PREPARATION AND CHARACTERIZATION OF NANOCOMPOSITE FILMS

G. Carotenuto, L. Nicolais, Department of Materials and Production Engineering, University of Naples Federico II - Piazzale Tecchio, 80 - 80125 Napoli, Italy

The incorporation of nanosized inorganic particles into a polymeric matrix represents the most important problem in the nanocomposite fabrication. Success in manufacturing materials for optical devices can be achived only if the particle aggregation is avoided. This paper describes the preparation of a polymeric nanocomposite containing a well-dispersed red pigment synthesized using nanosized titania particles.

Introduction

Nanocomposites are an interacting mixture of two phases, one of which is in the nanometer size range (1). In the last few years, these materials have become a major part of new materials synthesis all over the world for application ranging from mechanical to optical, magnetic, and dielectric (1,2). The composite materials between polymer and ceramic particles in the micrometer scale range are opaque. Light scattering, responsible for their opacity, can be suppressed decreasing the dimensions of the filler to a nanometre scale range. Therefore, the nanocomposites can act as optically homogeneous materials with modified optical and mechanical properties. Nanocomposite films can be used as optical filters, non linear optical, or ultrahigh refractive index materials (3).
This paper describes the preparation of agglomerate-free nanocomposite thin films, in which uniform nanosized spherical TiO_2 particles containing dyes are dispersed in a poly(methyl methacrylate) (PMMA) matrices. These samples have been characterized by scanning electron microscopy (SEM).

Experimental

To produce the TiO_2 particles, a 2 mol dm^{-3} $TiO(NO_3)_2$ solution was heated at 95°C for 10 min, which resulted in a precipitate of broad size distribution. The nanosized fraction was separated by centrifugation at 10,000 rpm for 15 min, which caused larger particles to settle. The finely dispersed nanosized solid was then purified by repetitive centrifugation and washing with deionized water. The red pigment was synthesized by adding 300 cm^3 of a 0.02 mol dm^{-3} aqueous solution of D&C Red#6 dye into 30 cm^3 of a dispersion containing 200 g dm^{-3} of the purified titania particles. The system was then stirred for 15 min in an ultrasonic bath and, finally, the pigment was separated by centrifugation at 5,000 rpm. In order to well disperse the pigment in the polymer, the particles had to be thoroughly dehydrated. For this purpose, the solid was washed with ethanol to remove water, and rinsed twice with propylene glycol methyl ether acetate (PMA) to remove the alcohol. The pigment was then dispersed in PMA (100-200 g dm^{-3}) using an ultrasonic bath, followed by mixing with a poly(methyl methacrylate) (M_W=30,000)/PMA solution (50wt% polymer). The excess solvent was evaporated in vacuum under stirring at room temperature until the desired viscosity was achieved. The films were obtained by depositing the pigment/polymer composite on cleaned glass plates using a spin coater. The thickness of the film was controlled by adjusting both the PMA content and the spinning speed. Finally, the films were cured under vacuum at 70°C for 5 min.
Morphology, substructures, and thicknesses of the films were examined by SEM. The plates were broken by cutting from the back surfaces (which were not coated with the composite films) with a diamond cutter, and the fractured surfaces were then examined.

Results

The SEM picture of the anatase TiO_2 particles is shown in Figure 1. The particle diameter ranges from 10 to 15 nm. Films containing 50 wt% pigment were obtained by spin-coating mixtures of pigment, polymer, and PMA (20 wt%), on glass plates.

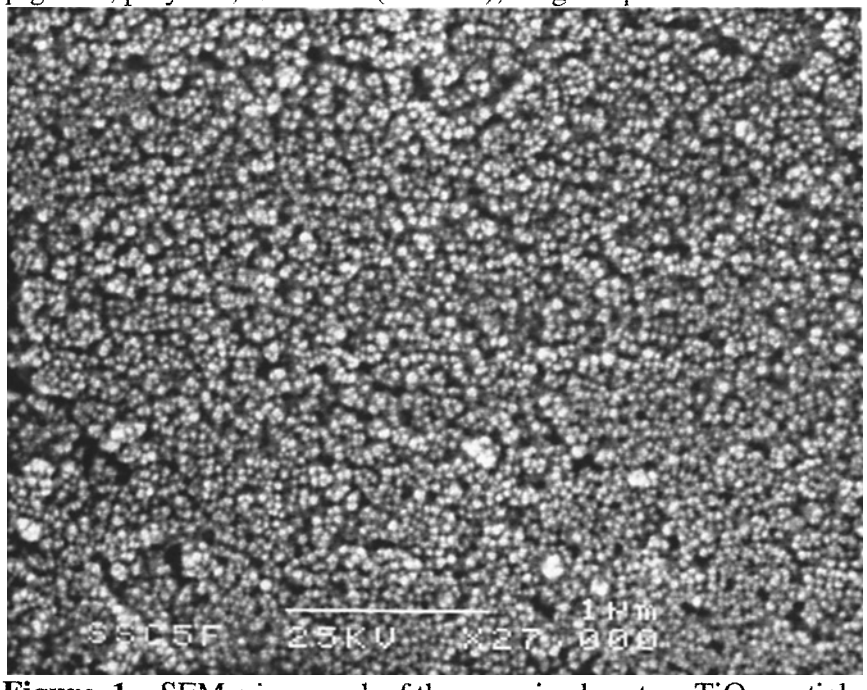

Figure 1 - SEM micrograph of the nanosized anatase TiO_2 particles.

The SEM study of the film cross-sections revealed that an insufficiently dehydrated pigment yielded films of low transparency, containing aggregates, cracks, and voids, see Figure 2.

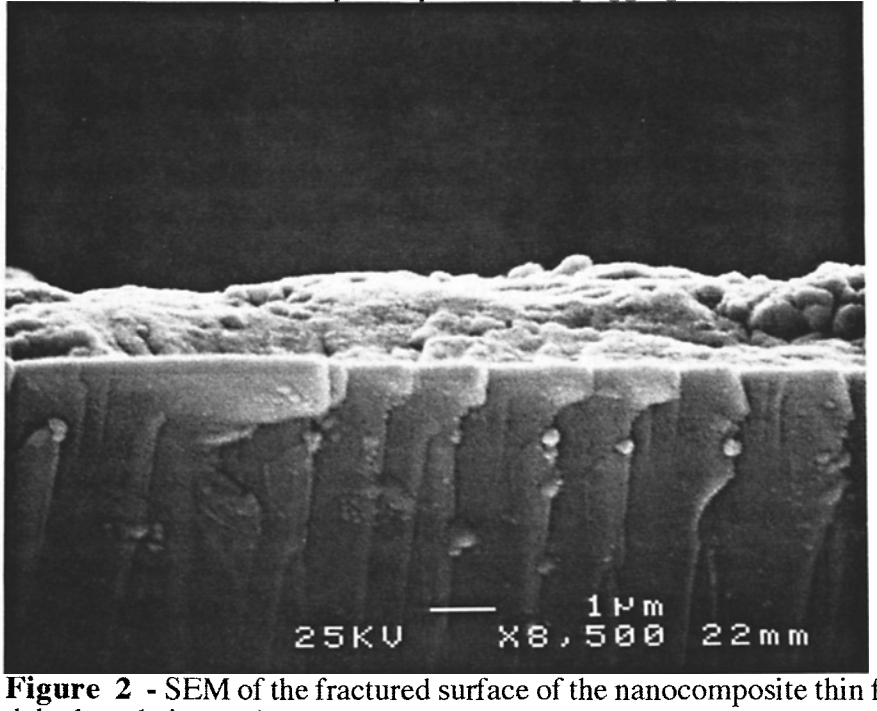

Figure 2 - SEM of the fractured surface of the nanocomposite thin film (50wt% of insufficiently dehydrated pigment).

The SEM picture of a nanocomposite thin film, containing 50wt% well-dehydrated pigment, is shown in Figure 3, it illustrates a very smooth and uniforme film without voids and cracks. In addition, the absence of shrinkage indicates that the film solidification was not accompanied by a significant densification.

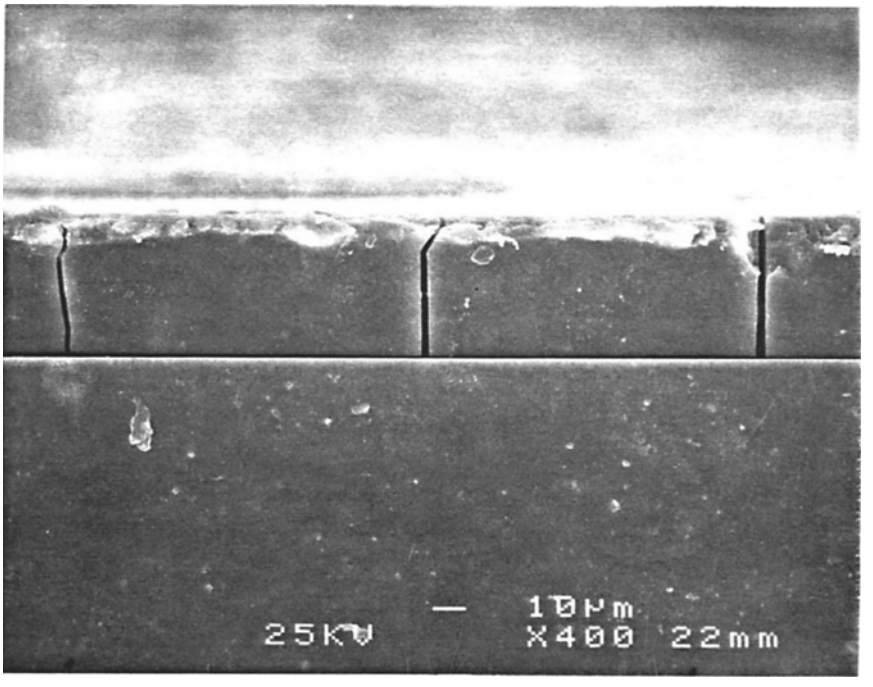

Figure 3 - SEM of the fractured surface of the nanocomposite thin film (50wt% of well-dehydrated pigment).

Discussion

The major problem in the preparation of TiO_2-PMMA nanocomposites is the mixing of the inorganic particles with the macromolecular matrix in order to achieve an uniform dispersion.

When the inorganic surface of the particles contact the polymer solution the only possible interactions at interface are by hydrogen bonds between the methyl-ester groups of PMMA and the hydroxyl groups contained on the particle surface. These interactions are not strong, and consequently, the resulting dispersion is not uniform because many particles are agglomerates. If the surface of the particles is organically modified, operation that can be realized by reaction with an organic dye, each particle results hydrophobic and can interact with the not polar macromolecular segments. This situation produces a remarkable improvement in the quality of the dispersion.

In addition, the nano-size TiO_2 particles are synthesized in aqueous solutions, using process of precipitation in homogeneous phase. These reactions can be controlled to yield uniform particles of different structure, shape, and size. When used as filler for composite materials, they cannot be dried before the introduction in the hydrophobic polymeric matrix, because an agglomeration process can follow. To obtain a good dispersion the water surrounding the dyed particles must be accurately removed. It is possible to eliminate totally the water first washing the particle with ethanol (water-mixable solvent), and then removing it by washing several times with an organic solvent, in which the ethanol is soluble. In the present case the organic solvent was exactly the polymer solvent.

Conclusions

The preparation of a new nanocomposite material, produced in form of thin film via spin-coating deposition technology, has been investigated. The SEM characterization of the nanocomposite cross sections shows as with particles modified by an organic dye the dispersability in the polymer solution is enhanced, and films with high smoothness and uniformity can be obtained.

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