Photoelastic Studies of Residual Stresses around Fillers Embedded in an Epoxy Matrix

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Summary: A photoelastic method was used to investigate the residual stresses in thermoset matrices during curing and cooling generated around spherical and high shape ratio fillers modelled by glass beads and glass or carbon fibers,respectively . Two types of reactive systems were selected: i/ based on a stoichiometric mixture of epoxy prepolymer and diamine comonomers –polycondensation- ; ii/ based on a mixture of epoxy prepolymer and an anhydride –chain polymerization-. A mapping of the residual stresses was obtained after curing process and after hydrothermal aging. From such a method, the location of the maximal stresses and the extend of residual stresses field can be discussed as a function of the geometry of the inclusions, the nature of the matrix, and the aging. The photoelastic method can be effective for various types of fillers and polymer matrices in order to select the proper associations of components for composite materials.

KEYWORDS: photoelasticity, residual stresses, epoxy, fiber, hydrothermal aging

Introduction

Residual stresses are important factor influencing the strength of filled polymers. The origins of residual stresses are usually differences in thermomechanical properties of constituents. Residual stresses strongly influence the overall strength and durability of polymer-based composites. As a consequence, they are still the subject of many investigations. They are usually observed during polymer processing at a temperature higher

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than the temperature of use. The residual stresses may be induced during curing of thermoset resins such as epoxy containing fillers (fibers, particles as beads or flakes) as polymerisation occurs by increasing temperature followed by cooling to room temperature. In fact, there are two origins of the residual stresses in thermoset-based composites: differences in thermal expansion coefficients, which lead to thermal stresses, and shrinkage during curing of matrix around fillers due to chemistry.

Photoelastic method

The state of stress around a filler inclusion embedded in a matrix was intensively modelled in the past by finite elements methods. These methods, usually effective, have some limitations in modelling of real properties of materials as they require on input the initial parameters, the interface properties, boundary conditions, etc.

Another very efficient way of studying residual stresses is photoelasticity , which is based on changes of polarization and phases of light passing through the stressed material[1]. The measurements of two dimensional states of stresses or strains by photoleasticity is relatively easy and cheap. In the case of volume (three dimensional, 3-D) stresses, the "frozen stress" photoelastic method is often used. This method requires to slice the material into thin layers which are analyzed by two dimensional conventional photoelasticity with polarized light. However, the "frozen stress" method cannot be applied to materials with small inclusions.

Few years ago, we made an effort to develop a 3-D photoelastic method of stress analysis for a limited case of a single axisymmetric inclusion embedded in a transparent matrix[2] . The method was successfully applied for the analysis of stresses around a single bead embedded in an epoxy resin matrix as an external tensile stress is applied and for the determination of residual stresses[3]. The method is based on Aben's concept of the characteristic parameters[4] for the description of optical properties of the birefringent matter and the Jones's matrix calculus for the description of light transmission[5]. The sample is divided into thin concentric cylindrical shells. Three Aben's characteristic parameters, i.e primary and secondary characteristic directions and characteristic retardation describe the

changes of polarization of light transmitted through the stressed material. These measurable parameters are the input data for the calculation of secondary stresses acting in plane perpendicular to the light path in the material. The calculations are begun far from the inclusion, where the light path through the stressed area is so short, that the stresses along the light path are uniform. The principal stresses are then determined directly from the characteristic parameters. The complicated 3-D object may be represented as a sequence of thin uniform sub-elements on the light path, which are parts of concentric cylindrical shells. Each of these sub-elements is a birefringent plate. The assembly of these elements is considered as the representation of the optical properties along the light path in a whole object, according to the equivalence theorem. Our method permits the determination of the principal stresses differences while the individual stresses may be further separated by using stress equilibrium conditions.

The photoelastic method was applied to study the stress state around spherical inclusions in an epoxy resin. In the present work, we modified and applied our method to the study of residual stresses around different types of model inclusions such as graphite and glass fibers which model the case of fillers with a large shape factor, L/D, embedded in an epoxy resin matrix. The analyzed stresses result from the shrinkage during matrix polymerization and from the thermal expansion misfit between matrix and fibers. The method was also used to study the influence of hydrothermal aging on the level of residual stresses for both systems with high shape ratio –fibers- and spherical –beads- inclusions.

Experimental

Materials

The samples were prepared by embedding inclusions in an epoxy-based reactive system followed by a curing to reach the completion of conversion. Two types of chemistry for the epoxy network building were considered. In the first an Epoxy prepolymer (Polysciences) was cured with dodecenylsuccinic anhydride as a hardener in the presence of 2,4,6-tri(dimethylaminoethyl)phenol (DMP 30) as initiator, i.e the curing proceed from a

chain polymerization. The resin was cured for 3 hours at 120°C and then cooled down to room temperature. The second route of matrix building was based on curing DGEBA prepolymer with 4,4'-methylene-bis-[2,6-diethleneaniline] (Lonza) as hardener (polycondensation reaction). The DGEBA/amine system was cured for 4 hours at 135 °C and post-cured at 190 °C for 4 hours. All reactions were conducted for a ratio of epoxy-to-anhydride and epoxy-to-amino hydrogen equal to1, which lead to fully crosslinked networks as revealed by DSC. The details of the curing procedure with amine were described earlier by Zinck et.al.[6].

Two types of fibers were used: graphite DG 114 (Celanese Adv. Eng. Composites) and sized E-glass fibers referred as P122 (Vetrotex Int.). Both fibers have a typical diameter of 17-20 μm. Short and long single fibers were embedded in the central plane of 1 mm-thick samples. Several samples with E-glass fibers were aged for 16 days in distilled water at 20°C. Untreated glass beads (International Enzymes Ltd.) of 250 μm-diameter were also used in the studies of hydrothermal ageing. The composites were submerged in distilled water for 16 days at 20°C or for 4 days at 90°C. The water absorption was controlled during the experiments by thermogravimetric analysis.

Photoelasticity measurements

The changes in optical properties around inclusions were studied by means of the 3-D photoelastic method (Figure 1). The micropolariscope based on polarizing microscope was equipped with sensitive CCD camera (0.003 lux), frame grabber card, and a PC computer. The illuminating light was filtered by a 546 nm monochromatic filter. The 10-bits frame grabber card could resolve a 1024 gray levels with in the scanning area of 768x576 pixels. Using such an equipment, it was possible to measure very small retardations, all below the first order isochrome.

For the samples containing spherical fillers, i.e. glass beads, it was relatively easy to measure the optical retardation and then to calculate stress components. As the knowledge of photoelastic constant of the matrix is required for such calculations, the photoelastic constant of materials were determined from the retardations measured for a samples without inclusions

stretched uniformly to 1% of strain. The determined values were:1.9 x 10^4 N.m/fringe for Epoxy/anhydride and 2.7 x 10^4 N.m/fringe for DGEBA/amine matrix.

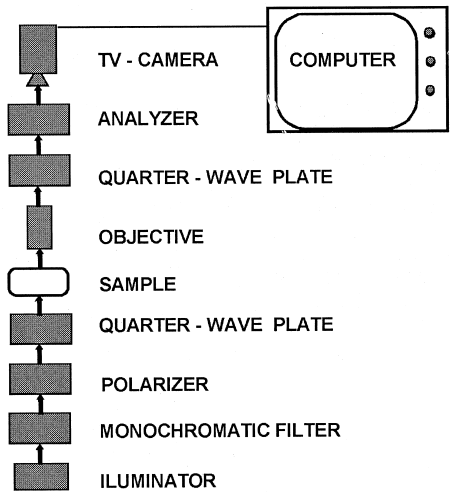

Fig. 1. Schematic representation of the automated micropolariscope.

Results and discussion

Samples with high shape ratio fillers, i.e. short fibers

A typical photoelastic integrated image for a short glass fiber embedded in a DGEBA/amine epoxy resin is given in Figure 2a. The residual stress pattern is typical for this type of microcomposites. From the maps of the characteristic directions and retardation it can be evidenced that the stresses are concentrated in the vicinity of fiber ends. The distance range of the influence of fiber ends on the residual stresses remains short. In the fiber axis direction, the distance under stresses is about 150 μm. From the birefringence analyses, one can see that the stresses increase drastically close to the interface.

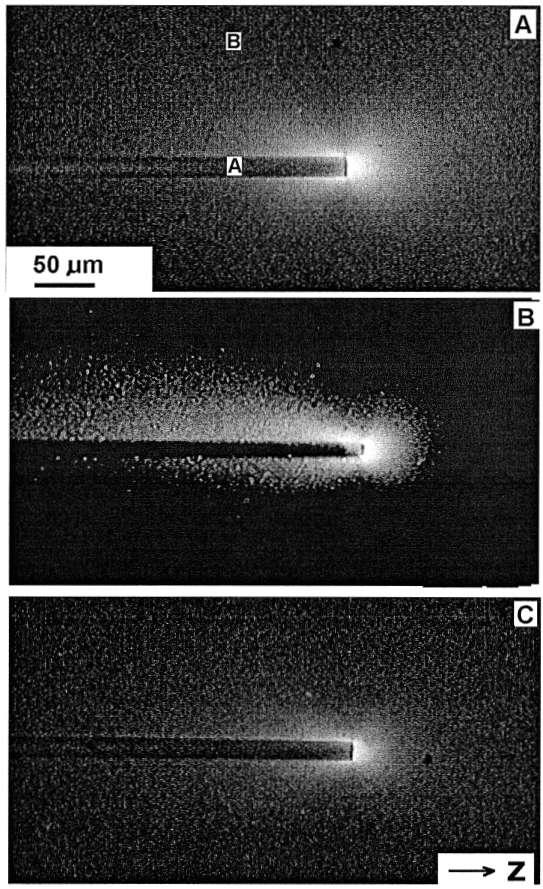

Fig. 2. The photelastic images of residual stresses present in the epoxy matrix around a glass fiber. (a) DGEBA/amine sample after curing; (b) Epoxy/anhydride sample after curing; (c) DGEBA/amine sample after 16-days of water aging at 20°C.

Much lower stresses in the matrix along the fiber far from the fiber ends were observed. Their distance of influence (AB direction in Figure 2a) was approximately 70 µm away from the fiber surface. Differences between the two types of epoxy matrices can be noticed. In fact, for the Epoxy/anhydride matrix, stresses perpendicular to the fiber, in a plane

locate in the middle of its length, are observed even at a distance of 120-140 μm (Fig. 2b) whereas for the DGEBA/amine matrix (Fig. 2a), the birefringence along the glass fiber is evidenced only very close to the fiber end.

The hydrothermal aging of samples with embedded fibers was performed in water at 20°C but also at 60°C. A picture of the DGEBA/amine sample after treatment in the water during 16 days at 20°C is given in Figure 2c which is the same as observed in Figure 2a. Measurements of the optical retardation vs. distance from the fiber end in the fiber direction are presented in Figure 3. The stresses partially relax in the vicinity of the fiber ends at distances from 10 to 100 μm. The relaxation of the stresses along the fiber was much smaller. The water was removed from the sample under vacuum at room temperature for one day. Water desorption leads to almost complete recovery of the initial stresses as it is detected in photoelastic images. This observation conforms to other earlier findings.

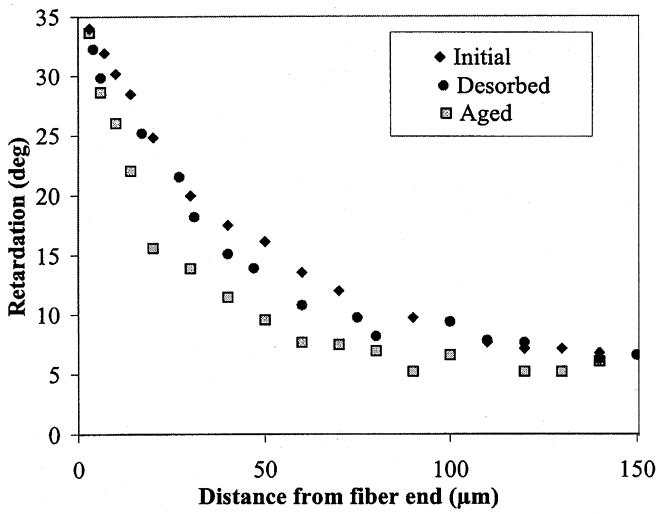

Fig. 3. Optical retardation in a DGEBA/amine-based matrix in the z – axis direction, after hydrothermal treatment and subsequent water desorption.

Hydrolysis phenomena such as chain scission were not evidenced at 60°C, by infra-red and NMR analyses and the water diffusion was found to follow a pseudo-Fickean process. The

plasticization of the network leads to a decrease in the glass transition temperature from 158 to 124°C from 1.8 wt. % of water uptake at the equilibrium state. Thus, the glass transition temperature of the aged sample is well above the aging temperature and the influence of hydrothermal aging on the tensile modulus was found to be negligible.

The approximated calculations of residual stresses as the function of the distance of the fiber surface can be performed by using Nairn & Wagner's approach[7,8]. In this model a cylindrical geometry with infinite length of fiber is assumed. Three stress components σ_θ - tangential-, σ_r –radial-, and σ_z -along the fiber axis- were calculated for both epoxy/glass fiber systems using previously determined parameters[3,6] (Figures 4a and 4b). In DGEBA/amine system (Figure 4b), the stresses are nearly 30 times higher than in Epoxy/anhydride based resin (Figure 4a).

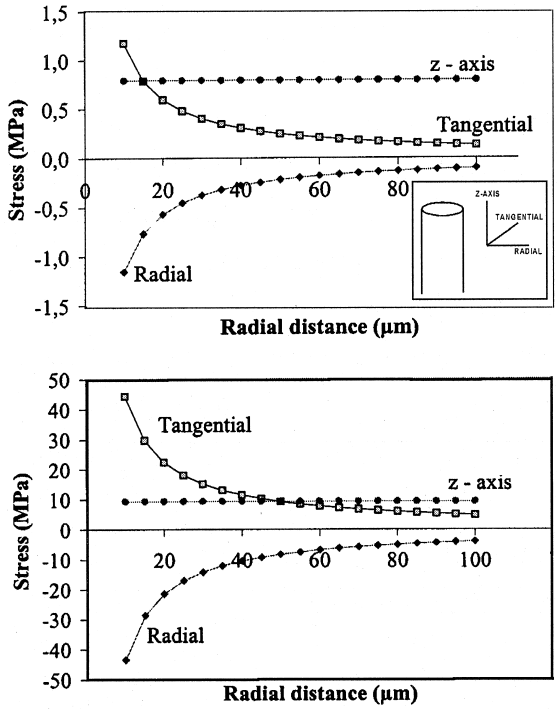

Fig.4. Stress distribution around a glass fiber (diameter 10 µm) according to Nairn & Wagner's approach: (a) Epoxy/anhydride-based and (b) DGEBA/amine-based microcomposites.

The characteristic directions are radial in the vicinity of the fiber and are perpendicular to the fiber axis in a distance from the fiber end. In both systems the radial stress, σ_r, is compressive in character while the tangential stress, σ_θ, acts in tension. The σ_z stress along the fiber axis extends for a large distance from the fiber axis without decreasing. The σ_z stress in DGEBA/amine system is about 9 MPa and can be observed using the micropolariscope, whereas in the Epoxy/anhydride-based microcomposite, the σ_z stress is about 0.75 MPa and cannot be detected by photoelasticity.

Samples with spherical fillers, i.e. glass beads

The optical patterns around isolated glass beads are given in Figure 5. Due to the curing of the microcomposite at high temperatures, large bright areas are visible around inclusions using micropolariscopic investigation. These areas correspond to non-uniform stressed zones of the epoxy matrix. From Figure 5a, it can be deduced that optical effect is more pronounced in DGEBA/amine-based system than in Epoxy/anhydride system (Fig. 5c). In addition, hydrothermal treatment decreases the brightness of photoelastic images (Fig. 5b) which indicates a lower stress state for aged specimen.

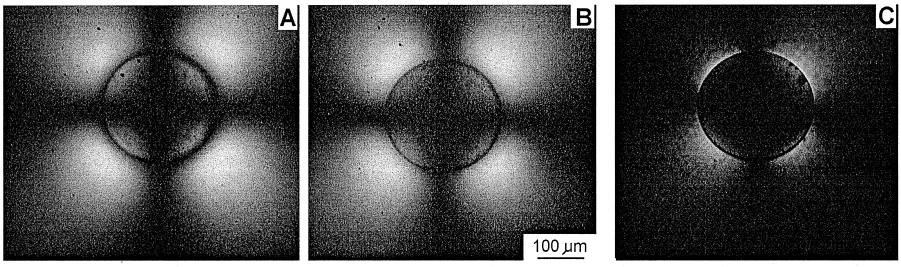

Fig 5. Photoelastic images of epoxies with glass beads: (a) DGEBA/amine matrix after curing; (b) the same sample as (a) after water immersion, for 4 days at 90°C; (c) Epoxy/anhydride matrix after curing.

The measured characteristic retardations of light were used for stress calculations. Due to the

point symmetry of isolated bead-matrix system, the stresses in all radial directions are the same but their values depends on the distance from the inclusion. At each point of the matrix only two components of stress tensor are independent: radial, σ_r, and tangential, σ_θ. In Figure 6, the results of stress determination in DGEBA/amine matrix are presented, while in Figure 7 the stresses for the Epoxy/anhydride matrix are plotted against the distance from the inclusion surface. The radial stresses are approximately twice of the tangential ones. A negative sign of radial stress values means a compression state of stress. The maximum values are: -26 MPa and -12 MPa for DGEBA/amine and Epoxy/anhydride matrices, respectively. The distance from the surface for which significant stresses are observed is 2.7 and 2.4 times of the inclusion radius in DGEBA/amine and Epoxy/anhydride matrices, respectively. These observations emphasises the large influence of the type of matrix for the level of residual stresses generated during curing and cooling.

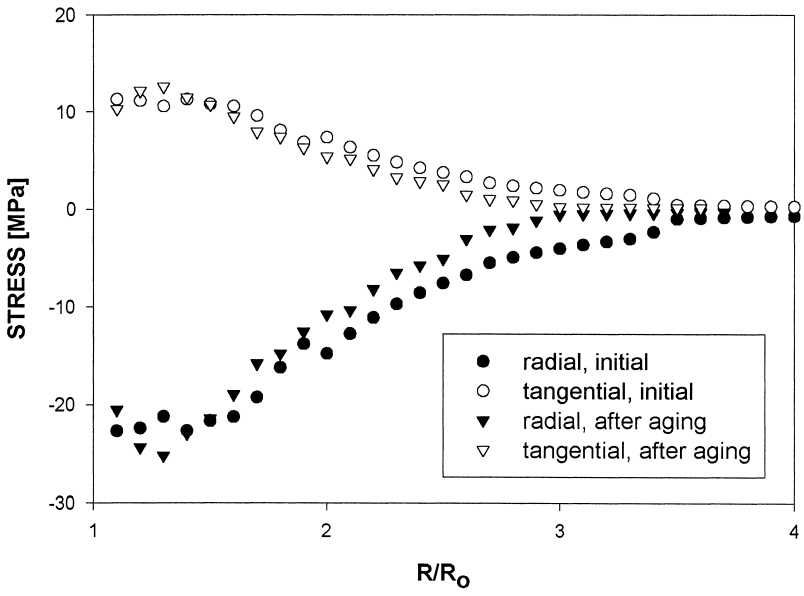

Fig 6. Stress distribution around glass bead in DGEBA/amine matrix.

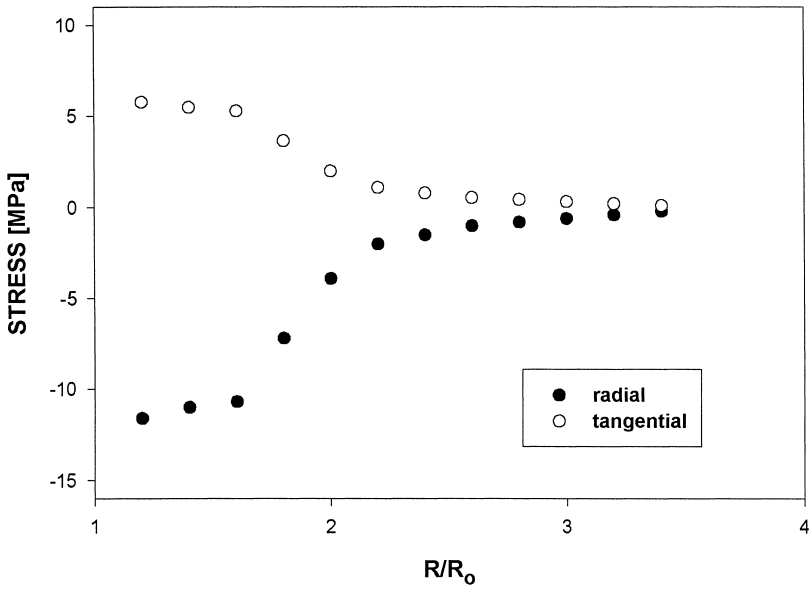

Fig. 7. Stress distribution around glass bead in Epoxy/anhydride matrix.

As reported, the state of residual stresses are sensitive to water uptake. Changes of stresses distribution in amine cured matrix after hydrothermal treatment are given in Figure 6 and similar tendencies are observed in the Epoxy/anhydride matrix. In both cases the stresses are lower for the aged samples. The lager decrease of radial stress is about 10 % below the initial level. The stress relaxation due to hydrothermal treatment is reversible as the initial values are recovered after 7 days of drying in air.

Samples with long fibers

For specimens based on the same epoxy embedding long fibers, the largest residual stresses concentrate near the fibers tips, similarly as for the short fiber-based microcomposites. However, in the part of samples, including both matrices, we observed that in the matrix between fiber ends the residual stresses extend far from the fiber surface, as observed previously. Examples of birefringence patterns due to a long distance stresses are

given in Figures 8 and 9. The distance for which their presence is evidenced, detected in micropolariscope, is 300-500 μm. Observation in micropolariscope reveals that these stresses are axisymmetric around fiber axis and their amplitude is much lower than the short range stresses at fiber tips. As a consequence, long fibers can transfer stresses to the matrix for large distances (300-500 μm). In the opposite, the zones of the matrix which are far from the fibers can load to the fiber as a stress is applied. Thus, it is evident that long range interaction of long fibers with epoxy matrix indicates the effective reinforcing effect of long fibers. The load transferred from the fiber to the matrix can be significant even if the level of stresses remains low, due to the large extend of interaction. In all the cases, if there is a sign of large range of residual stresses around long fibers, the reinforcing should be very effective, providing that the matrix will not be overloaded. In such a sense the presence of long range residual stresses in composites is favourable for reinforcement.

Conclusions

The observations by photoelasticity demonstrate the complex nature of the residual stresses around spherical and high shape ratio fillers in epoxy matrices. Their range and values depended on the nature of matrix, i.e. the related chemistry, curing conditions, and fiber surface treatment. For high shape ratio fillers as fibers, the residual stresses concentrate in restricted areas near fiber ends. In Epoxy/anhydride matrix, the stress field is larger but the maximum values are lower than in DGEBA/amine system. Hydrothermal aging strongly influences the stress distribution in epoxy matrices around fillers. The stresses partially relax due to water absorption of the matrix but after drying initial values can be retrieved. For long fibers, the presence of long range residual stresses shows the effective transfer of stresses in fiber - matrix system.

The presented approach can be applied to various types of fillers having different sizes and shapes and for measuring the overlap of stress field around particles. This photoelastic method can be used also for the control of curing / cooling processes and for measuring the efficiency of stress transfer in various fiber-matrix systems.

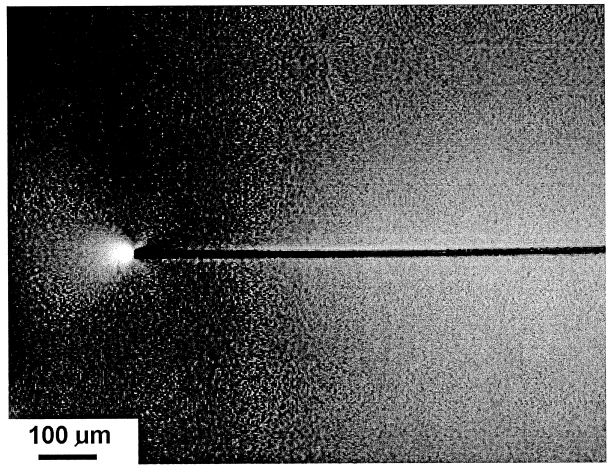

Fig. 8. Birefringence pattern around an isolated long glass fiber in the DGEBA/amine matrix.

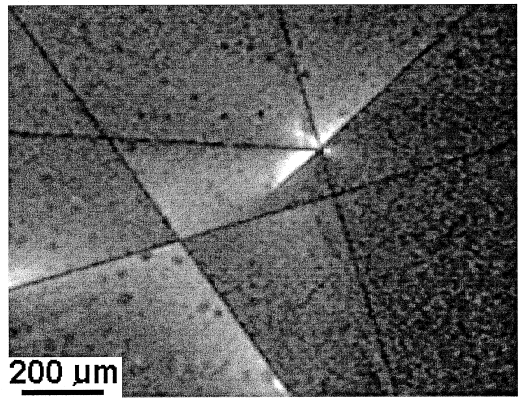

Fig. 9. Integrated photoelastic image for an assembly of long graphite fibers in Epoxy/anhydride epoxy matrix (fiber thickness is 19 µm).

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