Possibility for the Light Stabilization of Polycaproamide for Fiber Production

N. Simeonov, S. Todorova

University of Chemical Technology and Metallurgy, Str. Kliment Ohridski 8, 1756 Sofia, Bulgaria

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ABSTRACT: A considerable setback of polyamide fibers, especially polycaproamidefibers (PCAFs), is their low light resistance. This leads to changes in their appearance and their physicomechanical parameters under ambient atmosphere conditions and as a result of the effect of sunlight. This setback could be compensated to a certain extent by the introduction of suitable light stabilizers in the fiber mass. Depending on its efficiency, each light stabilizer is added at a concentration of 0.2–5% with respect to the mass of the polymer. We have investigated two possibilities for introducing the light stabilizer into the fiber mass. In the first one, the composition was finished immediately after the fiber spinning, and in the second one, polycaproamide granules were processed with a solution of light stabilizers before their melting. J Appl Polym Sci 100: 4921–4924, 2006

Key words: polyamide fibers; light stabilization; light stabilizer

Polyamide fibers and especially polycaproamide fibers (PCAFs) possess a specific complex of valuable properties, such as high mechanical strength, elasticity, wear resistance, and resistance to microorganisms, which lead to their widespread applications in techniques and for everyday needs.

Besides these valuable characteristics, PCAFs exhibit certain significant setbacks; one of them is their low light resistance. This leads to changes in their appearance and their physicomechanical parameters under ambient atmosphere conditions and as a result of the effect of sunlight.[1,2]

This setback could be compensated to a certain extent by the introduction of suitable light stabilizers in the fiber mass. Depending on its efficiency, each light stabilizer is added at a concentration of 0.2–5% with respect to the mass of the polymer.[3]

There exist two main groups of light stabilizers according to the mechanism of their activity:[1]

1. Light stabilizers that inhibit the reactions characterizing the processes of aging. These are the substances that link the free radicals originating in the polymer as a result of light irradiation or that interact with the products from the polymer transformation, such as hydroperoxides, leading to the formation of compounds with higher light resistance. These can also react with the polymer macromolecules at the location of their reactive links and end links, which are mainly attacked by light.
2. Light stabilizers that are characterized by their ability to absorb light in the ultraviolet (UV) spectrum and transform it into heat that does not affect the fibers. These compounds are so-called UV absorbers. They prevent the formation of excited states in the polymer molecules. Maximum efficiency is exhibited by the light stabilizers that absorb UV light of almost the same wavelength as the polymer.[4,5]

A number of substances that can be used to a lesser or greater extent than UV absorbers are being produced in or imported into Bulgaria.

The basic characteristics of some of them are presented in Table I.

It is interesting to investigate the possibility of using these substances for the light stabilization of PCAFs.

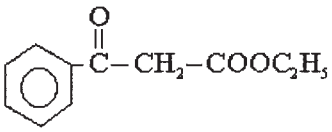
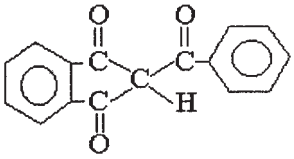
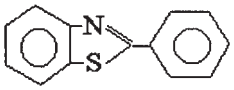
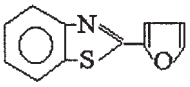
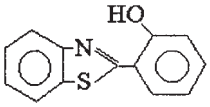
In a number of experiments, we followed the effects of ethyl ester of benzoyl acetic acid (EEBA) and 2-benzoyl 1,3-indiandine (SA-10) on the light resistance of PCAFs.

Taking into consideration the production scheme of the PCAFs, we studied two possibilities for introducing the light stabilizer into the fiber mass: in the first one, the composition was finished immediately after the fiber spinning, and in the second one, polycaproamide (PCA) granules were processed with a solution of light stabilizers before their melting.

The following was necessary for the realization of these experiments:

Correspondence to: N. Simeonov (nsimeonov@gbg.bg).

TABLE I
Basic Characteristics of Some Light Stabilizers

Symbol	Formula	Name	Solubility		Temperature of melting (°C)
			Water	Organic solvent	
EEBA		Ethyl ester of benzoyl-acetic acid	No	Heptane	—
SA-10		2-Benzoyl-1,3 indiandine	No	Ethanol, acetone	109
BI-1		2-Phenile benztiazole	No	Ethanol	114
BI-2		2-Furyl-benztiazole	No	Ethanol	105
BI-3		2-2-Hydroxyphenile benztiazole	No	Ethanol	125

*

1. Investigating the possibility of the preparation of stable emulsions of light stabilizers dissolved in the respective organic solvent with the finishing of the composition.
2. Studying the stability of the light stabilizers upon heating to the temperature of spinning (T_Φ) of PCAFs.

Stable emulsions were prepared with a non-ionogenic dispersive agent on the basis of polyglycoethers of high fatty alcohols.

Samples of PCAFs whose surfaces were treated with the light stabilizers EEBA and SA-10 were UV-irradiated under standard conditions for 150 h.

The changes in the parameters mostly affected by light—the whiteness, strength, and elongation—were determined as percentages of the initial values. The results are presented in Tables II and III.

Significant changes in the appearance of the fibers were observed by the 50th hour of the irradiation. After that, the respective parameters changed slowly, reaching their final values. The investigated substances showed a certain light-stabilizing effect, but it was comparatively weak, probably because of the too intensive irradiation.

It was necessary to study the resistance of the light stabilizers with which the PCAFs were treated to washing and similar types of wet processing. In the case of nonirradiated fibers, the stabilizers were not stable and were washed away from the fibers. In the case of fibers irradiated for over 50 h, however, the light stabilizers could not be extracted. Probably in the process of irradiation, some interaction took place between the light stabilizers and PCAFs.

Another possibility of introducing the UV absorbers into the fibers was also investigated: in the PCA granules before their melting. To remain active, the stabilizers had to be heat resistant up to T_Φ of the fibers, that is, 275°C.

The heat resistance of the investigated substances was determined by differential thermal (DT) and thermogravimetric (TG) analysis. The results are shown in Figures 1 and 2, respectively.

The results of these analyses showed that SA-10 could be used for introduction into the PCA granules. At 280°C, it lost only 4% of its mass, and this could

TABLE II
Changes in the Whiteness as a Percentage of the Initial Value as a Result of the UV Irradiation of PCAF

Sample	Irradiation (h)				
	10	25	50	100	150
1	18.34	41.62	62.80	69.91	74.26
2	15.68	37.54	56.96	60.31	64.23
3	14.13	35.97	55.36	58.78	62.83

1 = PCAF not subjected to additional processing; 2 = PCAF treated with EEBA (2% from the mass of the fibers); 3 = PCAF treated with SA-10 (2% from the mass of the fibers).

TABLE III
Reduction in the Strength (*R*) and Elongation (*E*) after the UV Irradiation of PCAF

	Irradiation									
	10		25		50		100		150	
Sample	*R* (%)	*E* (%)	*R* (%)	*E* (%)	*R* (%)	*E* (%)	*R* (%)	*E* (%)	*R* (%)	*E* (%)
1	43	32	57	64	77	87	82	90	81	92
2	36	27	53	48	76	84	78	88	78	89
3	35	28	51	45	72	82	79	85	75	86

The percentages are from the respective values for the nonirradiated PCAF. 1 = PCAF not subjected to additional processing; 2 = PCAF treated with EEBA (2% from the mass of the fibers); 3 = PCAF treated with SA-10 (2% from the mass of the fibers).

have been due to its humidity; up to that temperature, the DT curve did not show any processes leading to significant changes in its chemical structure.

To prove these results, the UV spectra of SA-10 were obtained after heating to temperatures determined from the DT curve. The spectra shown in Figure 3 show that SA-10 was stable enough under heating and could be added to the PCA granules. The other products exhibited significant mass losses under heating, and that made them unsuitable for addition to melted PCA.

The addition of light stabilizers to the melt was made in the following way: the PCA granules were treated with an acetone solution of SA-10, and then the acetone was evaporated. The prepared granules contained 1.5 or 3.9% stabilizer.

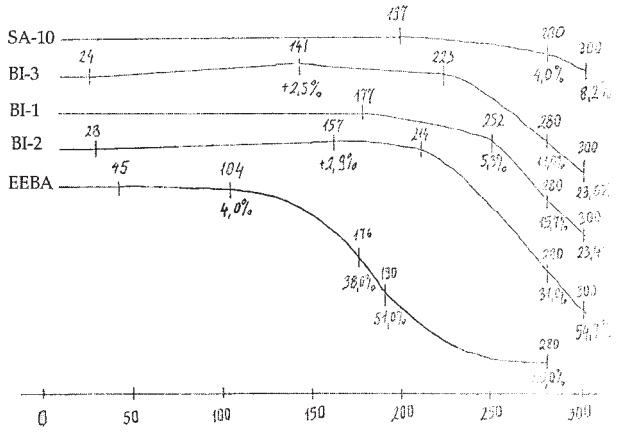


Figure 1 TG curves of the investigated light stabilizers.

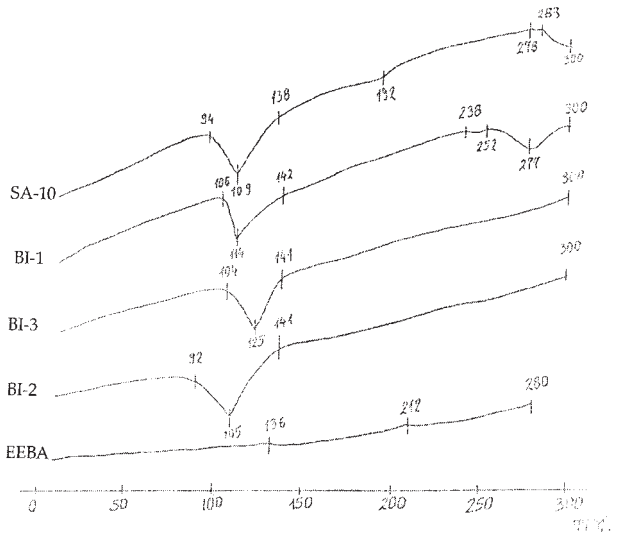


Figure 2 DT curves of the investigated light stabilizers.

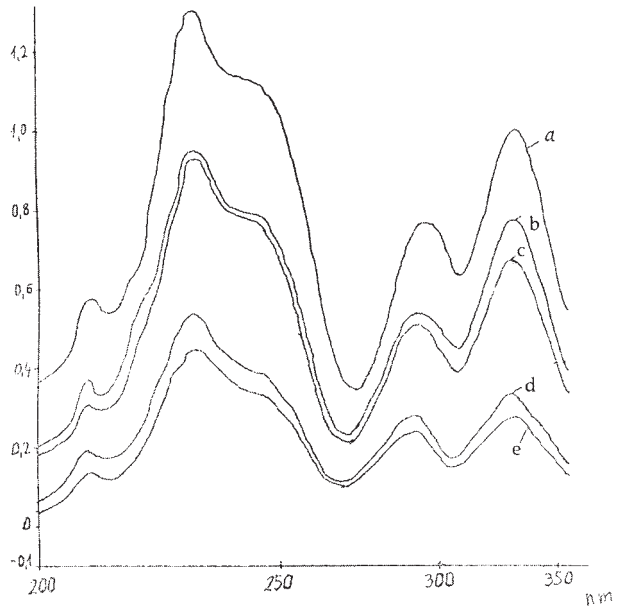


Figure 3 UV spectra of SA-10: (a) no heating, (b) heating to 110°C, (c) heating to 175°C, (d) heating to 192°C, and (e) heating to 280°C.

TABLE IV
Maximum Degree of Elongation (%) for PCAF with Different Contents of the Light Stabilizer SA-10

Sample	Light stabilizer (%)	Irradiation (h)				
		0	10	20	30	40
1	0	837	539	500	446	343
2	1.5	760	735	719	711	700
3	3.9	864	829	813	805	791

TABLE V
Reduction of the Mechanical Strength (*R*) and Elongation (*E*) Depending on the Period of Irradiation of PCAF with Different Contents of the Light Stabilizer SA-10

Sample	Light stabilizer (%)	Irradiation (h)							
		10		20		30		40	
		R (%)	*E* (%)	*R* (%)	*E* (%)	*R* (%)	*E* (%)	*R* (%)	*E* (%)
1	0	17.7	19.5	28.1	37.3	35.0	42.3	45.7	65.1
2	1.5	15.2	12.6	19.4	15.5	21.4	19.7	24.5	24.7
3	3.9	12.1	8.8	15.7	12.3	17.7	15.6	19.8	20.5

At the same time, the granules were treated with acetone only, without any stabilizing agent, so all the samples were under the same conditions. From all these granules, fibers were spun on Brabender laboratory equipment under the following conditions:

- For granules without a light stabilizer, a T_Φ value of 275°C, a velocity of spinning (V_Φ) of 2.7 m/min, and filler drawing of 175%.
- For granules containing 1.5% light stabilizer, a T_Φ value of 265°C, a V_Φ value of 1.1 m/min, and filler drawing of 588%.
- For granules containing 3.9% light stabilizer, a T_Φ value of 265°C, a V_Φ value of 0.56 m/min, and filler drawing of 1240%.

In the spinning process, it was established that the samples containing a light stabilizer had lower T_Φ, and this meant that the light stabilizer exerted a plasticizing effect. Moreover, the viscosity of the melt was reduced, and the produced fibers had different cross sections.

Samples from the fibers were UV-irradiated for 40 h. Every 10 h, the fibers were tested for their physicomechanical parameters, the average degree of polymerization (ADP), and the possibility of orientation by drawing. The results are presented in Tables IV–VI.

The results obtained for the possibility of orientation by drawing, the changes in the mechanical parameters, and the ADP of the fibers after irradiation proved the light-stabilizing effect of the product SA-10. The intensive irradiation did not reveal the real light-stabilizing effect of the product under ambient conditions, which should be expected to be much better expressed.

TABLE VI
Changes in the ADP of PCAF with Different Contents of the Light Stabilizer SA-10 Depending on the Period of Irradiation

Sample	Light stabilizer (%)	Irradiation (h)				
		0	10	20	30	40
1	0	529	446	417	398	364
2	1.5	501	483	465	448	431
3	3.9	498	486	471	463	450

The investigations led to the following conclusions:

- The substances synthesized as UV absorbers proved to a different extent their light-stabilizing effects in the case of PCAFs. The strongest light-stabilizing effect was exhibited by the product SA-10.
- To evaluate qualitatively the light-stabilizing effect of the products, it was necessary to investigate the aging of the fibers under standard atmospheric conditions.
- The UV absorber SA-10 exhibited a certain plasticizing effect in the PCA melt.
- The addition of more than 1.5% SA-10 in PCA made possible orientation by the drawing of PCAFs even after UV irradiation for 40 h.
- SA-10 exhibited its light-stabilizing effect in PCAFs both after the treatment of the surface of the fibers with it and after its addition to the PCA mass.

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