



Fig. 2. True stress-strain curves of high and low density polyethylene. Curves 1 and 3 refer to the yielding and nonyielding regions of a sample of high density polyethylene, annealed. Curve 2 refers to an annealed sample of a low density polyethylene. Jaw rate (nominal) = 1%/min.

biaxial orientation versus uniaxial tension in low density polyethylene is probably related to the difficulty in the former of producing a state or orientation in which biaxial flow can occur.

It would seem, therefore, that the purely thermal approach^{1,2} to cold-drawing in a material such as Marlex 50, in which one would postulate elevation of the temperature to that approximating the loss peak at the melting point, is not a completely tenable explanation, and that the dependence of drawability on crystallite orientation is the more important factor.

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Migration of Copper Through High Purity Poly(methyl Methacrylate)*

Migration of copper from a metal surface into solid poly(methyl methacrylate) in contact with it has been observed

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when the purity of the monomer is high, with especial emphasis on low water content.

The monomer was purified so that the water content was below 0.04% (by the Karl Fischer reagent method), the inhibitor having been removed to well below 1 p.p.m., and other impurities having been similarly reduced. The purified monomer was transferred and partially polymerized in a lamp-grade nitrogen atmosphere at 70°C. and poured onto the prepared metal surfaces, either in an atmosphere of nitrogen or with less than 15 seconds exposure to air. The polymer completely filled the constant thickness gap between the metal plates. Copper metal surfaces were prepared to yield a clean surface free from a thick oxide layer by grinding with Al₂O₃ under reagent grade toluene. Assembling was accomplished rapidly by a technique which had previously been shown to yield the same adhesional strength and electrical pattern¹ on adhesional break as when the entire operation was carried out in lamp-grade nitrogen. The assembled samples were polymerized at 40°C. and cured at 100°C.

After breaking, it was observed that the polymer layer was colored green for some distance (at least 3×10^{-3} cm.) into the polymer. The region gave a positive spot test for copper by the *o*-toluidine test which detects down to 0.003×10^{-6} g.; the sample taken from the interior of the polymer in each case was several milligram, so that the concentration of copper was at least of the order of 1 in 10^6 .

No copper migration was observed with an identical procedure if the water content of the original monomer had been reduced only to 0.10%.

If traces of acrylic, methacrylic, or other acid had been present because of degradation during polymerization, a copper salt or soap could be responsible for the migration. The mobility of the product would be favored by removal of H₂O. In view of the low temperatures used during preparation, a different process appears more likely.

Water is known to bond to polyacrylic acid molecules by an H-type bond, and differences are observed when the water is displaced by other molecules. The absence of the nonmigrant water would leave volume for the copper migration. Cu(II) complexes with polyacrylic and poly-

methacrylic acids^{2,3} where the acids provide both covalent and coordinate linkages. The covalent, coordinate linkages are also observed in "etching primers"⁴ where one Cr atom, covalently linked to two O's not of the carboxyl group, is coordinately bonded to the double-bonded O, and another Cr atom is covalently linked to the ionic O. Morawetz² shows a distribution of coordination of a Cu(II) over 0, 1, 2, 3, and 4 carboxylates per copper atom. The interference to chelation by hydrogen bonding in polymethacrylic acid would be minimized in PMMA because of the less electropositive character of the H.

Two-dimensional drawings of the PMMA molecules with bond angle configurations determined by Fisher, Taylor, and Hirschfelder models indicate that in the tightly constructed PMMA configuration the double-bonded O to double-bonded O distances are from 3.4 to 4.5 Å. for a large number of atoms, both within a single chain and between chains; the O—O distances in other complex structures is of the order of 1.97/0.707 or 2.80 Å. It appears likely that distributions of interchain configurations will provide such geometrical relationships between locations of doubly-bonded oxygens, and that the metal could travel from one to the next. Coordination bond could therefore be broken under the influence of (1) new coordination bonds which could immediately form, (2) concentration gradients of Cu(II), (3) an electric field gradient, and (4) shifting and mobility of charges within the interior of the polymer. Crank and Park⁵ have suggested that the dependence of the diffusion constant (in polymeric materials) on the history of the diffusion process may be due to changes in configuration or structure of the polymer which proceed at a rate comparable to that of diffusion, or to stresses exerted by one part on others and arising from swelling.

The migration may therefore be similar to the migration in polyacrylic acid observed by other investigators, except that the covalent linkage to the copper is supplied not by the polymer, but by (1) other atoms involved in the migra-

tion, or (2) the migration of (+) charged Cu atoms, thus being integrally associated with the observed metal to polymer charge transfer at the interface. Polymer contacts to metal of short duration⁶ produce a (+) polymer; only after a great many contacts and/or macroscopically observable metal transfer is a (-) polymer observed. This may be supporting evidence for the occurrence of the metal migration during the short initial time interval during which the polymer is still polymerizing.

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