CRYSTALLIZATION KINETICS OF DYED NYLON 6

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ABSTRACT

Isothermal and non-isothermal crystallization of polyamide 6
coloured with selected organic pigments was examined by DSC.
It was found that the activity of pigments is connected with
their chemical nature and with reduction of the free energy of
formation of critical size nuclei. Blue pigment and Red lake are
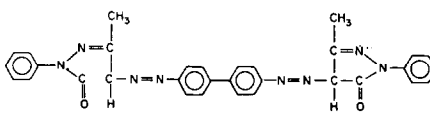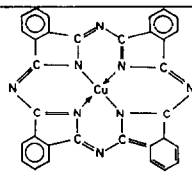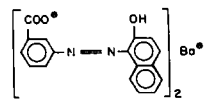substances which accelerate crystallization of nylon 6.

INTRODUCTION

Nylon 6 is widely applied in many fields and for this reason
is usually coloured with pigments, mainly obtained by synthesis.
Introduced foreign substances, according to their size, shape,
concentration, surface energy of the particles, distribution
affect kinetics and thermodynamics of polymer. In turn the mecha-
nical properties of nylon are governed by the supermolecular
structure.

The purpose of this paper is to determine the effect of some
organic pigments on the crystallization rate of polyamide 6 by
the use of DSC.

EXPERIMENTAL

In table 1 pigments used as nucleating agents are presented.
The homogeneous blending of the additives into the base polymer
was attained by melt mixing in the Brabender laboratory extruder.
The kinetics of isothermal and non-isothermal crystallization was
investigated in a standard DSC cell of the Du Pont 990 thermal
analyser. The measurements were carried out in nitrogen on samples
of 5 mg. All calculations were performed with the aid of a mini-
computer.

TABLE 1

Organic pigments

Pigment	Formula	Molec. weight
Pigment Orange G		631
Copper Phthalocyan. Blue B		577
Lake Red BB		426

RESULTS AND DISCUSSION

Experimental data were analysed in terms of the Avrami equation

$$\ln (1 - x) = - Kt^n \qquad (4)$$

where:x is the relative degree of crystallinity referred to the state of equilibrium, K is the constant of crystallization rate, n is the exponent depending on the type of nucleation and on the geometry of the crystallite growth. Some typical plots in Avrami co-ordinates are presented in fig.1. As can be seen from the data summarized in table 2 the initial portions of crystallization isotherms of pure polamide 6 can be fitted to the Avrami function with exponents ranging from 3.4 to 3.8 which formally corresponds to three-dimensional growth of the crystalline

Fig.1. Crystallization isotherms at 471 K: a/ 1% of Blue, b/ 1% of Red, c/ colourless PA 6, d/ 2% of Orange.

structures on thermal and athermal nuclei. The same results have been obtained by Gurato [1] and Ishibashi [2]. In some papers [3,
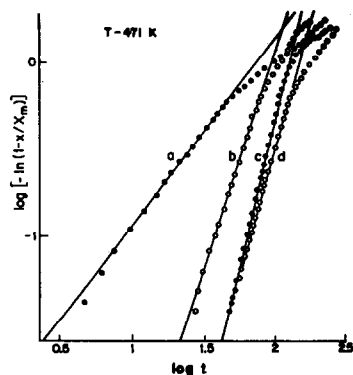
4, 5] high values of n up to 10 are reported for initial stages
of crystallization. However, those results can be described
with n=4 from the start of crystallization if the time scale is
corrected for the induction period.

TABLE 2

Kinetic parameters of isothermal crystallization of nylon 6
containing organic pigments

Sample	471 K		473 K		475 K		478 K	
	n	$t_{1/2}$	n	$t_{1/2}$	n	$t_{1/2}$	n	$t_{1/2}$
colourless	3.7	100.3	3.8	168.9	3.8	446	3.7	1421
Orange 0.5%	2.5	93.7	2.6	228.0	2.7	490	2.7	1609
Orange 1%	2.7	115.2	2.8	316.2	2.7	708	2.8	1630
Blue 0.5%	1.0	56.3	1.2	99.1	1.1	335	1.2	1060
Blue 1%	1.1	48.8	1.3	92.4	1.3	296	1.3	983
Red 0.5%	2.5	94.2	2.5	140.4	2.6	395	2.5	1097
Red 1%	2.7	71.3	2.6	123.3	2.5	370	2.7	965

The presence of pigments lowers the value of n since the con-
tent of heterogeneous nuclei is increased and crystallization
gradually turns into diffusion-controlled process. From the
classical equation [5] describing the crystalline phase growth
the surface free energy of fold-containing surfaces σ_e was cal-
culated:

$$\sigma_e = 6.24 \times 10^{-2} \text{ J/m}^2$$

It was assumed that crystallization occurs only on heterogeneous
crystal nuclei and is controlled by secondary surficial nucle-
ation. This result is in very good agreement with $6 \cdot 10^{-2}$ obtai-
ned by Magill [6] obtained from spherulitic growth rates.

Binsbergen [7] found that the active nucleating agents are
insoluble in the polymer melt and their physical state is a
fine dispersion of small crystals. As regards their chemical
nature, the agents consist of both hydrocarbon groups and either
polar groups or a condensed aromatic structure. The crystals of
active agents consist either of parallel layers or of parallel
rows of molecules. As a result, such arrangement of molecules
enables polymer molecules to assume a stretched conformation
over some distance, making crystallization much easier.

Among the selected pigments B Blue is the most active agent

accelerating crystallization of polyamide 6. In this case the
half-times of crystallization are twice as short. Moreover, this
agent causes changes in the mechanism of crystallization. Lower
values of n (about 1) would imply induction only the development
of fibrils, which subsequently do not organise into spherulites.
The activity of B Blue is probably connected with its structure
ie a regular packing of parallel stacks of the flat ring systems.

BB Red can also be numbered among nucleating agents. However,
in this case the presence of polar group OH in the hydrocarbon
part of molecule exerts an influence on the activity. The Avrami
exponent is in the range between 2.4 and 2.7. It corresponds to
a disc-like growth from instantaneous nuclei. G orange does not
from crystals with parallel layers or rows and is not a nucle-
ating agent.

The results of non-isothermal crystallization are in good
agreement with isothermal crystallization data. For samples
coloured with pigments temperatures of maximum crystallization
rates are shifted, which testifies to smaller undercooling. The
temperatures of DSC peaks reflect nucleation abilities of B Blue
and BB Red.

According to Gurato [1] the equation for cooling crystalliza-
tion at constant rate can be stated as

$$- \ln\left[a\left(2T_N - T_m^0\right) \, T_n^0/T_N^2(\Delta T)^2\right] = -\frac{4b_0 \, \partial \, \partial_e T_n^0}{K \Delta h_m T_N \Delta T} - \text{const.} \quad (2)$$

where: a is the cooling rate,
T_N is the temperature of de-
viation from the baseline on
the thermogram, T_m^0 is the
equilibrium melting point of
the polymer, T is the degree
of undercooling, h_m is the
heat of fusion per unit vo-
lume, b_0 is the monolayer
thickness, ∂ is the surface
free energy of the lateral
surface.

Test of equation (2) are
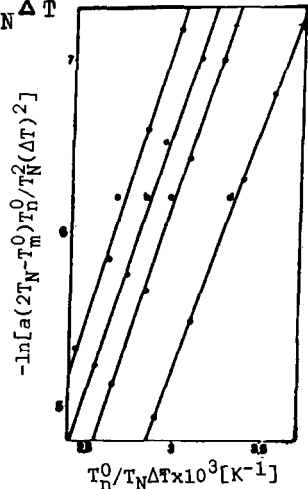shown in fig.2 for some sam-
ples.

The basic assumption of

Fig.2. Test of equation (2) for:
a/ 1% Orange, b/ colourless
PA 6, c/ 1% Red, d/ 1% Blue.

most theories of heterogeneous nucleation is that the total in-
terfacial free energy of the crystalline embryo is reduced by a
foreign phase which provides part of the interface to be formed.
This causes reduction in the activation free energy and a decre-
ase in the degree of supercooling required for nucleation.

Our results correspond to this idea since the slopes of
straight lines in fig.2 connected with the free energy of forma-
tion of a critical-size nucleus are different for PA 6 contai-
ning pigments. Apparent values of parameter δ_e calculated from
the equation are: colourless nylon $6.35 \cdot 10^{-2}$, Orange $7.36 \cdot 10^{-2}$,
Blue $5.41 \cdot 10^{-2}$, Red $6.02 \cdot 10^{-2}$ J/m. These remain in good agreement
with the observed rates of crystallization. The surface free
energy of nylon 6 coloured with B Blue is reduced by 20% which is
reflected in faster crystallization. The nucleation abilities of
the pigments can be arranged into the following series:

$$B \text{ Blue} > BB \text{ Red} > \text{no pigment} > G \text{ Orange}$$

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