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COMMISSION ON POLYMER CHARACTERIZATION AND PROPERTIES
WORKING PARTY ON STRUCTURE AND PROPERTIES OF
COMMERCIAL POLYMERS*

AGING EFFECTS IN 16 YEARS ON MECHANICAL PROPERTIES OF COMMERCIAL POLYMERS

(Technical Report)

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Aging effects in 16 years on mechanical properties of commercial polymers (Technical Report)

Abstract - Experimental results are presented on the static mechanical properties of 6 kinds of thermoplastics stored for 16 years under standard conditions (20°C, 65%R.H.) and at some constant temperatures ranging from -20°C to 40°C. Changes in the tensile strengths (yield strength and breaking strength at small strain) at 20°C storage temperature are less than 1% for PMMA, POM, ABS and PE, and nearly 7% for PS and PVC. Changes in the compressive yield strength at 20°C storage temperature are 4-6% for PMMA, PS, ABS and PE, 11% for PVC, and 20% for POM. Changes in the flexural yield strength at 20°C storage temperature are less than 2% for PMMA and POM, 5-6% for PVC, ABS and PE, and -8% for PS. Changes in the modulus of elasticity in flexure are 3-5% for PMMA, PS, POM and PE, and 6-7% for ABS and PVC. Higher storage temperature results in a large effect on strength changes for PVC, ABS and POM; it seems that the storage temperature of 40°C excites an unusually strong influence on the strength. Some discussions are made on the enhancement of yield strength.

INTRODUCTION

Cooperative research works on the aging of commercial polymers were started 16 years ago by the industrial research institutes attached to the Ministry of International Trade & Industry (MITI) of the Japanese Government. The final reports (refs.1, 2) were published in 1981. The reports include the results on the yearly changes of mechanical properties (stress-strain relation, creep, fatigue, impact, etc.) at room and higher temperatures, the weatherability, dimensional changes, molecular characteristics, and so on, for typical commercial polymeric materials that had been stored under various conditions for 5 years. The East Asia (formerly, the "Japanese") Sub-group of IUPAC WP IV-2-1 had a great interest in the reports at that time, in connection with the rising importance of environmental problems of macromolecules, and decided to take up a follow-up research on some mechanical properties as a project starting in 1983. This report describes the aging effect in 16 years on mechanical properties of commercial polymers plus some additional results, as well as discussions made within the Sub-group. We believe that it is now pertinent to publish the results of the research in PAC.

Table 1. Materials tested.

Material	Grade	Characteristics
PMMA	Acrilite S, No.001	As Cast-polymerized
PS	Denka Styrol, NW-1-301	General-purpose, As Extruded
PVC	Geon 103E	Rigid, As Pressed
ABS	Cycolack, GS-E	As Pressed*
POM	Dulacon, M-25	As Extruded
PE	Kobe Polysheet	Low Density, As Extruded

* Two extruded sheets are pressed together, such that their machine directions are perpendicular to each other.

Table 2. Initial properties of materials tested.

		PMMA		PS		PVC		ABS		POM		PE	
		av.	σ	av.	σ	av.	σ	av.	σ	av.	σ	av.	σ
Tensile	Yield Strength [MPa]	—	—	—	—	72.3	0.39	43.3	0.20	64.3	1.08	30.2	0.49
	Breaking Strength [MPa]	82.3	1.27	39.8	1.96	—	—	—	—	—	—	—	—
Compressive	Strength [MPa]	105	2.94	100	0.98	80.7	2.06	63.9	0.39	80.4	4.41	25.6	5.39
Flexural	Strength [MPa]	87.7	2.85	57.2	2.94	99.0	6.86	63.6	0.49	79.7	0.69	25.7	1.67
	Modulus [GPa]	3.17	0.13	3.21	0.14	3.38	0.04	2.04	0.02	2.97	0.09	1.66	0.10

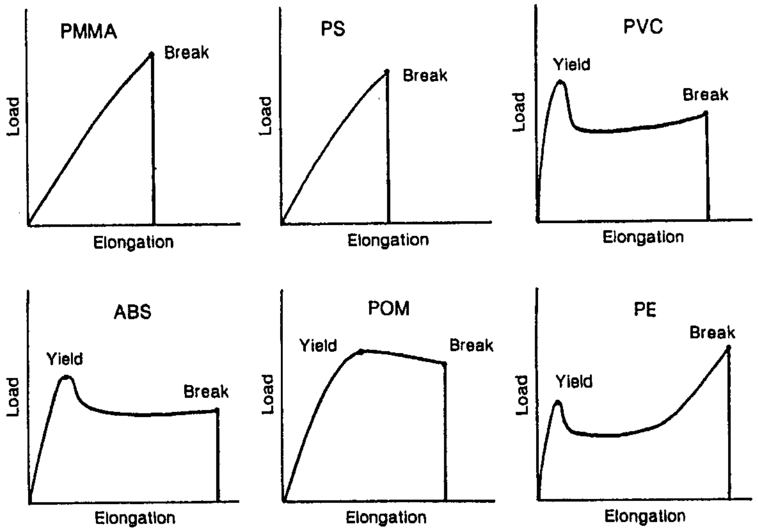

Fig. 1. Load-elongation curves for materials tested.

Temperature changes have been believed to be the principal catalyst for chemical reactions that produce the deterioration of plastics under outdoor exposure. However internal stress is repeatedly induced, according to Blaga et al. (ref.3), due to the difference in thermal expansions between the damaged surface layer and the interior, when changes in the outdoor exposure are accompanied with ultraviolet rays. This leads to a fatigue which creates cracks on the surface. Accordingly, when the temperature is considered in a study of weatherability, the temperature difference and number of cycles are important.

However, in a previous co-operative study (ref.4), the authors have noticed an interesting result that an increase in the tensile strength occurred with 8 kinds of PVC and 3 kinds of PMMA after stored in a dark room for several years. Furthermore, it was shown that the magnitude of the increase is almost the same as that of outdoor-exposed specimens. In this case, since the samples were stored for many hours under isothermal conditions, strengthening of the polymer structure is predominant rather than deterioration. Thus it is believed that measurements on the mechanical properties still have important significance when these materials are stored for a long time under isothermal conditions. In this study, 4 temperatures, -20, 0, 20, and 40°C, have been used as the storage temperatures in order to study the effects of temperature.

In this paper, results of measurements on the mechanical properties for 6 types of thermoplastics, polymethyl methacrylate (PMMA), polystyrene (PS), polyvinyl chloride (PVC), ABS resin (ABS), polyoxymethylene (POM), and polyethylene (PE), stored under standard conditions (20°C and 65%R.H.) and isothermal conditions for 16 years, together with discussion on the enhancement of yield strength, are reported.

EXPERIMENTAL

Materials

Commercial names and fabrication methods for the 6 kinds of materials tested in this study are shown in Table 1 (ref.5). The initial mechanical properties of the materials tested are shown in Table 2, where av. and σ imply the average value and the standard deviation, respectively. Load-elongation curves for these materials are also shown in Fig.1. The polymers used in this study can clearly classified into two groups according to their characteristics; yielding (PVC, ABS, POM, and PE) and non-yielding (PMMA and PS) materials.

Storage of samples

For long-term storage of the specimens, 4 types of facilities equipped with adequate isothermal temperature controllers were employed:

(1) A thermo-hydrostatic chamber for the standard condition.
(2) A freezer for the storage temperature -20°C.
(3) A refrigerator for the storage temperature 0°C
(4) A hot-air isothermal drying chamber for the storage temperature 40°C.

Shape of test specimens and test methods

A sufficient number of rectangular strips used as the test specimens were machined from materials in both the extrusion direction (lengthwise), and the perpendicular direction (crosswise). After that, the strips were thoroughly mixed and were stored in the respective atmospheres.

Of the strips stored under the standard condition, test specimens were taken out and machined with a shaper. The tests have been conducted in accordance with the standard JIS test method. For the strips stored at other temperatures, small-sized test specimens were adopted because of the small inner size of the storage facilities. The shape of the test specimens, the number of the test specimens, and the test speed are shown in Table 3.

Table 3. Test conditions.

Material	Temperature stored	Size of specimen	Number of specimens	Test speed
		Tensile		
PMMA, PS, PVC, ABS, POM	Standard conditions	Type 1 of JIS K 7113 (=ISO 527)	5 per axis	10 mm/min
	-20, 0, 20, 40 °C	Half size of type 1 of JIS K 7113 (=ISO 527)	3 per axis	
PE	Standard conditions	JIS K 6781 (~ISO 527)	5 per axis	50 mm/min
	-20, 0, 20, 40 °C	Half size of JIS K 6781 (~ISO 527)	3 per axis	
		Compressive		
PMMA, PS, PVC, ABS, POM, PE	Standard conditions	Thickness : 3 mm Width : 10 mm Hight : 20 mm	5 per axis	5 mm/min
	-20, 0, 20, 40 °C	Thickness : 3 mm Width : 5 mm Hight : 6 mm	3 per axis	
		Flexural		
PMMA, PS, PVC, ABS, POM, PE	Standard conditions	Thickness : 3 mm Width : 10 mm Length of span : 120 mm for modulus 48 mm for strength	5 per axis	2 mm/min
	-20, 0, 20, 40 °C		3 per axis	

RESULTS

1. Treatments of test results

Results on all the tests indicate that the yield strength and the fracture strength of non-yielding polymers can be evaluated sufficiently. However, the number of test specimens is insufficient to give significant results for some properties. This is partly due to the fact that the surface condition has a large effect on the elongation at break, but relatively little effect on the yield strength (ref.6). Under the condition that the strain at fracture of non-yielding materials is the same magnitude as the yield strain, the stress at fracture was used as a strength parameter. In general, it is very hard to keep the conditions which influence the test results constant for a long time. Therefore, study was carried out focusing on whether there exists a year-to-year variation of the static strength, and how the storage temperature influences the results. The experimental results are arranged and illustrated in accordance with the following methods:

1) The yearly results on the test specimens under standard conditions are reported by using the percentage difference from the first measured values as the criterion. When values are measured in two directions, the individual directional values obtained are compared with the initial directional values. Then the average of the two directional values is used.

2) When investigating the influence of the storage temperature in the vicinity of room temperature, the temperature dependence is calculated from the difference relative to the value measured at each individual year at standard conditions. The results in this case are calculated in a similar manner as 1).

2. Test results under standard conditions

PMMA PMMA is known to have a good stability against outdoor exposure. The results are shown in Fig.2. The tensile strength (strength at break) exhibits an upward trend in each of the first 5 years. However, increment is very small, approximately 2.5% at the 5th year. Compressive strength decreases after an initial increase of 5% in the 1st year, and the strength reverts to the initial value in 4-5 years. The flexural strength decreases in the 1st and 2nd years, but later recovery is seen. In 4-5 years, the strength increases approximately 5%. However, judging from Fig.8, it is believed that this value may be slightly too large. Regarding the modulus of elasticity in flexure, no change is seen within the stored time.

After 16 years, the individual variations are very small; 0.1% in tensile strength, 2.8% in the modulus of elasticity in flexure, and 2.2% in flexural strength. Nevertheless, the compressive strength increased 10.1%. Comparing with the values obtained from small-sized test specimens (Fig.8), it is believed that the true change of the compressive strength is closer to 5%.

PS The general purpose-PS is a resin so brittle that it is prone to producing crazes. In the first 5 years, as seen from Fig.3, the tensile strength (strength at break) first increases approximately 8% in the 1st year and after that it decreases. With the compressive strength, yearly variations are almost absent, but the strength tends to increase. The same is true for flexural strength, but tends to be decreased slightly. With the modulus of elasticity in flexure, the value increases almost 3% and seems to settle there.

After 16 years, the factors including tensile strength, compressive strength, and modulus of elasticity in flexure are increased by 6.5%, 6.1%, and 4.6%, respectively. However, the flexural strength is decreased by 7.8%.

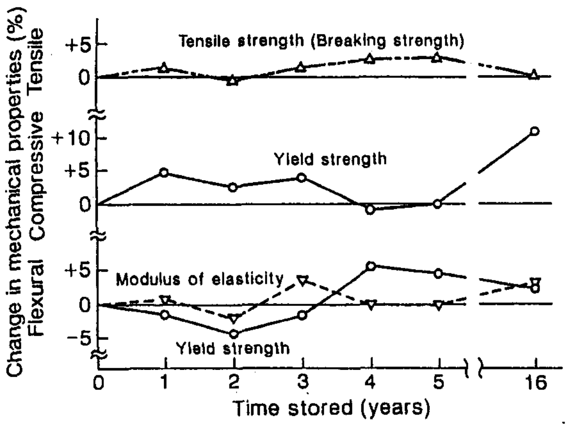

Fig. 2. Performance of PMMA stored at standard conditions.

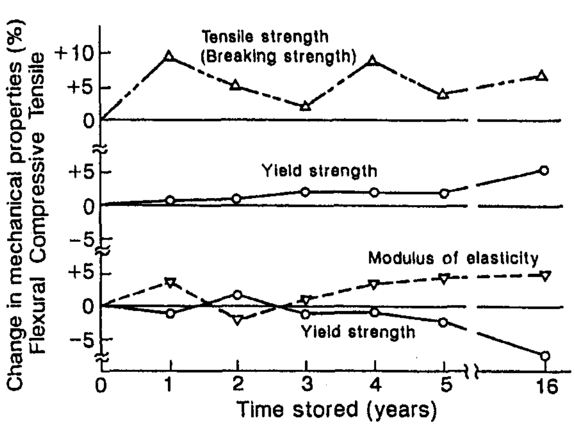

Fig. 3. Performance of PS stored at standard conditions.

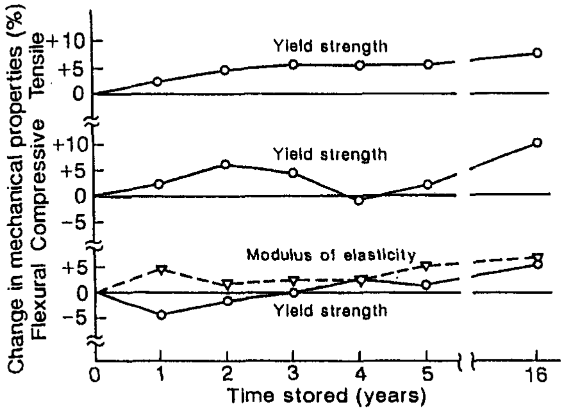

Fig. 4. Performance of PVC stored at standard conditions.

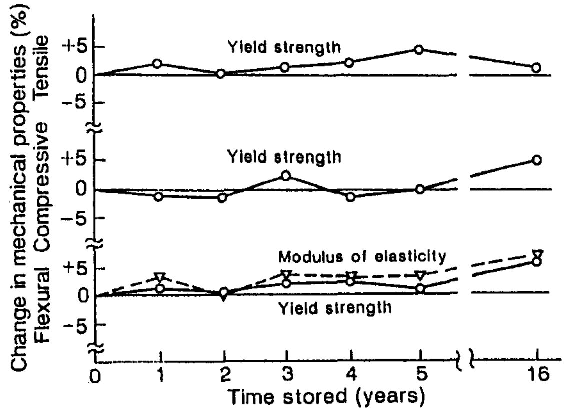

Fig. 5. Performance of ABS stored at standard conditions.

PVC Strength characteristics of PVC appear to be enhanced as time progresses as shown in Fig.4. In each of the first 5 years, the tensile strength (yield strength) increases almost linearly reaching 5% after 3 years, and after that maintains a fixed value. This yield strength increase agrees with the results obtained in the previous co-operative study (ref.2). The compressive strength increases by 5% by the 2nd year, and later tends to decrease. The flexural strength value decreases 3% in the 1st year, and after that reaches to an almost fixed value.

After 16 years, the individual properties are all enhanced; 7.2% in the tensile strength, and 10.9% in the compressive strength. For the flexural properties, the increases are 6.1% in the modulus of elasticity and 5.0% in the strength.

ABS ABS exhibits rather good results as a function of time (Fig.5). In the first 5 years, a yearly variation is difficult to see in the tensile strength (yield strength). Little change in strength is noticed until the 4th year after a slight increase in the 1st year. In the 5th year, another slight increase can be seen. No yearly variation is seen with the compressive strength. The flexural strength has a slight increase until the 4th year and then reverts to the initial value.

After 16 years, the individual properties have been enhanced by 1.1% in the tensile strength, 4.8% in the compressive strength, 7.1% in the flexural modulus of elasticity, and 5.8% in the flexural strength.

POM POM is a crystalline high polymer. In general, a very slight increase in strength is noticed throughout (Fig.6). In the first 5 years, the tensile strength (yield strength) remains constant except for an approximately 2% increase in the 2nd year. However, the strength reverts to the initial value in the 5th year. The compressive strength value is unchanged except for a 3% increase in the 1st year. With the flexural strength, the value slowly recovers after being decreased 5% in the 2nd year. The modulus of elasticity in flexure changes proportionally to the flexural strength after an initial increase of 2.5% in the first year.

After 16 years, a 0.8% increase is seen in the tensile strength, and a 20% increase in the compressive strength. The value of compressive strength is too high but the reason can not be explained. The flexural properties show a 5.0% increase in the modulus of elasticity in flexure, and a 1.3% increase in the strength.

PE PE is also a crystalline polymer. The strength characteristics are hardly changed with time (Fig.7). During the first five years, an approximately 2.5% increase is seen at the 2nd year in the tensile strength (yield strength) and then the value eventually decreases. In the 5th year, the value reverts to the initial strength. Since the degree of change is small, it is concluded that no time variation is produced. For the compressive strength, an approximately 4% increase is seen in the 2nd year. No change occurs after that. The modulus of elasticity in flexure has a slight increase with time.

After 16 years, a 0.2% decrease is seen in the tensile yield strength and a 3.7% increase in the compressive strength. In flexure, a 6.5% decrease is noticed in modulus of elasticity, and a 4.8% increase is seen in the strength.

3. Storage temperature dependence of mechanical properties

PMMA In the first five years, no yearly change can be seen in the tensile strength (Fig.8). Although large scatter is noticed in the flexural strength at various storage temperatures, the data seem to be free from any variation.

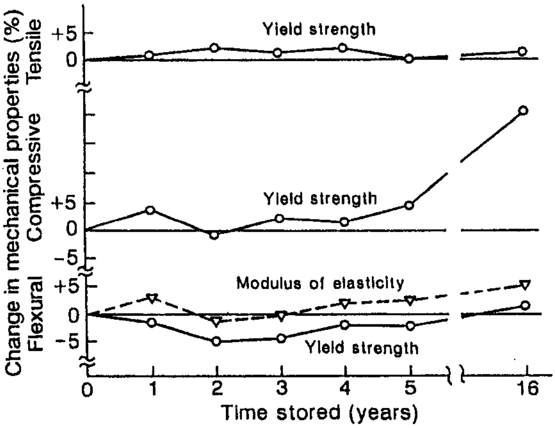

Fig. 6. Performance of POM stored at standard conditions.

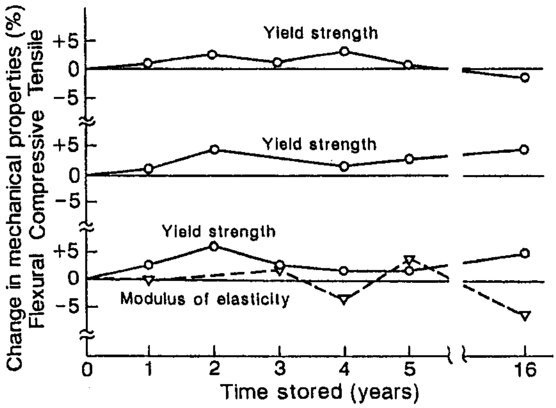

Fig. 7. Performance of PE stored at standard conditions.

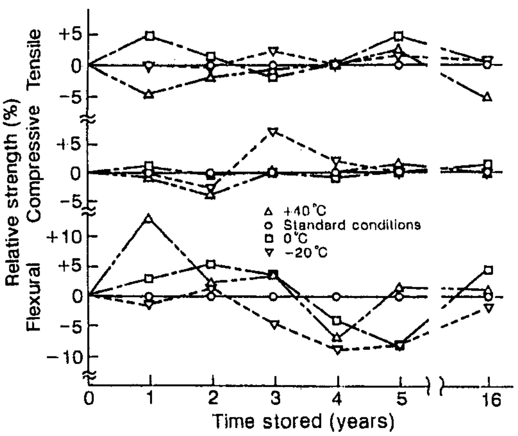

Fig. 8. Relative strengths based on values of standard conditions vs. time stored for PMMA.

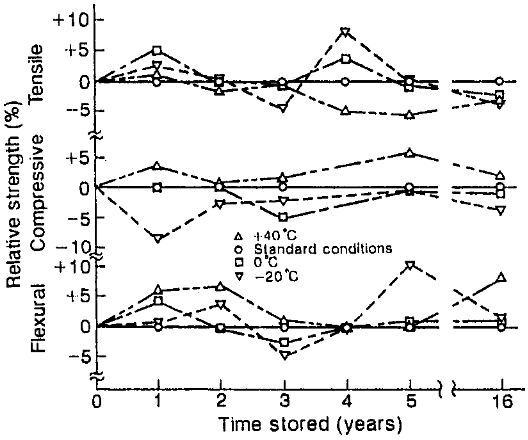

Fig. 9. Relative strengths based on values of standard conditions vs. time stored for PS.

After 16 years, the tensile test results show that the change is almost 0% except the 40°C sample. Kraft paper was placed onto the surface of the specimen of PMMA in order to retain the surface luster. Since the kraft paper adhered too firmly to the surface of PMMA at 40°C, some damage was inflicted to the surface when the paper was removed. This could be a cause of the 5.2% decrease in strength. In the compressive strength, no change is caused by differing storage temperatures. The flexure value at 0°C increases by 4.3%, but the change is very slight at other temperatures.

PS The influence due to the storage temperature can be seen very explicitly as shown in Fig.9. Although the low temperature sample is much higher in strength than the high temperature sample in the 1st year, the reverse is seen after 5 years. The compressive strength value increases at the storage temperature of -20°C until the 4th year, but no yearly variation is seen at other temperatures. The compressive strength is high when the storage temperature is high, and low when the storage temperature is low.

The flexural strength value increases in the 1st and 2nd years. After that, the value decreases and no yearly variation seems to be exhibited after the 3rd year.

After 16 years, largest change in the tensile strength is -3.7% at -20°C. The compressive strength decrease is 3.7% at the same temperature. The flexural strength exhibits a rather large increase, 8.2% at 40°C. However at other temperatures the increases are all less than 2%.

PVC In the first two years, the tensile yield strength increases with individual storage temperatures, all exhibiting the same tendency. Afterwards, the strength shows relatively little change. The results are shown in Fig.10. When the storage temperature is 40°C, the strength shows remarkable increase compared with other storage temperatures. It is judged that year-to-year variations do not exist with respect to the compressive yield strength. When the storage temperature is 40°C, the behavior of compressive yield strength is the same as those of the tensile strength. With respect to the flexural strength, no yearly variation is noticed for storage temperatures of -20°C and 0°C. However when the temperature is 40°C, the behavior is similar to those of the tensile and compressive strength.

After 16 years, the following changes are noted; -8.6% at -20°C, -6.9% at 0°C, and 4.7% at 40°C with respect to the tensile yield strength. The changes in the compressive yield strength are -4.9% at -20°C, -3.5% at 0°C, and 5.4% at 40°C. The modulus of elasticity changes by -6.4% at -20°C, -3.7% at 0°C, and 5.2% at 40°C. The flexural strength shows similar tendency as the modulus of elasticity in flexure. These values were arranged in the order of temperature, wherein the difference between the -20°C and 40°C values was almost 10%.

ABS In each of the first 5 years, no yearly variation is seen in the tensile yield strength at the individual storage temperatures (Fig.11). Influence of the storage temperature is not significant either. With the compressive yield strength, the values measured in the 3rd year are rather high, and those in the 4th year are rather low. Taking this fact into account, the yearly variation of the compressive strength is believed to be nil. It is found that the strength values increase with increasing the storage temperature. No yearly change in flexural strength is noticed. When the storage temperature is 40°C, the strength exhibits a higher value than those at other temperatures.

After 16 years, the tensile yield strength shows relatively small changes of 2.5% at -20°C, 2.8% at 0°C, and 1.8% at 40°C. The changes in compressive yield strength are -3.7% at -20°C, -1.4% at 0°C and 2.5% at 40°C. The flexural yield strength values exhibit the same tendency as the compressive strength.

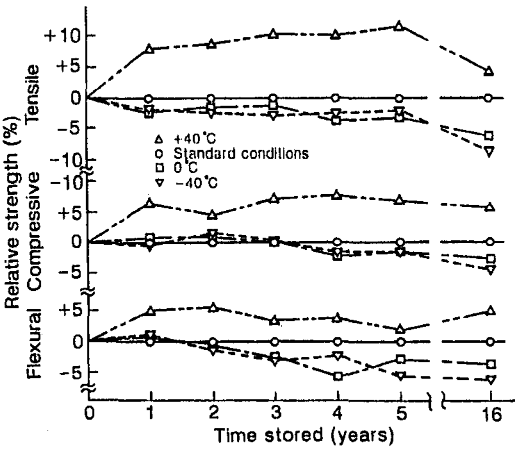

Fig. 10. Relative strengths based on values of standard conditions vs. time stored for PVC.

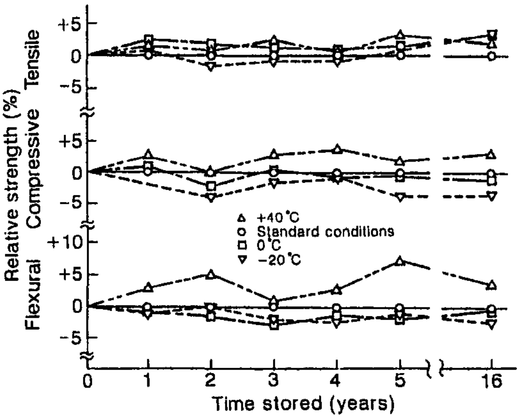

Fig. 11. Relative strengths based on values of standard conditions vs. time stored for ABS.

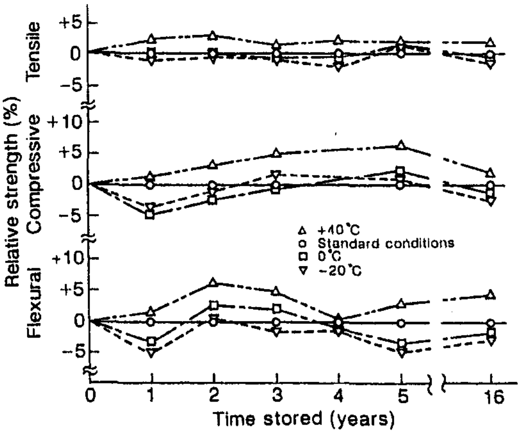

Fig. 12. Relative strengths based on values of standard conditions vs. time stored for POM.

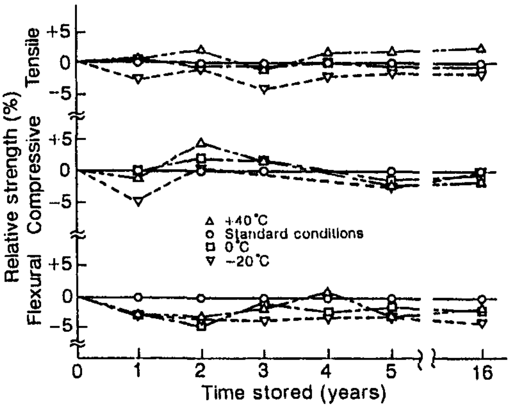

Fig. 13. Relative strengths based on values of standard conditions

POM In the first 5 years, the tensile strength (yield strength) at different temperatures exhibits almost the same trends except for the storage temperature of 40°C, and no year-to-year variation is noticed (Fig.12). However a rather high strength value is seen when the storage temperature is 40°C. At 40°C, the compressive strength increases until the third year, then remains relatively constant. The influence of the storage temperature is the same as that of the tensile strength. With respect to the flexural strength, the order of the strength change at each year is in accordance with that of the storage temperature.

After 16 years, the changes in tensile yield strengths are -1.3% at -20°C, -0.8% at 0°C, and 1.4% at 40°C. Meanwhile the flexural strength changes are -2.6% at -20°C, -1.5% at 0°C, and 4.5% at 40°C. The compressive strength values exhibits the same tendency as the flexural strength.

PE In each year, as seen from Fig.13, the tensile yield strength shows the same trends at all storage temperatures. Although there is almost no distinction between the data at 20°C and 0°C, these values are in between the 40°C and -20°C values. The compressive strength remains fixed after a slight increase in the 2nd and 3rd year. No explicit relationship between the strength and the storage temperature is established. With the flexural strength, very little year-to-year variation is seen. Very similar behavior is noticed in the properties except for 20°C.

After 16 years, the changes in tensile yield strength are -1.5% at -20°C -0.5% at 0°C, and 2.3% at 40°C. The compressive strength changes are -1.3% at -20°C and -2.0% at 40°C. The flexural strength changes are -4.2% at -20°C, -2.1% at 0°C, and -1.6% at 40°C.

DISCUSSION

1. Mechanism of enhancement of static strength

As a part of this study, measurements on the molecular weight distribution have been made on PMMA, PS, PVC, and PE samples which have been stored in the vicinity of room temperature for 3 years. The results strongly indicate that no change occurs in the molecular weight and the molecular weight distribution for 3 samples except PE to an appreciable extent in this temperature range (ref.7). In the present section, some considerations will be given about the role of residual stress and strain.

Relaxation of residual stress A specimen having compressive residual stress on the surface layer and tensile residual stress in the central portion as illustrated in Fig.14 is considered. In this case, it is believed that relaxation of the residual stress is produced due to the long-term annealing, and the tensile yield strength (or the fracture strength) and the compressive strength are increased. On the other hand, the flexural strength will be decreased due to the decrease of the compressive stress on the surface. In addition, it is assumed that at higher storage temperature the progress is accelerated. According to So et al., compression is developed on the surface layer and tension prevails on the inside during the extrusion of plates such as PC (ref.8). Thus the distribution illustrated in Fig.14 is obtained. However, the magnitude of residual stress for specimen may be within the instrumental errors in the measurement. It may be difficult to expect the existence of residual stresses high enough to explain the increase of the static strength.

Recovery of residual strain It is widely known that thermal shrinkage is produced when molded articles are heated near the glass transition temperature. It is thought that the amount of the recovery is related to the degree of enhancement of the static strength, since the strain incurred while processing the sample is recovered as time lapses. We assume that

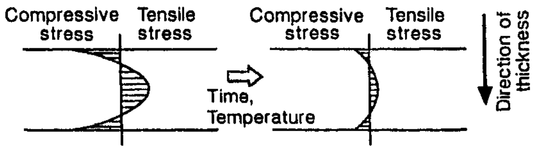

Fig. 14. Change of distribution of residual stress.

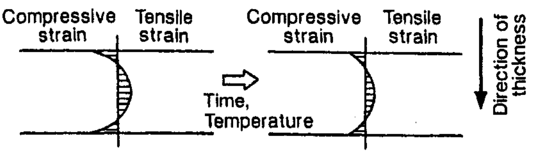

Fig. 15. Change of distribution of residual strain.

yield (or fracture) is generated when the sample reaches a fixed strain (particular to each material). Since both the tensile and compressive strengths are enhanced, it is necessary to introduce the concept of co-existence of tensile residual strain and compressive residual strain. Also, when a situation, where the flexural strength is decreasing as the strength is recovering, is considered, the strain distribution appears in a form similar to the case of the relaxation of the residual stress. The distribution of the residual strain in this case is illustrated in Fig.15. Since the balance of tensile and compressive forces is not needed in this model of residual strain, there is no need to include such an equilibrium of strain. This is an advantage over the residual stress model. It is also easily understood that press forming and extrusion produce different residual strain distributions in the materials.

Strength enhancement by changes of internal structure If the internal structure change allows hardning the material, the tensile, compressive and flexural strengths would be simultaneously enhanced. It is widely known that crystallization and spherulites formation influence the mechanical properties with crystallizable polymers such as POM and PE. The density is related to the extent of crystallization, thus the variations of the densities of POM and PE stored in an isothermal room at 20°C for 3 years were measured (ref.9). The densities tend to decrease as time lapses, although the variation is just 0.1%, not a large change in the density. Therefore, at this moment, it is difficult to explain the enhancement of the static strengths of POM and PE in terms of the increased crystallinity.

Regarding the spherulites, conclusion can not also be stated because observation has not been made yet.

2. Comparison of degree of enhancement of static strength with annealing effects

As a cause of the enhancement of static strength, relaxation of the residual stress previously discussed, and/or recovery of the residual strain have been considered. This means that molecular chains, that are unstabilized when the sample pieces are molded, reach a stabilized state after a certain time at the storage temperature. Thus a time (100 hours) believed to be sufficient for complete annealing at temperatures higher than 40°C, the

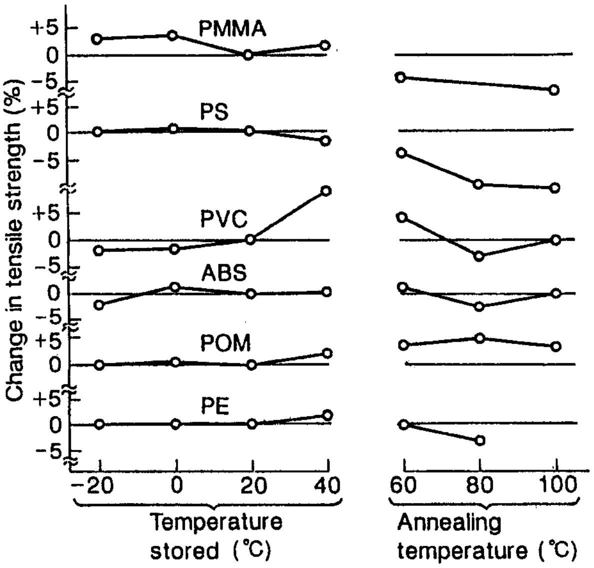

Fig. 16. Relation between strengths obtained after 5 years storage and strengths obtained after 100 hours annealing.

maximum storage temperature used in this experiment, is used for annealing experiment, and the results were compared with the values for samples stored at individual temperatures for 5 years, with respect to the tensile strength (Fig.16).

The results indicate that the data of the long-term stored samples agree well with the annealing data for PMMA, PS, ABS, POM, and PE. Rather large discrepancies appear for the PVC data. PVC especially features a considerable degree of strength enhancement after long-term storage at 40°C. When good agreement exists, it is inferred that the data from the long-term storage exhibit stabilized values at each temperature. One the other hand, when good agreement does not exist, it is believed that some enhancement factor other than stabilization of the molecular chains is induced in the long-term storage or a thermal deterioration reaction occurred in the annealing.

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