

| | |
|-------|------------------------|
| [100] | 6.9 GPa (a axis) |
| [010] | 8.6 GPa (b axis) |
| [110] | 2.2 GPa |
| [111] | 0.7 GPa |
| [001] | 312.5 GPa (fiber axis) |

Comparison between the experimental and theoretical results indicates that anisotropic behaviours of highly uniaxial and biaxial drawn high modulus films reflect the much weaker intermolecular forces between chains. Furthermore, it is suggested that the polymer chains composed of side-way free uniaxial drawn films and simultaneous biaxial drawn films are in more highly extended states in comparison with those of successive biaxial drawn films.

Acknowledgment

The present paper was performed under the management of the Research Association for Basic Polymer Technology for High Performance Plastics sponsored by Agency Industrial Science and Technology, MITI.

References

1. P. Smith and P. J. Lemstra, *J. Mater. Sci.*, **15**, 505 (1980)
2. H. Kiho and K. Asai, *Kobunshi Toronkai Preprint (Japan)*, P.835 (1974)
3. K. Furuhashi, T. Yokokawa, K. Ohsawa and K. Miyasaka, *Kobunshi Gakkai Polymer Preprint (Japan)*, **32**, (4) 874 (1983)
4. M. Matsuo and R. St. J. Manley, *Macromolecules*, **15**, 985 (1982)
5. M. Matsuo, *Kobunshi Gakkai Polymer Preprint (Japan)*, **32**, (4) 841 (1983)
6. K. Tashiro, M. Kobayashi, H. Tadokoro, *Macromolecules*, **11**, 914 (1978)
7. I. M. Ward, "Static and Dynamic Properties of the Polymeric Solid State", p.173 (1981) D. Reidel Publishing Co.

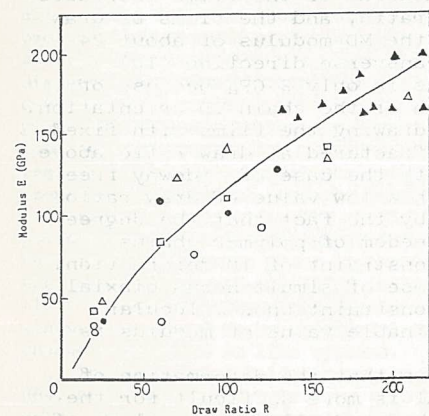


Figure 1. Relation between modulus and draw ratio for UHMWPE films made from various gel sheets by side-way free uniaxial drawings. (○) 0.7M PE, 1% decaline (●) 0.7M PE, 5% decaline (△) 1.9M PE, 1% decaline (▲) 1.9M PE, 5% decaline, obtained by zone drawing (□) 2.7M PE, 1% decaline

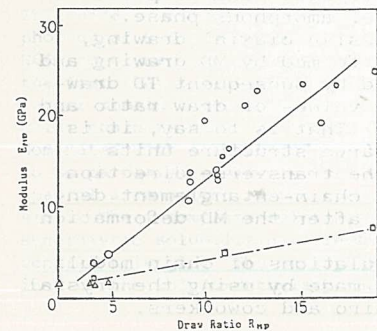


Figure 5. Relation between draw ratio of MD and modulus of MD for biaxial drawn UHMWPE gel films. (○) constrained uniaxial drawing, (△) successive biaxial drawing, (□) simultaneous biaxial drawing

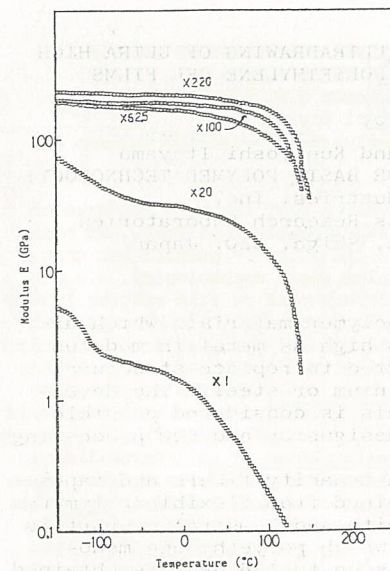


Figure 2. Dynamic Young's moduli for UHMWPE films made by side-way free uniaxial drawing. Sample of 220 draw ratio is obtained by zone drawing. Other samples are obtained by ordinary drawing.

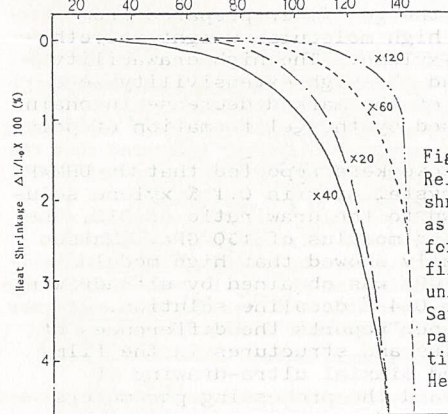


Figure 3. Relation between heat shrinkage and temperature as a function of draw ratio for ultra drawn UHMWPE films made by side-way free uniaxial drawing. Sample: 0.7M PE gels prepared in 1% decaline solution. Heating rate: 5 C/min.

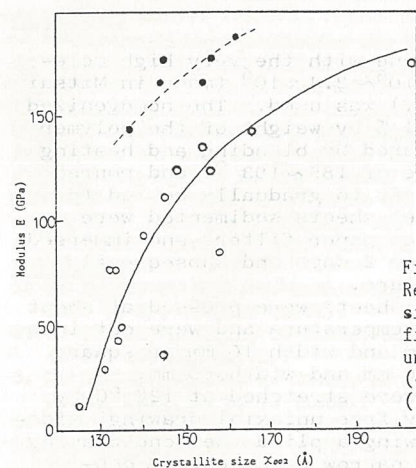


Figure 4. Relation between crystallite size and modulus for UHMWPE films made by side-way free uniaxial drawing. (○) ordinary drawing (●) zone drawing

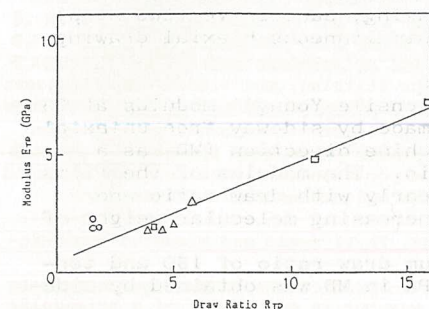


Figure 6. Relation between draw ratio of TD and modulus of TD for biaxial drawn UHMWPE gel films. (○) constrained uniaxial drawing, (△) successive biaxial drawing, (□) simultaneous biaxial drawing

EFFECT OF HUMIDITY ON BEHAVIOR OF POLYMERS

by
Marion F. Mecklenburg
Department of Mechanical Engineering
and
Pedro Albrecht
Department of Civil Engineering
University of Maryland, College Park, Maryland 20742

The adverse effect of relative humidity on the mechanical properties of polymers has been generally recognized, though few studies have allowed test specimens to equilibrate fully to the ambient environment. Water vapor absorption into those polymers that absorb water takes considerable time, and straining polymers alters water absorption capacity. Additional complications arise since most polymers exhibit considerable viscoelasticity; they tend to creep under fixed loads and to stress relax under fixed displacement constraints. If the polymer is to equilibrate to the environment, then it must also equilibrate to an applied load or displacement. This suggests that at least four variables are involved in equilibrium: temperature, water content (which is related to RH), stress and strain. If one considers the equilibrium moisture isotherm (EMI), two of these variables are constant: temperature, which is a fixed value, and stress, which is normally zero. However, the specimen swells with changes in RH, so the "strain" is not constant. This swelling behavior is measured in the equilibrium swelling isotherm (ESI). Measuring the mechanical properties of a material as a function of temperature and RH must require an "equilibrium" stress-strain curve if one exists.

The effect of RH on the mechanical properties of collagen and "neat" epoxy adhesives was measured in carefully controlled environments; some of the results are discussed below. The following properties of collagen were measured: (1) The standard EMI where the specimen is allowed to freely swell, but additionally this test was performed by desiccating a specimen previously restrained at 86% RH. Fig. 1 shows that the restrained specimen retains considerably more water than the unrestrained. (2) The ESI, Fig. 2. (3) The equilibrium stress-strain curves at 28°C and 5%, 30% and 50% RH. These tests were performed by rapidly straining the specimen a specified amount and allowing it to stress relax until there was no further stress decay. The specimen was incrementally strained after stress equilibrium was reached, developing the plots shown in Fig. 3. It took 1 to 2 seconds to load the specimen and about 24 to 48 hours to reach equilibrium. The specimens were cut from cast films 0.002 to 0.003 in (0.05 to 0.075 mm) thick into strips 0.2 in (5 mm) wide. The source of the collagen was rabbit skin glue. (4) Stress recovery at fixed length (strain) vs. RH at 28°C. Specimens of collagen were restrained at different RH values and then desiccated. The stress developed was measured and plotted as shown in Fig. 4.

These tests related the following quantities, all measured at equilibrium: (1) stress versus strain at constant RH; (2) water absorption versus RH for restrained and unrestrained specimens; (3) length (and volume) change versus RH; and (4) stress versus RH for restrained specimens. Since each pair of parameters is related to all others, it would seem that tensile stressing and environmental stressing of polymers in equilibrium should also be equivalent. This is shown in Fig. 5 where the various tests are plotted on a stress versus elongation coordinate system. The equilibrium stress-elongation plots were constructed from the equilibrium stress-strain plots (Fig. 3), and were all initialized to 5% RH. In this way the various curves begin at elongations corresponding to the free swelling of the unrestrained collagen specimens of the same length due to increases in RH from 5% to 30% and to 50%. An additional abscissa was plotted in terms of RH to identify, for convenience, the free elongations (swelling) corresponding to increases in RH above 5%. The vertical plots show the stress developed at various RH values for specimens restrained at 50% and 70% RH and allowed to desiccate. The black dots indicate stress levels reached at the indicated RH. The agreement is remarkable considering that the data were obtained with different specimens and types of

tests. The ability of a collagen specimen to reach equilibrium points of stress, strain, temperature and RH by two distinct paths suggests a relationship between the mechanical strain energy applied to the specimen by stretching and the strain energy developed by stressing due to environmental changes. At RH values above 80% collagen was unable to demonstrate an equilibrium stress-strain curve. In other words stress relaxation was total. The EMI for collagen shows a dramatic water uptake above 80% RH, and mechanical properties deteriorate rapidly in this region.

Similar tests are being performed on neat epoxy adhesive specimens. These include various two-part and film epoxy adhesives cured at various temperature and time periods. Certain preliminary conclusions can be reached. (1) For those adhesive systems that demonstrate large response to water vapor as measured by the swelling isotherm, there is a dramatic loss of mechanical properties with increase in RH. Equilibrium stress-strain curves exist at the benign environments and do not exist at the high RH levels. (2) Stress recovery occurs with the desiccation of restrained epoxy specimens similar to the collagen, and the magnitude of change in stress levels due to desiccation appears to coincide with the changes in stress levels developed in the equilibrium stress-strain curves. (3) If it can be assumed that the material has yielded in the flatter region of the equilibrium stress-strain curve, then environmental stressing can also induce yielding. (4) A specimen stressed at equilibrium in a low RH environment will, under fixed load conditions, creep to failure if the RH is increased. Under fixed displacement conditions, it will stress relax completely if the RH is sufficiently increased. (5) Rapidly straining a specimen can greatly overestimate its mechanical properties. (6) Rapidly loaded specimens will stress relax when held under fixed displacement. While this behavior often has been attributed to bond breaking, there is sufficient evidence to suggest that further uptake of water during straining occurs. This is evidenced by the change in the collagen EMI due to restraint. Since more water is held, more water sites are available, suggesting straining can cause an alteration of water vapor currently present. It is quite possible that additional water uptake and reorganization of water vapor present can induce stress relaxation.

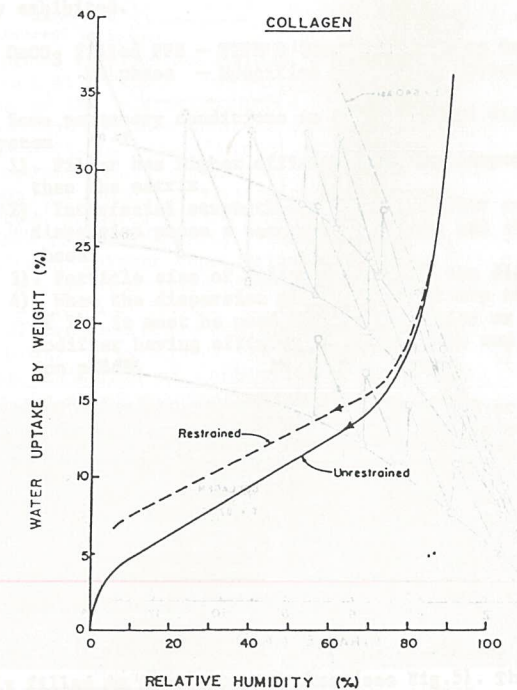


Fig. 1 Equilibrium moisture isotherm for collagen

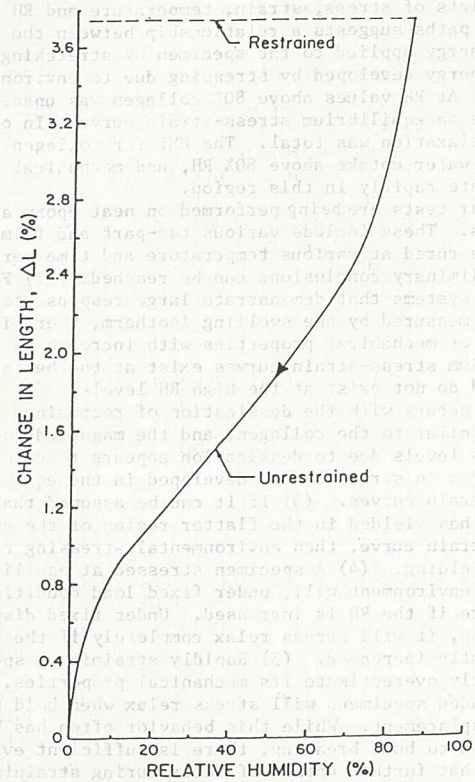


Fig. 2 Equilibrium swelling isotherm for collagen

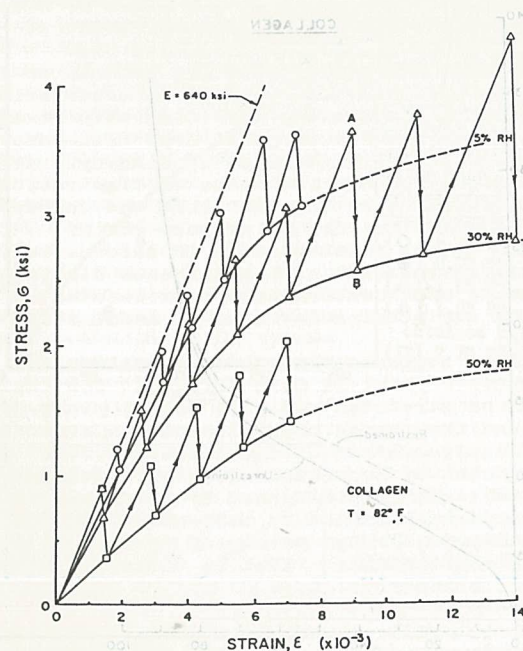


Fig. 3 Equilibrium stress-strain curves for collagen

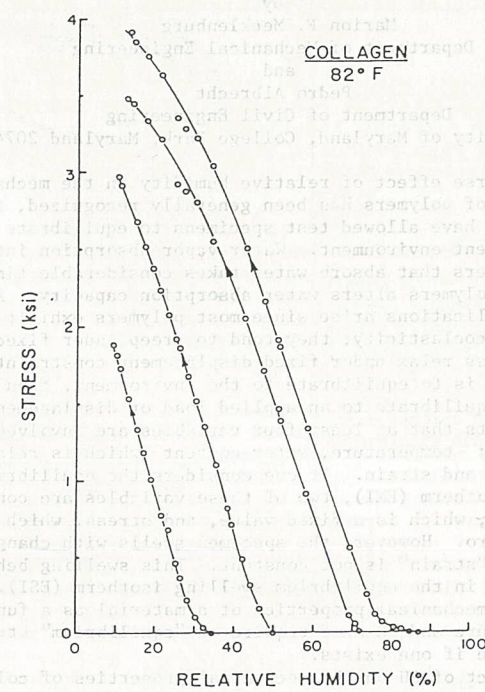


Fig. 4 Effect of changes in RH on stress of restrained collagen specimens

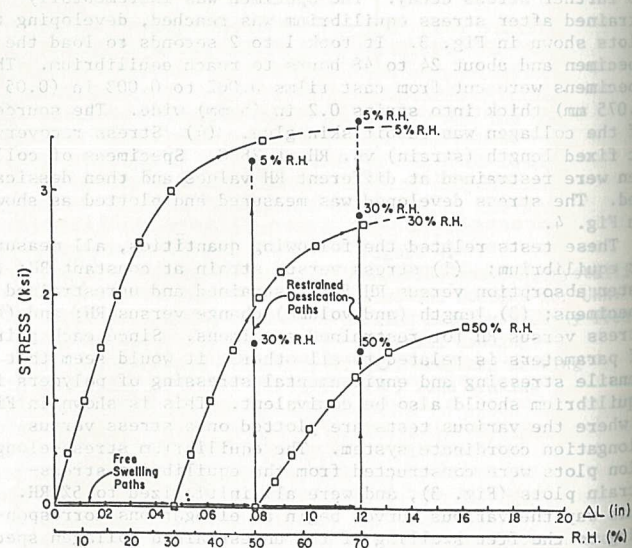


Fig. 5 Comparison of tensile stressing and environmental stressing of collagen

IMPROVEMENT OF IMPACT RESISTANCE OF CALCIUM CARBONATE FILLED POLYPROPYLENE AND PROPYLENE-ETHYLENE BLOCK COPOLYMER

by
Hideaki Nakagawa and Hironari Sano
PLASTICS LABORATORY, MITSUBISHI PETROCHEMICAL CO., 1 TOHOCHO, YOKKAICHI, MIE 510, JAPAN

Introduction

When an inorganic filler is added in a polymer, generally its rigidity may be improved, but its impact strength may be reduced compared to unfilled polymer (e.g., refs. 1, 2). Impact resistance of a filled polymer will be expected to improve by considering as following

- 1). increase of the number stress concentration point and their homogeneous dispersion,
- 2). dispersion of impact stress (wider distribution of the stress concentration sites),
- 3). prevention of development from micro crack to macro crack,
- 4). increase of micro plastic deformation ability in the matrix,

For the mechanism of impact resistance of propylene-ethylene block copolymer (PPB), we have been primarily experimented from the fractography by considering the molecular and solid structural factors (3-5). The result was revealed PPB has a structure as shown in Fig. 1. And upon the application of impact, micro cracks occur at PE/EPM interface in the numerous dispersion phases, but development of these cracks is inhibited by the EPM phase. So PPB shows higher impact strength than PP. That is, PPB has the abilities of 1)~3) described above.

The purpose of the present work is to investigate the relationship between the dispersion morphology of CaCO₃ and the behavior of impact fracture for CaCO₃ filled PPB and PP using fractography and instrumented charpy impact tester.

Experimental

The polymers used in this work were iso-polypropylene (PP, MFR=5) and propylene-ethylene block copolymer (PPB, MFR=5, ethylene content=7.2 wt%) which were made from Mitsubishi Petrochemical Co.. Nine calcium carbonate (CaCO₃) varied the diameter (0.07 to 7.0 μm) were used as filler (see Table 1). They were made from Maruo Calcium Co. and Shiraiishi Kogyo Co.. No. 1~No. 6 were precipitated colloidal CaCO₃ and were treated with some higher fatty acid, and the others were crushed type and did not treat.

Polymers and CaCO₃ (20 wt%) were blended with RA1010 and RPH (each 0.1phr) in a supermixer and afterwards, these compounds were extruded at 240°C using PCM-30 (Ikegai Iron Co.). Injection sheets were prepared using Meiki SJ-35 under the condition of 240°C, 500Kg·cm⁻², 70rpm.

Impact strength were measured by means of Izod and Dupont impact tester. Stress-strain curves were obtained using instrumented charpy tester.

The dispersion morphology of CaCO₃ in the composites and the fractography were observed by means of SEM (Hitachi HHS-2R). The specimens were carefully sliced (see Fig. 2) by the ultra microtome (Sovall Porter-Blum MT-2-B) under deep freeze condition (-90~-100°C) and afterwards, ion etching were applied on the cross section. The particle size (average surface area) of CaCO₃ in the composites were observed by means of optical microscope at magnification 400 and afterwards, were analysed using Image Analyser (Hamamatsu Hotonics C995-2).

Results and Discussion

1. CaCO₃ filled PP

Table 1 Shows the effect of filled particle size of CaCO₃ on the impact strength. It is observed that the strength increases up to 3μm but it decreases with further increasing the size. The optical microscope photographs revealed that the smaller particles tended to aggregate when CaCO₃ was filled smaller than 0.3μm. Fig. 3 shows the Dupont impact strength as function of the average surface area of CaCO₃ dispersed in the composites. It can be seen good correlation between the strength and the weight average surface area.

The impact stress-strain curve shows remarkable difference in the plastic deformation region among samples (Fig. 4). The specimens, that small size CaCO₃ was dispersed more homogeneously in the PP, was easy to plastic deformation. And from the fractography, it was observed that this behavior was correlated with amount of the minute cracks occurred at the interface of CaCO₃ PP.

Consequently, if a filler is dispersed homogeneously and finely in a polymer even if in the case of inorganic filler filled polymer, a large amount of impact energy is absorbed in the course of the formation of the many minute cracks. So if a composite can be satisfy such morphology, its impact resistance leads to higher than un-filled polymer.

2. CaCO₃ filled PPB - TYPE A

In the case of CaCO₃ filled PPB, even when the filler treated and did not with a higher fatty acid were used, they dispersed substantially in the PP matrix (Fig. 5). Fig. 6 shows the impact stress-strain curves. It is revealed that the dependence of the particle size shows similar characteristics in the case of the filled PPB. But PPB system didn't improve the impact strength (see Table 1). An PPB has a structure as shown in Fig. 1(3,4). When impact is applied to a PPB, cracks occur in the interface between the PE and EPM phases in the domains; since EPM exists between the crack and the matrix, growth of the crack is inhibited, and the impact energy is absorbed by occurrence of the crack and deformation of the EPM. So PPB has high impact strength. When impact was applied to a composite that CaCO₃ dispersed in the matrix portion, many cracks occur mainly in the matrix as in the case of the aforementioned the filled PP, and a phenomenon of crack formation was scarcely noted in the dispersed phases comprised of PE and EPM. Thus, the favorable impact strength of the PPB was not fully exhibited.

3. CaCO₃ filled PPB - TYPE B (Composite having CaCO₃ in the PE phase - Specified dispersion system)

Some necessary conditions in the specified dispersion system

- 1). Filler has higher affinity with the dispersed phase than the matrix.
- 2). Interfacial strength between the filler and the dispersion phase < between the matrix and the dispersion phase.
- 3). Particle size of filler << size of the dispersed phase.
- 4). When the dispersion phase don't satisfy the condition of 1), it must be used a modified filler or added a modifier having affinity to both filler and the dispersion phase.

CaCO₃ has scarcely affinity with PP and PE or EPM. But in the case of PPB used in this study, as molecular weight of PE and EPM components have higher than PP, CaCO₃ can't be easy to incorporate in the dispersed phase. So we used a maleic anhydride grafted HDPE (m-g-HDPE) as a modifier. Because it may be has good affinity with the PE component in the PPB and with CaCO₃ too. In this study, we used m-g-HDPE having 1% maleic acid and CaCO₃ of No. 6 in Table 1. M-g-HDPE was added when PPB and CaCO₃ was mixed in the supermixer. The composition in weight was PPB/m-g-HDPE/CaCO₃=64/16/20.

The resulting composite was found that CaCO₃ was wonderfully filled in the dispersed phase (see Fig. 5). The impact strength was far greater than expected (see Fig. 8).

Such high impact resistance was similar to the case of the unfilled PPB except following phenomenon. When impact