined by viscosity test under the same reaction conditions, and the longer the time flowing through the capillary, the higher the viscosity and the higher the molecular weight. The result is shown in Figure 1:

![Figure 1. styrene dosage and outflow time.](image1)

3.1.2 Determination of reaction temperature and time. According to the half-life of azobisisobutyronitrile, the experimental temperatures were selected at 61℃, 65℃, 69℃, 73℃ and 80℃ respectively. The viscosity test on PUV-3853 showed the highest viscosity of the product at 65℃. Therefore, it can be determined that the optimum temperature of the experiment is 65 ℃, the reaction time is 8 h, and the viscosity test results are shown in Figure 2:

![Figure 2. Reaction temperature and outflow time.](image2)

3.1.3 Determination of the amount of initiator. Azobisisobutyronitrile (AIBN) is the most commonly used azo initiator. AIBN is an oil-soluble initiator and is suitable for bulk polymerization, suspension polymerization and solution polymerization. AIBN has several advantages including it is relatively stable, safe to store and use, the decomposition reaction is relatively stable, only one kind of free radical is generated, and substantially no induced decomposition occurs, so it is often used for the
kinetic study for free radical polymerization. AIBN is a low-activity initiator whose decomposition temperature is 60–80°C and the decomposition activation energy is 129kJ/mol. Styrene 3853 mixed with the initiator in the proportions of 0.25%, 0.5%, 0.75%, 1%, 1.25% (molar ratio of initiator AIBN to raw material 3853) at 65 °C for 8 h. 10 ml toluene, the viscosity of different amounts of initiator was measured with a Ukrainian viscometer, and the result is shown in Figure 3:

![Figure 3. Initiator dosage and outflow time.](image)

As can be seen from the figure 3, when the dosage of initiator is 0.75%, the optimal dosage is used.

3.1.4 Infrared spectroscopy test. PUV-3853 was obtained by using azoisobutylonitrile (AIBN) as initiator at a reaction temperature of 65°C and a reaction time of 8 h. The results of the infrared experiments are shown in Figure 4:

![Figure 4. PUV-3853 infrared spectrum.](image)

The vibration value less than 1300 cm⁻¹ is the single bond, and the double bond vibration value between 1900-1500 cm⁻¹. C=C, C=O, N=O, C=N, etc. The vibration value is about 2400-2100cm⁻¹. For example, the absorption peak of carbon-nitrogen triple bond was generated by polyacrylonitrile(PAN) at 2240 cm⁻¹. C-H stretching vibration display a characteristic peak at 2875.8 cm⁻¹, carbonyl display the characteristic peak at 1719.6 cm⁻¹, intramolecular carbon-carbon double bond display the characteristic peak at 1636.5 cm⁻¹. The infrared spectra of the reaction product is shown in figure 4. According to the infrared spectral characteristics, we found that a new peak occurred at 1800-1700 cm⁻¹, indicating that the stretch vibration of C=C changed, indicating that chemical polymerization had taken place. After fracture, the peak becomes shorter, which indicates that the copolymerization of the polymer is obvious.
3.2 Mechanical properties

![Graph showing mechanical properties of ABS composites](image)

(a) Tensile strength  
(b) Impact strength

Figure 5. Mechanical properties of ABS composites.

It can be seen from Fig. 5(a) that when \( m(\text{PUV-3853})/m(\text{ABS}) = 0.1 \), the tensile strength is 45.41 KJ/m²; (b) it can be seen that when \( m(\text{PUV-3853})/m(\text{ABS}) = 0.1 \), the impact strength is remarkably improved. The tensile strength of ABS material before processing is 44.21 MPa, and the impact strength is 43.99 KJ/m². After PUV-3853 treatment, the tensile strength of ABS composite material can reach 45.23 MPa, and the impact strength can reach 48.32 KJ/m². The tensile strength of the composite material was increased by 2.31%, and the tensile strength of the composite material is increased by 9.84%, and the composite integration of the composite material is realized.

4. Conclusion

PUV-3853 was obtained when the reaction temperature was 65 °C, the reaction time was 8 h, and the amount of initiator was 0.75%.

PUV-3853 has good compatibility with ABS resin.

When PUV-3853 is added to 0.1% (mass fraction), the mechanical properties of the composite are optimal.

References

[1] Z.X.Lu, H.J.Yu, W.Dong. Research Review on Mechanism and Applicability of Hindered Amine Light Stabilizers[J]. Plastic Science and Technology, 2019, 47(04): 98-102.

[2] Geuskens G, Kabamba M. S. Photo−oxidation of polymers−Part V: A new chain scission mechanism in polyolefins, Polym. Degrad. Stab. 1982, 4(1): 69−76.

[3] Y. Ohkatsu, Search for unified action mechanism of hindered amine light stabilizers, Jpn. Pet. Inst. 51 (2008) 191-204.

[4] Z.Wang, P.S.Ning, Z.M.Ding. Research Progress of Hindered Amine Light Stabilizers[J]. Plastic Additives, 2012(01): 1-9.

[5] Wayne W.Y.Lau, J.Q.Pan, M.Yang. Polymeric Hindered Amine[J]. Plastic Additives, 2001(02): 1-7.

[6] Z.P.Zhang. Synthesis of Hindered Amine Light Stabilizer Tinuvin-770[J]. Hebei Chemical Industry, 1998(02): 43-45.