

# Poly(phenylene oxide) Composites Containing Crosslinked Polystyrene Microspheres. II. Dark Crosses Observed in Microscope

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## Synopsis

Extinction phenomena observed between crossed polaroids in microscope were classified into three groups: (1) Poly(2,6-dimethyl-1,4-phenylene oxide)/polystyrene composite with crosslinked polystyrene microspheres. Negative dark crosses were observed in the shells of the spheres, the cores of the spheres were completely extinct. The crosses disappeared at 170°C, which is 20°C above  $T_g$  of the matrix polymer. (2) Polycarbonate composite with glass beads. The dark crosses were positive and outside the glass beads. The crosses disappeared at 130°C, which is 20°C below  $T_g$  of the matrix polymer. (3) *In situ* polymerized composites with crosslinked polystyrene microspheres. The dark crosses were the same size of the spheres. They were negative in poly(methyl methacrylate) and poly(vinyl acetate) and positive in polystyrene. The disappearing temperatures of the crosses were 150, 110, and 285°C, respectively. The first two groups of phenomena are explained as the photoelastic effects caused by the thermally induced stresses. The last group is due to the inhomogeneous swelling or contracting of polystyrene networks in the matrices.

## INTRODUCTION

Owing to the mismatch of thermal expansion coefficients of a matrix and a filler in a composite, there is a thermally induced stress. For a polymer composite with an inorganic filler this stress is a squeezing force on the filler exerted by the matrix upon cooling, because the polymer matrix has a much larger coefficient of thermal expansion. The direct effects of this mismatch are the decreases in Young's modulus and tensile strength of the composite, as compared with the expected values in the unstressed state.<sup>1</sup>

Polymer composites containing inclusions of a crosslinked polymer have similar expansion coefficients and, therefore, only small thermally induced stresses. This could be looked as an advantage in the study of mechanical properties. In a previous paper the tensile properties of poly(phenylene oxide) composites with crosslinked polystyrene microspheres were reported.<sup>2</sup> In this article the same composites have been examined with attention to the existence of the thermal stresses. Some observations using a polarizing microscope will be reported and discussed in terms of photoelasticity related to the thermally induced stresses. In order to analyze the phenomena, some more composites have also been examined on purpose.

## EXPERIMENTAL

The composites were pressed into sheets at a temperature  $70^{\circ}\text{C}$  above  $T_g$  of the continuous matrix polymers. A polarizing microscope with a hot stage was used. Between crossed polaroids dark crosses, which were quite similar to that of spherulites of crystalline polymers, were observed. Micrographs were taken at room temperature. Then the temperature of the hot stage was increased at  $2^{\circ}\text{C}/\text{min}$ . The temperature at which the dark crosses disappeared was recorded.

## RESULTS

The extinction phenomena were classified into three groups:

1. Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)/polystyrene (PS) composite containing crosslinked PS microspheres. Crosslinked PS spheres were prepared from suspension polymerization. The spheres contain 8 wt % of divinylbenzene. The particle size is  $37\text{--}90\ \mu\text{m}$ . PPO/PS blend (50/50 w/w) was used as the matrix. A thin film of thickness of 0.1 mm was used for microscopic observation. As shown in Figure 1, the microspheres were divided into two parts: Negative dark crosses appeared in the shells of the spheres, while complete extinction was in the cores of the spheres. The crosses disappeared at  $170^{\circ}\text{C}$ , which is  $20^{\circ}\text{C}$  above  $T_g$  of the matrix, PPO/PS blend.

2. Polycarbonate (PC) composite with glass beads. The particle size of the glass beads is  $45\text{--}100\ \mu\text{m}$  in diameter. A film of thickness of 0.2 mm was used. The dark crosses were positive and outside the glass beads; their sizes were far

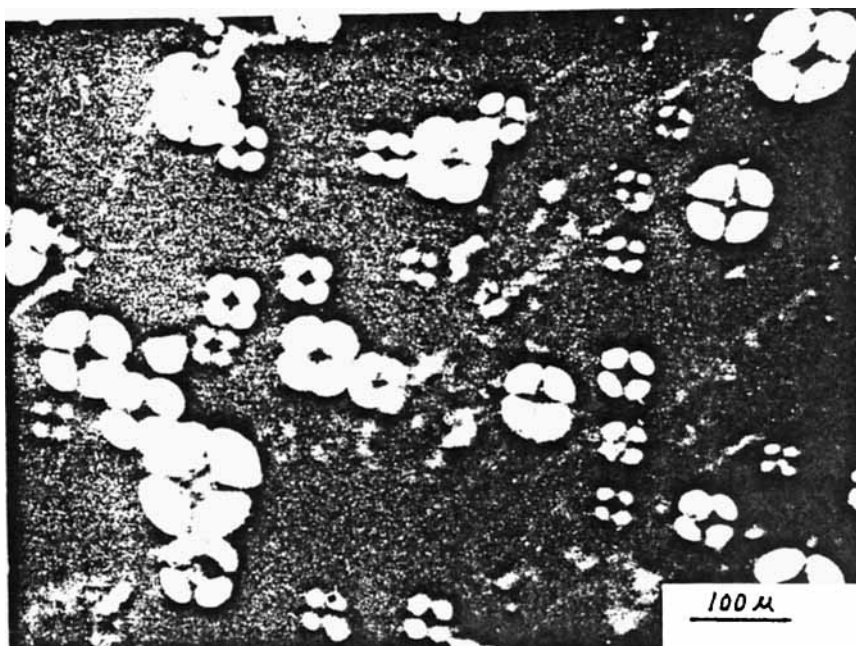


Fig. 1. A thin film of PPO/PS composite with crosslinked PS microspheres as observed between crossed polaroids in a polarizing microscope.

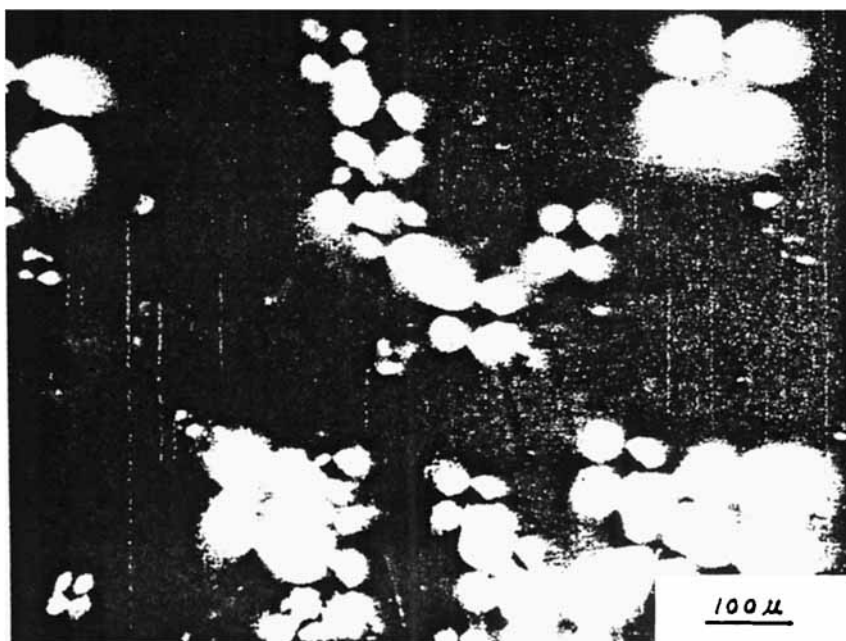


Fig. 2. A thin film of PC composite with glass beads (crossed polaroids).

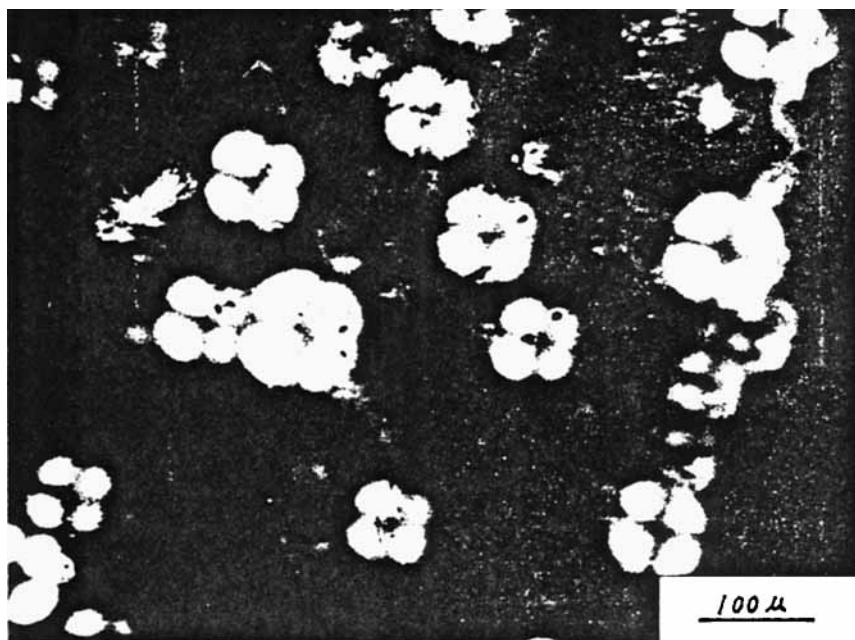


Fig. 3. A thin film of *in situ* polymerized PMMA composite with crosslinked PS microspheres (crossed polaroids).

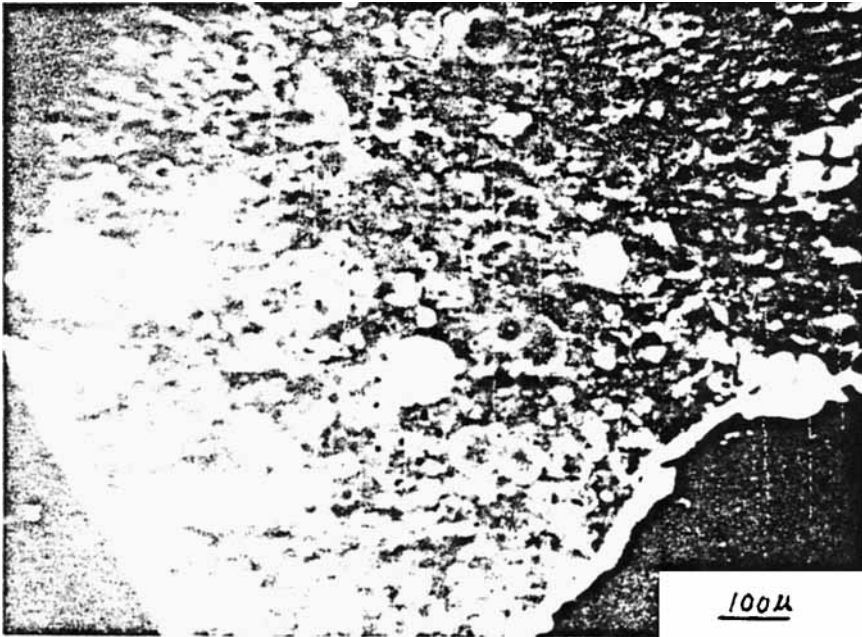


Fig. 4. A thin film of *in situ* polymerized PVAc composite with crosslinked PS microspheres (crossed polaroids).

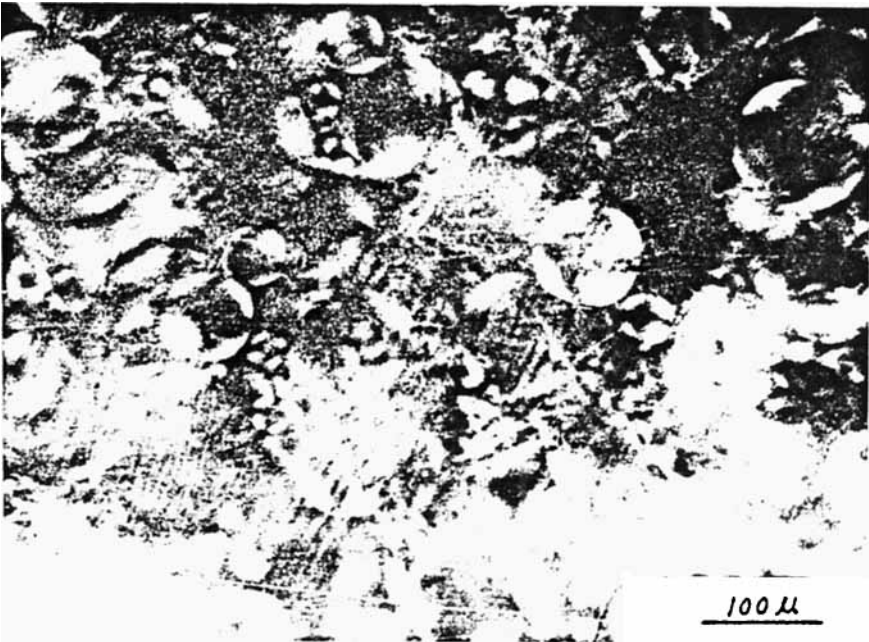


Fig. 5. A thin film of *in situ* polymerized PS composite with crosslinked PS microspheres (crossed polaroids).

TABLE I  
 $T_g$  of Composites

Sample	$T_g$ of crosslinked PS ( $^{\circ}\text{C}$ )	$T_g$ of matrix ( $^{\circ}\text{C}$ )
1. Crosslinked PS	120	
2. PPO/PS		147
3. PPO/PS composites, 30-70 wt % of filler	$122 \pm 2$	145
4. PVAc composite	126	43
5. PMMA composite	128	110
6. PS composite	130	90

TABLE II  
Densities and Expansion Coefficients of Polymers

Sample	$d$ ( $\text{g}/\text{cm}^3$ ), $25.2^{\circ}\text{C}$	$d$ ( $\text{g}/\text{cm}^3$ ), $51.7^{\circ}\text{C}$	$\alpha \times 10^4$ ( $\text{K}^{-1}$ )
PPO/PS	1.0682	1.0634	1.70
Crosslinked PS	1.0480	1.0418	2.24

larger than the beads, as shown in Figure 2. The crosses disappeared at  $130^{\circ}\text{C}$ ,  $20^{\circ}\text{C}$  below  $T_g$  of the matrix polymer.

3. *In situ* polymerized composites with crosslinked PS microspheres. Methyl methacrylate (MMA), vinyl acetate (VAc), or styrene were suspension polymerized in the presence of the crosslinked PS microspheres. The composite beads were then washed with water and dried in a vacuum oven at  $50^{\circ}\text{C}$ . The thickness of the films for microscopic observation was 0.1-0.2 mm. Figures 3-5 show the dark crosses of crosslinked PS spheres in PMMA, PVAc, and PS matrices, respectively. They were the same sizes of the spheres. The dark crosses were negative in PMMA and PVAc and positive in PS matrices. The disappearing temperatures were 150, 110, and  $285^{\circ}\text{C}$ , respectively.

DTA measurements were made for the studied composites on a Mettler TA2000 apparatus using a sample weight of around 10 mg. The glass transition temperatures are listed in Table I. In Table II are densities and expansion coefficients of the polymers. The densities were determined at 25.2 and  $51.7^{\circ}\text{C}$  by pycnometry, from which the coefficients of thermal expansion were calculated.

## DISCUSSION

Close observation of the micrographs shows that the dark crosses of these composites are quite different from that of spherulites. The later are usually called as Maltese crosses, having a radiating structure. Many concentric extinction rings are also seen on the later crosses. The reason of the extinction phenomena of spherulite is in the two different velocities of light along its radial and tangential directions. If the radial velocity is higher, the refractive index in this direction is lower than the refractive index in the tangential direction, a negative spherulite results. This, of course, is a reflection of its

inner structure. For the thermal stresses of spheres in a matrix Beck et al. gave the equations as follows<sup>3</sup>:

sphere:

$$\sigma_r = \sigma_t = P_0 = \frac{4(\alpha_s - \alpha_m)(1 + \nu_s)G_s G_m \Delta T}{6(1 - 2\nu_s)G_m + 3(1 + \nu_s)G_s} \quad (1)$$

matrix:

$$\sigma_r = (\alpha/R)^3 P_0 \quad (2)$$

$$\sigma_t = -0.5\sigma_r \quad (3)$$

where  $\sigma_r$  and  $\sigma_t$  are the stresses in the radial and tangential directions, respectively.  $P_0$  is the hydrostatic pressure on the surface of the sphere.  $\alpha$  is the volume coefficient of thermal expansion,  $G$  is the shear modulus,  $\nu$  is Poisson's ratio,  $a$  is the radius of the sphere,  $R$  is radial distance from the center of the sphere,  $\Delta T$  is the temperature decrease giving rise to the stresses, and subscripts  $s$  and  $m$  designate the sphere and matrix, respectively. From the stress-optic law,<sup>4</sup>

$$n_r - n_0 = c_1 \sigma_r + c_2 \sigma_t \quad (4)$$

$$n_t - n_0 = c_1 \sigma_t + c_2 \sigma_r \quad (5)$$

Some relations of refractive indices can be obtained as follows:  
in sphere:

$$n_r = n_t \quad (6)$$

in matrix:

$$n_r - n_t = 1.5(c_1 - c_2)\sigma_r \quad (7)$$

Since the optical constants  $c_1 \neq c_2$ ,  $n_r \neq n_t$ . This explains the birefringent pattern of PC filled with glass beads (Fig. 2). In PPO/PS composite with crosslinked PS microspheres, the spheres have a larger coefficient of thermal expansion and good adhesion with the matrix. A drawing force will be exerted on the matrix by the spheres when cooling down from the fabrication temperature. Therefore, it is anticipated that the shell and core of the sphere will be in different mechanical conditions. The shell is the inhomogeneous contracting part of the sphere owing to the tensile stress by the matrix, while the core is the homogeneous contracting part. The hydrostatic pressure on the inner surface of the shell is assumed to be zero. The stresses in the shell should be<sup>5</sup>

$$\sigma_r = \frac{a^3(R^3 - b^3)}{R^3(\alpha^3 - b^3)} P_0 \quad (8)$$

$$\sigma_t = \frac{a^3(2R^3 + b^3)}{2R^3(\alpha^3 - b^3)} P_0 \quad (9)$$

where  $a$  and  $b$  are the outer and inner radius of the shell, respectively.  $R$  is the radial distance from the center of the core in the shell, and  $P_0$  the hydrostatic pressure on the outer surface of the shell. The radial displacements at the interface between the microspheres and matrix are equal,<sup>5</sup>

$$\frac{1}{3}(\alpha_s - \alpha_m)\Delta T a - \frac{P_0 a}{E_s}(1 - 2\nu_s) = \frac{P_0 a}{2E_m}(1 + \nu_m) \quad (10)$$

From the above relation the same  $P_0$  as eq. (1) can be obtained. Hence  $n_r \neq n_t$  in the shell can also be deduced from the stress-optic law. This explains the dark crosses seen in Figure 1. In this paper the relative difference between the expansion coefficients of the two polymers is only 30%; the photoelastic effects by the thermally induced stresses are undoubtedly observed. The similar observations have been reported in the literature.<sup>6-8</sup>

The photoelasticity by the thermal stresses cannot explain the extinction phenomena seen in Figures 3-5. The thermal stress disappears at  $T_g$  of the matrix, but the birefringent patterns in Figures 3-5 disappear at very high temperatures, even at the temperature when the matrix is in molten state. The dark crosses here are mainly due to the inhomogeneous swelling or contracting of crosslinked PS networks in the matrices. With polymerization going, the originally homogeneously swelling networks will contract in PMMA and PVAc, or swell further in PS, because crosslinked PS is not miscible in PMMA and PVAc but in PS. These are not homogeneous because of great viscosity of the polymeric systems. Sternstein published a theory describing the stress distribution in the inhomogeneously swelling network.<sup>9</sup> They also studied the birefringent pattern of the network.<sup>10</sup> The theory completely explains the reported phenomena in Figures 3-5.

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Received October 1, 1985

Accepted October 27, 1986