

Pigment-induced crystallization in colored plastics based on partially crystalline polymers

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Abstract

Mold shrinkage of the colored plastics based on partially crystalline polymers is a well-known phenomenon and is assumed to be caused by pigment-induced crystallization of polymers. A systematic investigation has been carried out for a variety of organic pigments in polypropylene (PP) and polyethylene (HDPE) systems in order to clarify the correlation between the nucleation effect due to pigments and the mold shrinkage. Special attention was paid to the onset temperature of crystallization for both PP and HDPE systems as monitored by DSC (differential scanning calorimeter). In parallel, the crystallization rate was also studied in the isothermal process by depolarization method for PP while by dilatometry for HDPE systems. As a result, the mold shrinkage is found to become more significant as the onset temperature is higher and the crystallization rate is faster. This tendency is well correlated with the formation of small spherulites (diameter: less than 1 μm). These results lead us to conclude that the organic pigments in colored plastics serve as a nucleation agent for partially crystalline polymers to form small spherulites, causing the mold shrinkage to occur.

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1. Introduction

In the field of colored plastics, especially in polyolefins such as polypropylene (PP) and high density polyethylene (HDPE), organic pigments are known to remarkably affect the mold shrinkage or distortion [1–3]. Turnbull and Fischer [4] and Lauritzen and Hoffman [5] pointed out that additives and/or impurities initiate crystallization of partially crystalline polymers. In addition, a number of reports were also published on the nucleat-

ing effect in polymers due to pigments [6–12]. However, these are the studies based on the approach from the research area of polymers, not from pigments. For this reason, an attempt was made in the present investigation to clarify the influence of organic pigments on the crystallization of polymers and eventually the mold shrinkage in PP and HDPE systems. We believe that the present information could provide us with a guiding principle how to modify pigment surface or tailor pigments themselves.

Special attention has been paid in the present investigation to the onset temperature of crystallization in both pigment-loaded PP and HDPE systems as monitored by DSC (differential scanning

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colorimeter). In parallel, the crystallization rate was also studied in the isothermal process by depolarization method for PP while by dilatometry for HDPE systems. The former method is simple but still sufficient for slow crystallization processes as in the case of PP systems. However, this method is obviously insufficient for HDPE systems in which the crystallization proceeds quite rapidly; whereas dilatometry is adequate for this purpose.

2. Experimental

2.1. Materials and experimental conditions

Tables 1 and 2 detail the commercial PP and HDPE, as well as organic and inorganic pigments

used in the present experiment, respectively. The composition of the colored plastics is given in Table 3. The molding conditions are summarized in Table 4. The test plaque used for the injection-mold test has a dimension of 120×80×2 mm³.

2.2. Measurements

2.2.1. Mold shrinkage

The extent of mold shrinkage was measured for two directions: one is along the machine direction (MD) and the other is perpendicular to the machine direction (TD: transverse direction).

2.3. Onset temperature of the crystallization (T_p)

The onset temperature (T_p) of the crystallization was measured by DSC for both PP and HDPE

Table 1
Polyolefins used

Polymer	Trade name	Manufacturer	MFR ^a	Type
HDPE	Hi-zex 2208 J	Mitsui Chemical	8	High density polyethylene
PP	Mitsubishi Noblen MH-4	Mitsubishi Chemical	5	Isotactic homopolymer

^a Melt flow rate (g/10 min).

Table 2
Pigments used

Trade name	Manufacturer	Pigment class	C.I. name	Abbreviation
Iragazin Yellow 2GLT	Ciba	Isoindorinone	P.Y.109	2GLT
Iragazin Yellow 3RLT	Ciba	Isoindorinone	P.Y.110	3RLT
Cromophtal Yellow GR	Ciba	Condensed azo	P.Y.95	GR
Lithol Fast Yellow 1090	BASF	Quinophthalone	P.Y.138	1090
Cinquasia Red Y	Ciba	Quinacridone	P.V.19	Red Y
Cromophtal Scarlet R	Ciba	Condensed azo	P.R.166	Sc R
Lionol Green 2YS	Toyo Ink	Cyanine green	P.G.7	2YS
Lionol Green GLS ^a	Toyo Ink	Cyanine green	P.G.7	GLS
Heliogen Blue 6911K	BASF	Cyanine blue	P.B.15:3	6911K
Lionol Blue BLS ^a	Toyo Ink	Cyanine blue	P.B.15:1	BLS
TE Yellow	Toyo Ink	Mixture ^b	–	TE
Tipaque CR-50	Ishihara	TiO ₂	P.W.6	TiO ₂
Cd Yellow 2240	Orient Chem.	Cd yellow	P.Y.37	CdY
Toda Color 120ED	Toda	Iron oxide	P.R.101	Fe ₂ O ₃
Mitsubishi Carbon #45	Mitsubishi Chem.	Carbon black	P.BL.7	CB

^a Shrinkage-improved product.

^b Shrinkage-improved product by surface coating, and its composition: 2GLT/3RLT/TiO₂/Zn-stearate 17/6/60/17 (in weight).

systems. The test samples were heated, respectively, to 230 and 180 °C for PP and HDPE systems and then cooled at a rate of 5 °C/min. The exothermal peak upon crystallization gave the onset temperature.

2.4. Crystallization rate measured in the isothermal process for pigment-loaded PP and HDPE systems

The crystallization rate was measured in the isothermal process at fixed temperatures of 130 and 129 °C for PP and HDPE systems, respectively. The half time $t_{1/2}$ is defined as the time required for 50% crystallization. The following two different methods were employed for measurements.

The depolarization method, applied for PP systems, utilizes a pair of polarizers which are arranged in a cross-nicol position: no light transmission (dark). Then, some molten samples of colored plastics are placed between these polarizers. Light transmission occurs in proportional to the extent of the crystallization with elapsed time.

The intensity of transmitted light is used as the measure for the degree of crystallization.

Dilatometry, applied for HDPE systems, is a method to measure the change in volume caused by the crystallization of polymers, using a glass capillary together with mercury [13]. This method enables us to carry out a very precise measurement even for rapidly changing processes in a close temperature range.

2.5. Microscope observation

A polarizing microscope was used to observe spherulites of polymers which appear as a result of the crystallization. The size of the spherulite serves as a good measure of the crystalline state. When the nucleation frequency is high, we normally observe small spherulites. On the contrary, the spherulites grow up to large crystallites as the nucleation frequency decreases.

3. Results and discussion

3.1. Effect of pigments on the mold shrinkage in PP and HDPE systems

Figs. 1 and 2 show the MD/TD mold shrinkage in PP and HDPE systems loaded with a variety of pigments, respectively. In Fig. 1 for PP systems, the blank sample without any pigment finds itself at the lower-left corner in zone 1. MD shrinkage in PP systems is rather insignificant in all pigments. On the other hand, the organic pigments in zone 3 exhibit considerable TD shrinkage as compared with the blank sample in zone 1. The inorganic pigments in zone 1 (TiO_2 , Fe_2O_3 and Cd Y) are quite inactive for the mold shrinkage.

Table 3
Composition of colored plastics

Pigment type	Weight ratio of pigment/DA ^a /polymer	Measurements
Org. and inorg. pigments	0.2/0.07/100	Dilatometry
TE	0.65/0/100	
Organic pigments	0.1/0.1/100	Mold shrinkage and DSC
Inorganic pigments	0.2/0.1/100	
TE	0.65/0/100	

^a Dispersing agent: a mixture of Zn and Ca stearates for PP and Zn-stearate for HDPE.

Table 4
Molding conditions

Polymer	Temperature (°C)		Pressure (kg/cm ²)		Time for molding process (s)		
	Cylinder	Mold	Injection	Hold-on	Injection	Hold-on	Cooling
HDPE	240	40	80	40	5	3	15
PP	220	40	55	40	4	2	14

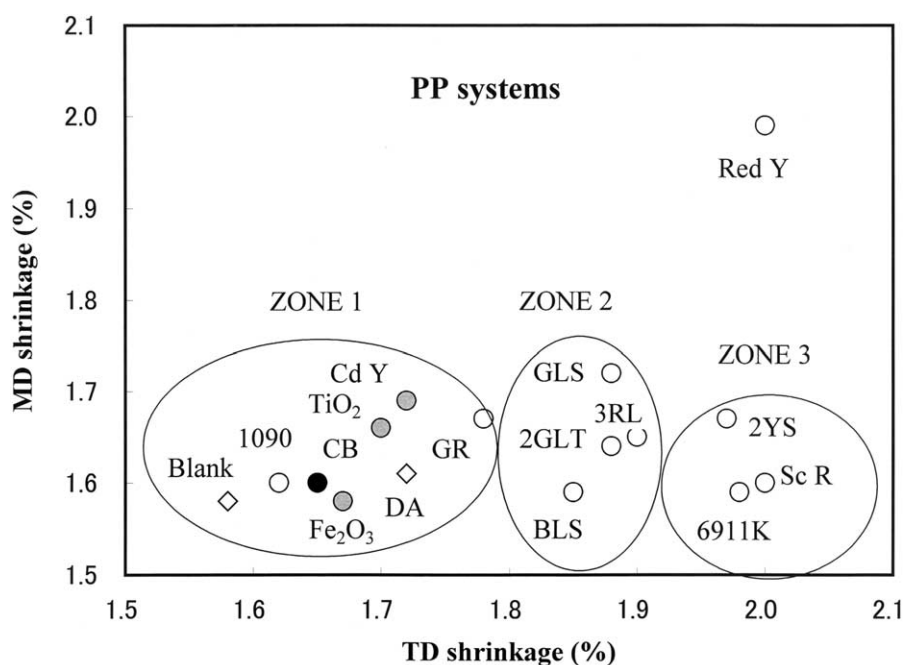


Fig. 1. MD and TD mold shrinkages in PP systems for a variety of pigments. Molding temperature: 220 °C. “Blank” denotes the plastic sample without any pigment while “DA” is the sample which includes only a dispersing agent (see footnote of Table 3).

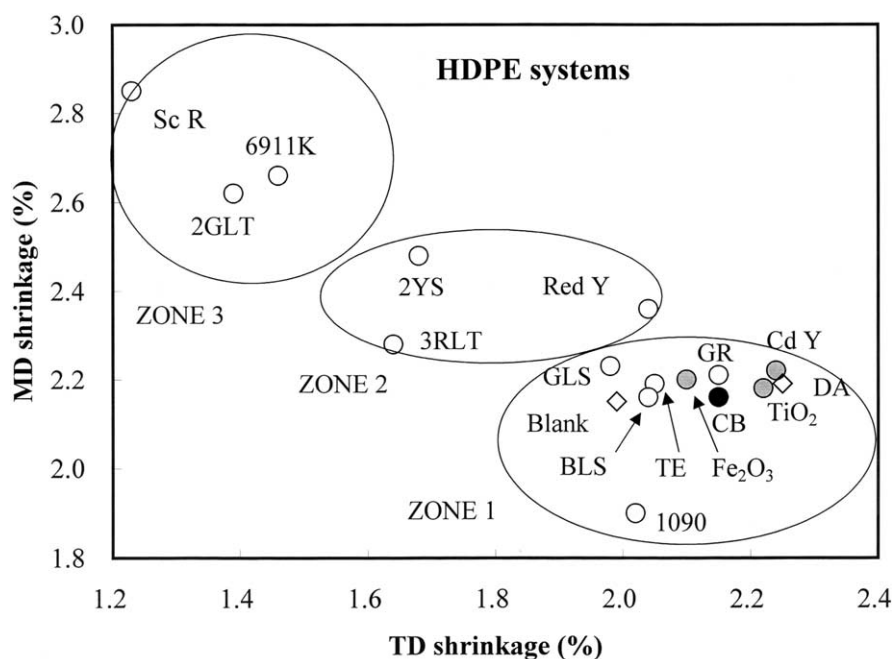


Fig. 2. MD and TD mold shrinkages in HDPE systems for a variety of pigments. Molding temperature: 240 °C. “Blank” denotes the plastic sample without any pigment while “DA” is the sample which includes only a dispersing agent (see footnote of Table 3).

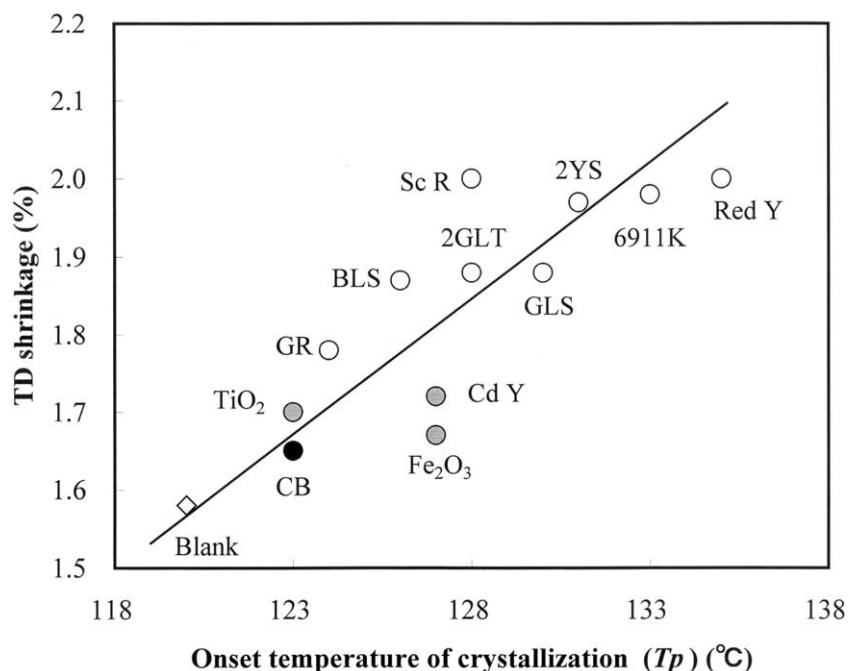


Fig. 3. TD shrinkage versus onset temperature of crystallization (T_p) in pigment-loaded PP systems.

In HDPE systems, the blank sample is present at the lower-right corner in zone 1. It is also to be noted that the organic pigments in zone 3 exhibit quite significant MD shrinkage but less TD shrinkage. The MD shrinkage causes appreciable distortion in molded products in practice. The inorganic pigments in zone 1 behave again nearly in the same way as the blank sample.

3.2. Correlation between the onset temperature of crystallization (T_p) and the mold shrinkage in PP and HDPE systems

Figs. 3 and 4 show the correlation between the onset temperature of crystallization (T_p) and the mold shrinkage in PP and HDPE systems, respectively. In both systems, a good linearity is recognized between the mold shrinkage and the onset temperature. The inorganic pigments in both systems exhibit insignificant mold shrinkage. It is also remarkable to note that the mold shrinkage of GR (condensed azo: CIBA) in HDPE systems is smaller as compared with that of the blank sample.

3.3. Correlation between the crystallization rate and the mold shrinkage in PP and HDPE systems

Fig. 5 shows the correlation between the time required for 50% crystallization ($t_{1/2}$) and the mold shrinkage in PP systems. The half time was measured in the isothermal process at a fixed temperature of 130 °C by means of depolarization method. Fig. 6 shows the same correlation for HDPE systems in which the measurements were made at 129 °C by means of dilatometry. Both PP and HDPE systems exhibit the same tendency that the decreased mold shrinkage is in line with increasing $t_{1/2}$, i.e. slow crystallization rate. In PP systems, Fe₂O₃ is found to be exceptionally inactive for the mold shrinkage.

Fig. 7 shows the three representative examples (1090, GR and 2GLT) of the detailed crystallization process as a function of time. The volume fraction of the crystallized phase (χ) is obtained by dilatometry measurements. The volume fraction of the non-crystallized phase ($1-\chi$) is then calculated and given in the present figure. It is to be

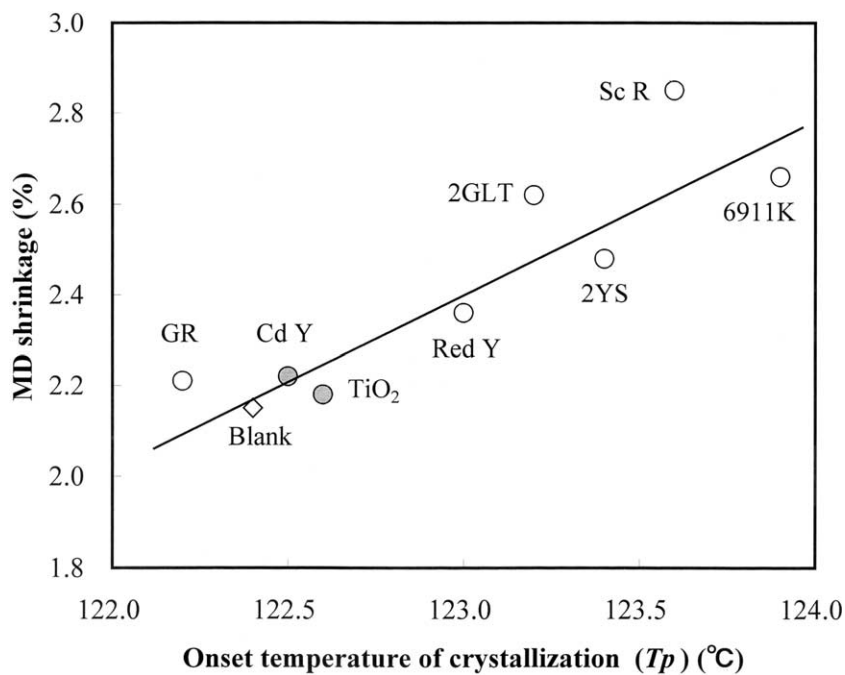


Fig. 4. MD shrinkage versus onset temperature of crystallization (T_p) in pigment-loaded HDPE systems.

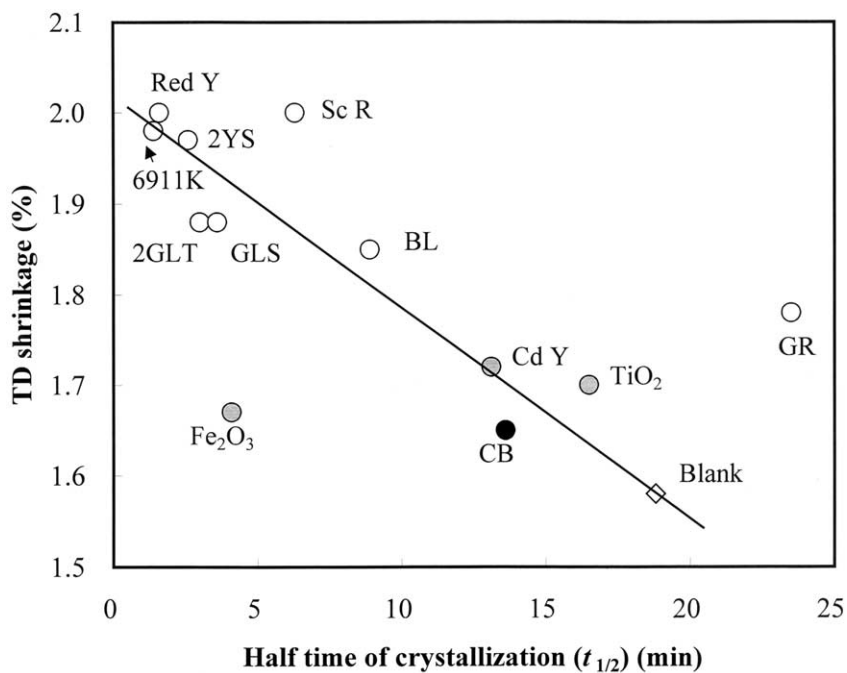


Fig. 5. TD shrinkage versus half time of crystallization in pigment-loaded PP systems measured in the isothermal process (130 °C) by means of depolarization method.

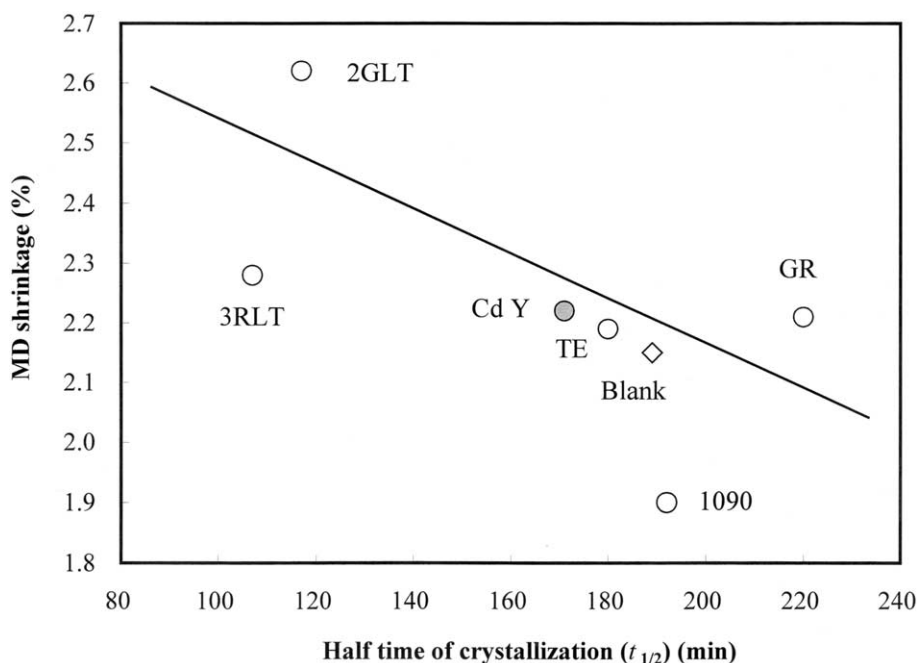


Fig. 6. MD shrinkage versus halftime of crystallization in pigment-loaded HDPE systems measured in the isothermal process (129 °C) by means of dilatometry.

noted that 2GLT (isoindolinone) shows an abrupt crystallization around 280 min. This phenomenon corresponds to a supercooling effect as found in water. The same effect was also observed in 3RLT (again isoindolinone) but not shown here. It is, however, not yet fully clarified whether the supercooling effect here is specific of isoindolinone pigments.

3.4. Correlation between the spherulite size and the mold shrinkage in PP systems

Table 5 shows the spherulite size in PP systems as observed by a polarizing microscope, together with the values for the onset temperature of crystallization (Fig. 3) as well as the time required for 50% crystallization ($t_{1/2}$) (Fig. 5). The “increase in T_p ” given in the table is measured relative to the onset temperature of the blank sample. Judging from the present table, the mold shrinkage as characterized by the increase in T_p (Fig. 3) and the fast crystallization rate (Fig. 5) becomes more significant as the spherulite size is smaller. The formation of small spherulites is equivalent to saying

that the nucleation frequency is high in PP systems. Unfortunately, the corresponding results in HDPE systems are not available because their spherulites are generally too small to observe by microscope. However, the same situation as that in PP systems is presumably also the case in HDPE systems.

It is also important to note that the inorganic pigments in Table 5 (which are inactive for the mold shrinkage) exhibit some increase in T_p in spite of slow crystallization rate and large spherulites. This would suggest that the spherulite size plays the most important role in the occurrence of mold shrinkage that exceeds other influencing factors such as high onset temperature and slow crystallization rate. In conclusion, the mold shrinkage becomes more significant as the nucleation frequency is increased in colored plastic systems.

3.5. Mechanism of the mold shrinkage

On the basis of the forgoing discussions, the mechanism of mold shrinkage can be explained in

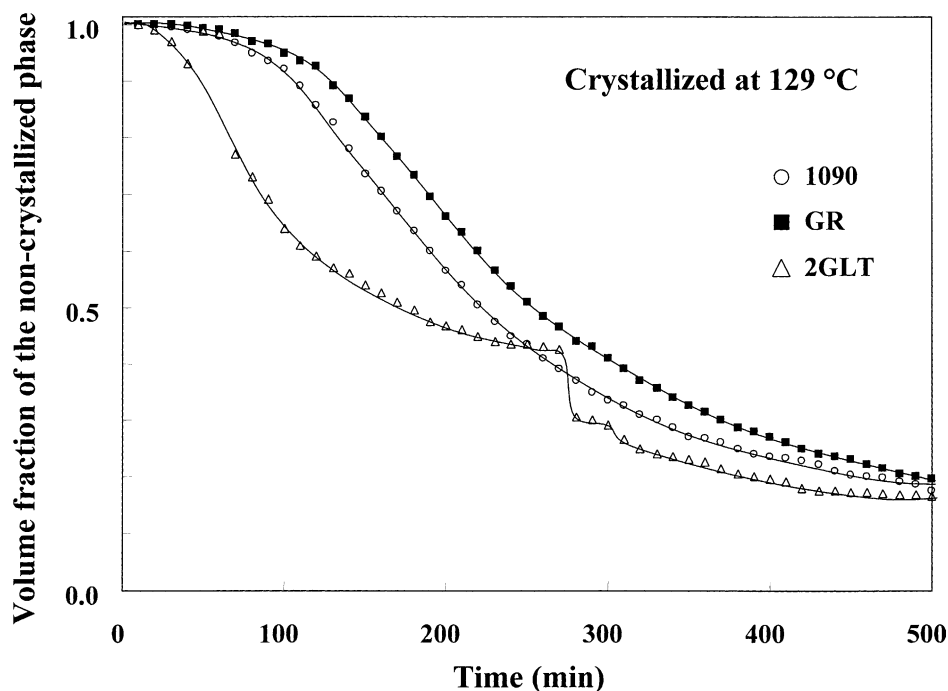


Fig. 7. The volume fraction of the non-crystallized phase is plotted as a function of time in the isothermal process of 129 °C. The volume fraction of the crystallized phase (χ) is determined by experiment [13]. Then, the volume fraction of the non-crystallized phase ($1-\chi$) is deduced as given in the present figure.

Table 5
Parameters for the crystallization process of PP systems

Pigment	Increase in T_p (°C)	$t_{1/2}$ (min)	Spherulite size ^a
Blank	0	18.8	Large
2GLT	0	3	Small
GR	4	23.5	Large
RedY	15	1.6	Small
ScR	8	6.3	Small
2YS	11	2.6	Small
GLS	10	3.6	Medium
6911K	13	1.4	Small
BLS	6	8.9	Medium
TiO ₂	3	16.5	Large
Cd Y	7	13.1	Large
Fe ₂ O ₃	7	4.1	Large
CB	3	13.6	Large

^a "Large": several 10 μm ; "medium": one to several 10 μm ; "small": less than 1 μm .

the following way. The presence of organic pigments in colored plastics enhances the nucleation frequency in partially crystalline polymers. This, in turn, induces a change in higher order structure of polymer systems. Then, the internal stress may remain in bulk or be propagated throughout the system during the cooling process, thus leading to the formation of a residual stress in polymers. This eventually brings about mold shrinkage in colored plastics.

4. Conclusions

Organic pigments are found to enhance the nucleation frequency of polymers that induces internal stress, i.e. a change in higher order structure of polymers. This may eventually lead to a residual stress which results in mold shrinkage of colored plastics. The present conclusion strongly

suggests that the surface treatment and/or surface modification of pigments play a decisive role for the suppression of mold shrinkage in colored plastics.

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References

- [1] Herbst M, Hunger K. *Industrial Organic Chemistry*. Weinheim: VCH; 1993.
- [2] Suzuki S. *Dyestuffs & Chemicals* 1977;22:69 [in Japanese].
- [3] Ando G, Suzuki S. *Industrial Materials* 1977;25:29 [in Japanese].
- [4] Turnbull D, Fischer JC. *J Chem Phys* 1949;17:71.
- [5] Lauritzen Jr JI, Hofman JD. *J Res Nat Bur Stds* 1961; 65A:257.
- [6] Silberman A, Raninson E, Dolgopolsky I, Kenig S. *Polym Adv Technol* 1995;6:643.
- [7] Jacoby P, Berstedt BH, Kissel WJ, Smith CE. *J Polym Sci, Part B: Polym Phys* 1986;24:461.
- [8] Filho DS, Oliveira CMF. *Makromol Chem* 1993;194:285.
- [9] Sterzynski T, Cab P, Lambla M, Thomas M. *Polym Eng Sci* 1997;37:1917.
- [10] Menges G, Sarholz R, Kruger E. *Plastverarbeiter* 1981; 32:59.
- [11] Wlochowicz A, Eder M. *Angew Macromol Chem* 1989; 171:79.
- [12] Turturro A, Olivero L, Pedemonte E, Alfonso GC. *Br Polym J* 1973;5:129.
- [13] Suzuki S, Miyashita S, Katabuchi H. *Jpn Soc Colour Mat* 2001;74:379 [in Japanese].