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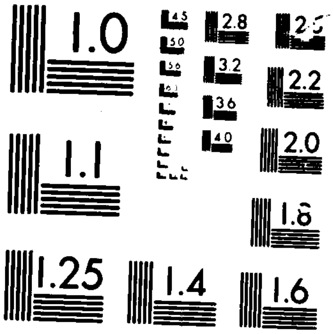

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The effect of a brittle surface layer on the mechanical behavior of polymers has been studied. The brittle surface layer has been simulated by laminating a thin film to a polymer or by ultra violet irradiation of the surface.

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Fracture mechanics theories have been utilized to account for the phenomenon of surface embrittlement. A criterion has been established suggesting that embrittlement will only occur when the dynamic stress intensity factor in the brittle layer reaches a value greater than the arrest toughness of the ductile substrate. It has also been shown that the embrittlement phenomenon can be described in terms of a critical crack velocity or critical thickness. It is shown that brittle films less than .005 inches thick can cause brittle failure of polymers such as polycarbonate and ABS. It is also shown that cracks can attain velocities of up to 200 m/sec when propagating through such films.

Keywords: Fracture mechanics.

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The Control of Polymer Mechanical Behavior by Surface Modification

Final Report

Lawrence J. Broutman

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Chicago, IL 60616

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1. Problem Statement

Surface embrittlement describes the phenomenon wherein normally ductile materials behave in a brittle manner as a result of a thin embrittled layer at their surface. Brittle behavior is viewed as failure of the polymer under tensile stress at a strain equal to or less than the yield point strain. The principal objective of this research is to determine the effect of a brittle surface film on the resulting mechanical behavior of a ductile polymer.

The thickness of a surface layer which can adversely affect the properties of a bulk polymer is small compared to the total thickness. Embrittlement typically results from thermal oxidation or ultra violet irradiation (outdoor weathering) as well as from purposely applied paints or coatings to the surface of a polymer. It might also occur as a result of processing or fabriaction of the polymer, typically caused by thermal oxidation. In more limited cases it can be caused by a surface structure (e.g., crystallinity) which is different from the bulk created as a result of processing.

2. Summary of Results

The effect of a brittle surface coating on the mechanical behavior of rubber-modified polymers in uniaxial tensile loading was evaluated for both SAN-coated ABS and PS-coated HIPS polymers. In both cases, the coating polymer was of the same basic chemical composition as the glassy matrix component of the rubber-modified, version so that the laminated structure may be simply regarded as a specimen whose surface layer was depleted of rubber particles. By lowering the molecular weight of the coating, the condition of decreasing matrix molecular weight of the surface layers due to long term environmental degradation was simulated. In the case of SAN-coated ABS, nine different SAN polymers were used, with the number-average molecular weight ranging from 18,000 to 90,000. On the other hand, HIPS was coated with five different PS polymers of molecular weight from 16,000 to 110,000.

In general, the coating thickness varied from about 25 to 150 microns although in some cases much thicker coatings were also used. These coatings were laminated onto one surface of the 3mm thick sheets of the ductile substrates so that the coating thickness represented from about 1-5% of the total sample thickness.

By far the most easily discernible change in the tensile behavior of the coated specimens was the severe loss of ductility based on the measurement of strain to failure or area under the stress-strain curve. Either of these was observed to be dependent on both the coating thickness and its molecular weight. For a given molecular weight coating, the ultimate elongation decreased rapidly as the coating thickness increased. The rate of decrease was especially pronounced initially for thin coatings, but became more moderate for thicker coatings. Eventually, a critical coating thickness was reached when the coated specimen failed in a brittle fashion evidenced by the absence of an apparent load drop at yield. Thus, at the critical coating thickness, the ultimate fracture strain of the coated specimen has been reduced to the yield strain of the uncoated polymer. The strain to failure of the coatings, determined in separate experiments by testing thin free films, was also of about the same magnitude as the ultimate fracture strain of the coated sample. However, the value of the critical coating thickness required to cause elimination of the yield point was observed to increase slightly with the coating molecular weight.

On the other hand, the embrittlement effect appeared to be more severe for coatings of sufficiently low molecular weight. Not only is the critical thickness required to eliminate yielding less than those for higher molecular weight coatings, but on increasing thickness, the ultimate fracture strain of the coated sample decreased to below the yield strain and eventually reached the ultimate fracture strain of the coating, which was lower than for coatings of higher molecular weights.

A brief summary of a possible mechanism consistent with the multiple crazing theory which can account for all of the observations above is presented below. Consider first a thin coating of a high molecular weight material in which stable crazes can form. Since the craze initiation stress is independent of molecular weight, crazes can form in the rubber-modified material as well as in the coating, whereas craze growth can terminate at the rubber particles within the ductile substrate in favor of crazing elsewhere. Crazes formed in the coating can increase in size unimpeded across the thickness of the coating. Craze thickening in the coating thus occurs simultaneously with multiple craze formation and termination in the substrate. This stage corresponds approximately to the macroscopic yielding evidenced by a load drop. With continued deformation, the rupture of the craze fibrils eventually leads to the formation of a true crack in the coating. When the coating thickness is less than the critical crack size required for unstable crack propagation, only slow, stable crack growth can take place. Due to the stress concentration created ahead of the crack tip, deformation of the substrate is preferentially localized there at the expense of further crazing elsewhere. This effectively reduces the amount of matrix material available for crazing and results in much reduction in ductility. Thus, provided that the coating is thin, macroscopic yielding is possible although much reduced for a coated specimen.

When the coating thickness exceeds the critical crack size for fast crack growth, the propagating crack impinges on the coating-substrate interface at a substantially higher velocity. This effectively enhances the local strain rate at the crack tip. According to the time-temperature equivalence principle, this may be interpreted as a reduction of test temperature or as an upward shift of the glass transition temperature of the rubber particles in the region of interest. In any case, it is reasonable to expect a reduction of the substrate fracture toughness so that a rapidly moving crack can propagate through the substrate with much reduced resistance. Thus, the ultimate fracture strain of the coated sample coincides with that of the coating polymer. Furthermore, the critical coating thickness required in this situation is equal to the critical crack dimension just prior to the onset of unstable crack growth. Further increase in coating thickness beyond the critical value is not expected to continue to reduce the ultimate fracture strain since the fracture characteristics of the coating depends not on its thickness but its molecular weight. Thus, increasing critical coating thickness with molecular weight is expected in light of the known observation that the mirror smooth slow crack growth region increases with the molecular weight.

When the coating molecular weight is below that required for stable crazes to form, the situation is slightly different. In this case, the fracture stress of the coating is lower than the craze initiation stress of the substrate, so that cracks are produced in the coating before any crazing can take place. The first crack is produced when the fracture strain of the coating is reached. Thereafter, stress build-up in the coating is due to shear stress transfer. As a result, it is expected that the number of surface cracks formed per unit length, or the crack density, increases with applied strain but decreases with coating thickness. For a thin coating, a large number of cracks are formed. Due to the stress concentration at the crack tips, multiple crazing is expected to occur only in the vicinity of the crack tips. This effectively reduces the amount of matrix material available for crazing, since the regions between crack tips remain relatively undeformed. Thus, the extent of multiple crazing is considerably reduced, leading to a drastic reduction in ultimate elongation. Increasing coating thickness decreases the number of cracks formed, thus further restricting the extent of crazing. The result is further reduction in ultimate elongation. With additional increase in coating thickness, there is an increasing probability that a crack will form such that the combination of crack depth, coupled with the prevailing stress in the specimen, produces the required stress intensity to enable the crack to propagate across the interface into the substrate in an unstable manner. Since the stress in the specimen continues to increase with applied strain, the instability condition can be achieved at a later stage even though the first cracks formed did not result in fracture. Eventually, a coating thickness is reached such that the first crack formed is sufficiently deep to enable it to propagate. As a result, the ultimate elongation of the coated specimen reduces to the fracture strain of the coating, and in the case of the lowest molecular weight coating polymer, is substantially below the yield strain of the uncoated substrate.

The effect of UV exposure was evaluated based on the standard tensile test at slow strain rate. The mechanical behavior of exposed samples was strikingly similar to those of coated specimens with thin coatings. As before, the elongation to failure was the most easily observed change in the resulting mechanical behavior. For ABS, there was an immediate although small reduction of ductility after only 20 hours of exposure. The ultimate elongation continued to decrease slowly with exposure time so that at the end of the 4.3 months exposure period, it has fallen from the unexposed value of 22% to 9%. The HIPS sample was, however, much more resistant to UV degradation. Over the same period of exposure, the ultimate elongation dropped form about 30% to 25%. This decrease was, however, only slightly more than the standard deviation of 3% normally associated with the measurements. The justification of the brittle layer method is certainly attested to by the observation that much longer exposure time would be required in order to bring about the same degree of embrittlement previously observed for coated specimens.

The surface embrittlement of ductile polymers has been explained using fracture mechanics principles. From fracture mechanics principles it was shown that the resistance of a polymer to surface embrittlement is greater the greater its crack arrest toughness. Further, it was predicted that a necessary and sufficient condition in order for a brittle layer to embrittle a ductile polymer is that the value of the stress intensity factor at the ductile-brittle interface during dynamic crack growth be greater than the crack arrest toughness in the ductile material. This hypothesis was verified by modeling the surface embrittlement process. A brittle material - ductile material duplex tensile specimen was designed. Measurements of crack velocity using this specimen showed that there is a critical crack velocity, V_C, above which the crack propagates through the interface and below which it arrests at the interface. The values of V_C obtained using the duplex specimen were the same as those determined from the respective $\dot{a}$ vs. K curves of the brittle and the ductile material. A compact crack line loaded specimen was used to determine the $\dot{a}$ vs. K curves for different polymers. Surface embrittlement was also modeled using a ductile material upon which a brittle coating was applied. These specimens not only allowed the measurement of a critical velocity, V_C, but also a critical thickness, t_C, necessary to cause embrittlement. These tests showed that it is possible for a crack to reach velocities of 300 to 400 m/s in brittle coatings which are less than 0.5 millimeters thick. The values of VC measured using these types of specimen are also identical to those determined from the $\dot{a}$ vs. K curves of the brittle coating and the ductile material. Crack arrest toughness measurements were made on a variety of polymers using the crack line loaded compact specimen and in the case of polycarbonate, the value was determined as a function of temperature.

3. List of Publications

"Surface Embrittlement Studies in Ductile Polymers", 2nd Intl. Conf. Proc., Polymer Sci, & Engr., Warsaw, Poland, Nov. 26, 1979 (with P. So).

"The Effect of Surface Embrittlement on the Mechanical Behavior of Rubber Modified Polymers", SPE Antec, May 1981; Poly. Eng. & Sci., 14, 22, 1982 (with P. So).

"A Fracture Mechanics Approach to Surface Embrittlement in Ductile Polymers", Proc. of 5th Churchill Conf. Deformation, Yield and Fracture of Polymers, Cambridge. England, April, 1982 (with L. Rolland, K. Thomson and S. Mostovoy).

"Surface Embrittlement of Ductile Polymers: A Fracture Mechanics Theory", Proc. of Soc. of Plastics Engineers Annual Tech. Conf., Chicago, IL May 1983; Poly., Eng. and Sci. Vol 25, 4 (1985) (with L. Rolland).

"Fracture Toughness and Crack Arrest in Polymers", Proc. 43rd Annual Technical Conference, Society of Plastics Engineers, April 29 - May 2, 1985 (with L. Rolland).

"The Fracture Behavior of Surface Embrittled Polymers", Proc. 43rd Annual Technical Conference, Society of Plastics Engineers, April 29 - May 2, 1985 (with Paul So).

"Effect of Coatings on the Fracture Behavior of ABS and Polycarbonate Polymers", 44th Annual Technical Conference, Society of Plastics Eng., May 1986 (with L. Rolland).

4. List of Scientific Personnel

Lawrence J. Broutman, Professor of Materials Engineering

Paul So, granted PhD in Metallurgical and Materials Engineering

Loic Rolland, granted PhD in Metallurgical & Materials Engineering

Dr. Gad Marom, Visiting Professor

Tat Wong, granted PhD in Metallurgical & Materials Engineering

Dr. Nachum Rosenzweig, Research Associate

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