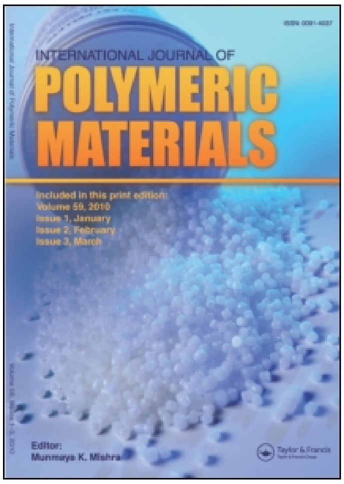

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A Comparison of Structural and Physical Changes of Polymers After Diffusion Stabilization From Polar and Non-Polar Media

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We present a comparative analysis of structural changes in the surface areas of diffusion-stabilized polymers, and of the corresponding changes in their mechanical and physical behaviour. The study yielded original data on the influence of diffusion compositions on stability and other properties of polymers.

KEYWORDS: Diffusion stabilization, structure, physical properties, nylon-6, x-ray analysis

Problems related to the choice of stabilizers and of their application techniques are still very important.[1] It was found experimentally, that stabilizers introduced by diffusion techniques open the ways of inhibiting destruction-related processes, and of supplying controlled effects to the surface layers of block polymers. So far, our attention was focused on diffusion from liquid solutions of a stabilizer and a solvent which acts as a plasticizer.[2] This is a two-stage process: first the solution is diffused in the polymer, and later it is fixed by a thermal treatment in air.[2,3] Suggestions on the stabilizing compositions and on technologic conditions are described elsewhere.[2,4]

Our studies with Nylon-6 indicate a transformation of a less stable crystalline structure to a more stable one, as the essential part of the process. The result is a more stable crystalline surface and an improved physical and mechanical resistance.

There exists no unique approach to the analysis of X-ray diffraction patterns of Nylon-6. The analysis presented in[2,5–7] which included a survey of examination techniques for Nylon-6, leads to a conclusion, that in block samples of Nylon-6 and especially in their surface layers in the absence of special treatments diffusion results in imperfect crystalline structures. Such polymers are subject to structural modifications under physical and chemical loads.[2,3,8,9] In the present study we maintain[2,5] that a metastable pseudo-hexagonal γ'-phase is formed on surfaces of

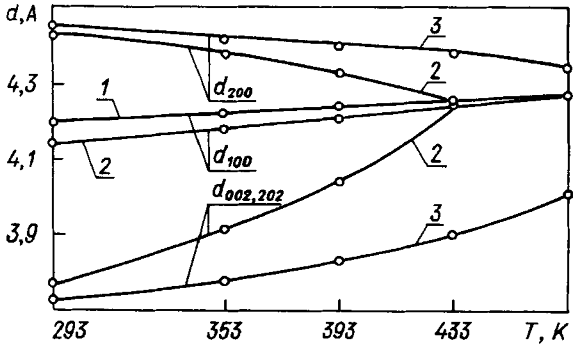

FIGURE 1 Change of inter-plane distances in untreated (1) and treated by poly-β-naphthol (2) and by 1,4-dihydroxy-benzene (3) Nylon-6 under an increase of temperature.

Nylon-6 blocks. It is easily subject to α transformation. Therefore diffusion stabilizers work mainly through the $\gamma' - \alpha$ transformation. But α-phase of block Nylon-6 is an imperfect crystal structure either,[2,5,6] so that its lattice is apt to change under a high heat load.[5,10] The changes lie in smaller distances between the main interference lines (200) and (002) of α-phase and in their approach to interference lines (100) of γ'-phase. It appears that α-phases resulting from $\gamma' - \alpha$ transformations due to different stabilizers have different thermal resistance rates.[11] So α-phase built by diffusion of a 5 per cent solution of poly-β-naphthol in ethanole and by a subsequent thermal treatment is not stable, and higher temperatures lead to significant changes of inter-plane distances d_{200} and $d_{002,202}$. But a stable α-phase may be introduced into Nylon-6 by a similar process with 1,4-dihydroxy-benzene (Figure 1).

Diffusion stabilization of filled polymers poses new problems. It has been shown[12] that in glass-reinforced Nylon-6 side effects of higher internal stress and lower impact elasticity are possible. Analogic effects have been observed in polymers with dispersed fillers under a diffusion stabilization. In our study we have applied to Nylon-6 titanium dioxide (1 per cent weight) as a well known structural agent, and metallurgical powder slag (10 per cent weight). The subsequent X-ray diffraction patterns (Table I) show that titanium dioxide improves the surface crystal structure on the account of γ'-phase. In the slag-filled polymer, the filler concentration exceeds its optimal value, so that regularity of the surface structure is similar to that unfilled polymers.

TABLE I

Crystal structures of modified Nylon-6

Filler	Treatment	Crystallinity, %	Modified fraction, %	
			γ'	α
Non-filled	Reference	18	18	—
	Diffusion stabilized	28	3	25
Titanium dioxide	Reference	43	43	—
	Diffusion stabilized	44	27	17
Slag filled	Reference	15	15	—
	Diffusion stabilized	29	2	27

TABLE II

Changes in crystalline structure of Nylon-6

Treatment	Temperature, K	Shift of interference lines (100), deg.	Change of crystallinity %	Relative change of modification rate, %	
				γ'	α
Original	323	−0.08	−2.3	−2.3	—
	373	−0.10	+13.5	+13.5	—
Diffusion	323	−0.10	−1.0	—	−1.0
stabilized	373	−0.15	−5.0	+5.0	−10.0

The structure of diffusion stabilized polymers is closely related to the filler. During diffusion stabilization from a 12.5 per cent solution of quinhydrone in ethanole followed by a thermal treatment, non-filled structures are improved by a partial $\gamma' - \alpha$ transformation (Table II). During diffusion of titanium dioxide filled Nylon-6, structural changes are limited to $\gamma' - \alpha$ transformation without any change in the regularity. Diffusion stabilization of samples with 3 per cent of molybdenum disulphide gave similar results. The slag-filled samples show a similar trend towards improved crystallinity with a complete $\gamma' - \alpha$ transformation (Table I).

High-temperature X-ray diffraction studies suggest that even optimal amounts of structural agents cannot build stable crystal surfaces. High-temperature X-ray diffraction patterns of samples containing 1 per cent titanium dioxide show more intensive interference lines (100) and considerably lower peaks shifted towards smaller angles (Table II): an indication of a non-filled polymer (Figure 1). As already noted, during diffusion stabilization a part of γ'-phase is transformed into α-phase. The remaining fraction of γ'-phase becomes more stable and less apt to change at high temperatures. The large fraction of γ'-phase observed at 373 K is related to a re-transformation $\alpha - \gamma'$. The stabilizer—induced α-phase is not stable and shows a tendency of inter-plane changes at high temperatures, when the typical interference lines become less intensive at a lower temperature of 373 K.

The above structural changes are in specific ways reflected in physical properties (Table III). The improved surfaces of original and slag-filled samples result in considerably higher strength. But in titanium dioxide filled samples re-arrangements of surface structures have insignificant effects on strength. The

TABLE III

Strength, modulus of tension elasticity and impact elasticity of untreated and treated Nylon-6

Filler	Treatment	σ, MPa	E, MPa	a_n, kJ/m^2
Unfilled	Original	39.7 ± 1.7	1400	11.7 ± 1.3
	Diffusion stabilized	56.5 ± 1.0	1391	11.0 ± 0.8
1% titanium	Original	40.3 ± 1.0	2022	33.8 ± 1.7
dioxide	Diffusion stabilized	42.2 ± 2.9	1453	12.0 ± 0.1
10% slag	Original	37.1 ± 0.4	2335	10.7 ± 0.9
	Diffusion stabilized	50.1 ± 3.2	2202	5.7 ± 3.5

fillers have significant effects on the deformation behaviour of diffusion stabilized polymers. The effect is most pronounced in titanium dioxide filled samples. With larger quantities of fillers the effect of stablilization on the modulus of elasticity is less pronounced, see.[12] Impact elasticity is most sensitive, it becomes considerably smaller in filled samples after the ordinary process of diffusion stabilization (Table III). Because of the very small amount of titanium dioxide filler (0.28 per cent weight) we ascribe considerable reduction of impact elasticity and the modulus of elasticity in such samples to re-arrangements of their structure and of the corresponding stresses. One of the ways of to decrease the stress is to prolong the cooling after the thermal treatment.[12]

In the next stage of our study we attempted to compose such media of diffusion stabilization, which would exclude plastification. We found that thermooxidation destruction was inhibited by certain mineral oils.[3] This is a probable explanation of the high efficiency of treatments in different oils.[9] As a result we composed oil stabilizer of Nylon-6.[13] Further studies showed a closeness of its action to the traditional compositions. The composition must be diffused at elevated temperatures (about 390 K) to ensure plastification and radical changes of the surface crystal structure. This composition applied to Nylon-6 gives a significant improvement of its crystallinity (from 18 to 36 per cent) of its surface with $\gamma' - \alpha$ transformation (Figure 2, curves 1, 2). The resultant trends of structural changes and of their rates are close to the earlier observations[2,3] on diffusion stabilization from plasticizer-stabilizer compositions. In the same manner we observe a partial $\gamma' - \alpha$ transformation and a partial modification crystallinity in titanium dioxide filled samples (Figure 2b), but in slag-filled samples the treatment gives a complete $\gamma' - \alpha$ transformatiön and a supplementary improvement of structure by α-phase (Figure 2c). In spite of the high temperature, the processing was insufficient for a complete structural transformation. The transformation was hampered by incomplete diffusion. The subsequent thermal fixation gives a supplementary improvement of the structure (Figure 2, curves 3). The rate of crystallinity becomes increases for 6 to 8 per cent, mainly by the increased fraction of α-phase. Note the more intensive interference lines (002, 200). Judging by the ratio of intensities $J_{200}/J_{002,202}$ this leads to a further movement of

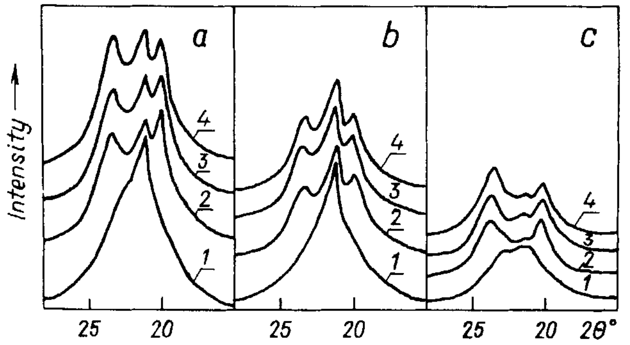

FIGURE 2 X-ray diffraction patterns of Nylon-6: a) original, b) 1 per cent titanium dioxide, c) 10 per cent slag. 1) untreated, 2) diffusion stabilized, 3) thermally treated, 4) heated at 433 K for 96 h.

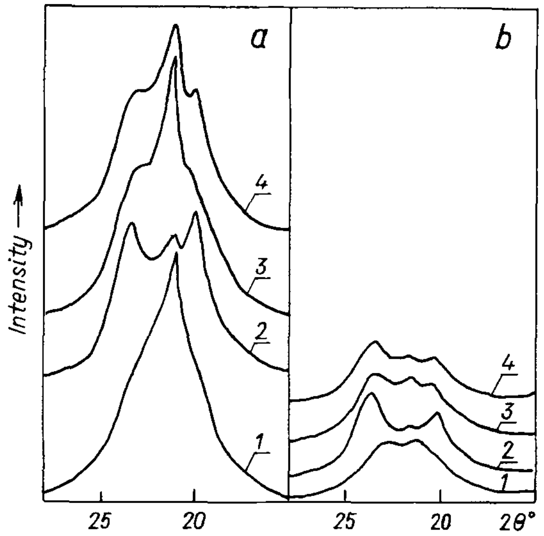

FIGURE 3 X-ray diffraction patterns of Nylon-6: a) original, b) 10 per cent slag. 1) untreated, 2) ethanol, 3) acetone, 4) ethanol–acetone mixture treated.

the lattice away from the ideal α-phase. A prolongation of the treatment to 96 h supplies poorer crystallinity to all samples.

When diffusion stabilization is performed without plasticizers and without plastification-enhacing conditions, crystallyne structures undergo minor changes. This was observed during diffusion stabilization of Nylon-6 from compositions of the same stabilizer in different solvents. We used solvents of different polarity levels—ethanol, acetone and their 50 to 50 per cent mixtures. Diffusion from a solution in ethanol (Figure 3, curves 2) gave the above described effect. Diffusion from a solution in acetone did cause $\gamma' - \alpha$ transformation, and no structural changes were observed (Figure 3, curves 3). In the mixture of solvents an additive effect was not achieved (Figure 3, curves 4).

Although the above diffusion compositions do not change the crystalline structures, they still may cause certain changes in the physical behaviour of polymers. Thus, diffusion of polycarbonate from a N-methyl-p-amino-phenol sulphate solution in water showed no changes in the crystalline structure,[14] but at a temperature rise the interference lines were strengthened ($\theta = 8.5°$). The increase rates are from 3.5 to 1.5 per cent in the temperature range from 293 to 333 K, from 18 to 5.5 per cent at 373 K, and from 9 to 3 per cent in the cycle 273–293–333–273 K, for untreated and treated samples, respectively. The more stable structures of diffusion stablized polymer samples explain the higher strength and lower deformation rates of diffusion stabilized polycarbonate.[14,15] Faster stress relaxation rates and certain influences of the fillers were also noted. The effect was mainly related to thermal treatment (Figure 4, curves 1, 3, 5). A prolonged treatment of polycarbonate in water is advantageous for its stress relaxation, even in thermally treated samples (Figure 4, curves 2, 3). Diffusion stabilized samples are more deformation resistant (Figure 4, curves 4, 5).

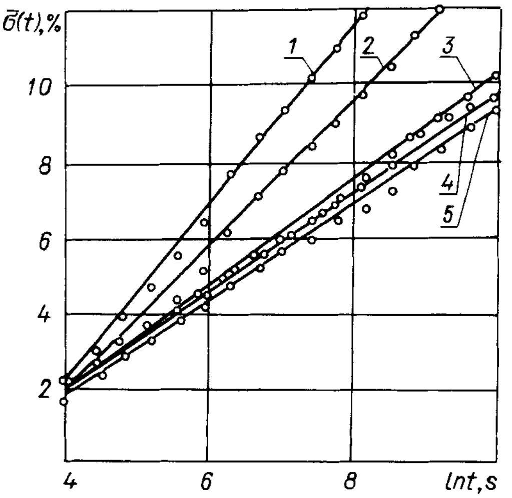

FIGURE 4 Relaxation rates of tension stress of polycarbonate samples: 1) original; 2, 3) thermally treated; 4, 5) diffusion stabilized; 1, 3, 5) before; 2, 4) after 1000 h in water at 293 K.

Polycarbonate samples acquire different physical features even for small differences of the penetrated layer thickness and of concentration. We have 20 to 50 mkm and 0.3 per cent and 250 to 500 mkm and 3 to 5 per cent, after non-plasticizing and plasticizing treatment, respectively.

Diffusion stabilization of polymer-group acetals[16] suggests a possibility of surface modification by compositions without plasticizers, same as for polycarbonate. The X-ray patterns show unsignificant modifications of surface crystallinity, but both strength and impact elasticity are significantly altered (Table IV). The effect is evidently related to the stabilizer applied, because this study was made in constant conditions.

From our study we concluded a possibility of modifying physical and mechanical properties of crystalline block polymers, first of all their strength and deformation resistance. The direct effect of diffusion stabilization, namely inhibition of destruction in agressive media by suitable distributions of the stabilizers has been described earlier.[3,4,17,18]

TABLE IV

Tension strength and impact elasticity of diffusion stabilized polymer-group acetals

Composition	σ, MPa	a_n, kJ/m^2
Original	60.0 ± 0.9	41.0 ± 4.4
Quinhydrone (12.5% in ethanole)	62.0 ± 1.3	40.4 ± 4.1
Hydroxylamine hydrosulphate (6% in water)	61.8 ± 2.4	35.0 ± 2.0
Tetramethylthiuram disulphide (6% in acetone)	—	58.7 ± 1.4
Tetramethylthiuram disulphide (0.4% in ethanole)	62 ± 2	42.6 ± 3.0
Potassa (46% in water)	60 ± 1	52.0 ± 2.7
Topanol (6% in ethanole)	62 ± 0.5	47.9 ± 0.6

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