A STUDY OF WEATHERING OF POLYAMIDE-6 UNDER STRESS*

Miroslav Raab† and Vladimír Hnát

Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences
162 06 Prague, Czechoslovakia

الخلاصـــة :

تُقَـدم هذه الورقة طريقة يتم من خلالها تقييم تعريض طبقات رقيقة (أغشية) من اللدائن إلى التدني أو التحلل الخارجي ؛ بفعل التأثيرات المتزامنة للإجهاد الميكانيكي ، والتلامس المباشر بين العينة والأنواع المختلفة من الموادِ الصلبة خلال فترة التعريض . وقد أظهرت نتائج الإجهاد (الشّـد) بعد فترة شهرين من التعريض لأغشية البوليمايد (٦) أنَّ التصدع غير المتشابه ينتشر في المادة خلال التدني أو التحلل ، وأنَّ هذا التصدع يتأثر بوجود ونوعية المادة الصلبة الحاملة للأغشية . أما بخصوص الحامل الفولاذي ، فإنّ التصدع يترافق مع عملية التلدن المتميزة .

ABSTRACT

A method is presented by which polymeric films are exposed to outdoor aging under simultaneous action of mechanical stress and the effect of direct contact between the sample and different solid materials during the exposure can be evaluated. The results of stress–strain tests for polyamide-6 films after two months exposure suggest that upon aging anisometric flaws develop in the material. The severity of the flaws is affected by the presence and type of the solid material supporting the film. In the case of a steel support, the flaw formation is accompanied by distinct plastification.

†To whom correspondence should be addressed.

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INTRODUCTION

During long-term mechanical loading of polymeric materials two processes compete: orientation and fracture. While orientation improves the resistance to degradation, the synergistic cooperation of mechanical stress and environmental attack facilitates chain scission and crack formation [1, 2]. Indeed, practical experience shows that mechanical loading during outdoor exposure of polymeric parts often plays a crucial role. In spite of this, however, the aging tests of polymers are usually performed without mechanical stress both under outdoor and laboratory conditions. Such tests then refer to the properties of polymers after storage but cannot give realistic information about their long-term behavior in service conditions. Outdoor tests of polymeric materials under stress are rather exceptional. Kaufman [3] used the ASTM D 1693-60T method for stress corrosion measurement also for weathering. ASTM methods have also been developed for evaluating ozone resistance of polymeric materials under stress, in ozone chambers (D 1149-86) and outdoors (D 1171-86). In the case of polyamides, it was shown that mechanical loading during weathering increases the degradation significantly, in both films and compact specimens [4].

This work describes a new method developed for accelerated outdoor aging of polymeric films. It assesses not only the effect of mechanical stress itself but enables also the influence of the contact of the film sample with a solid support to be studied. For example, changes of degradation processes due to the presence of metal ions [2, 5] can be studied during long-term outdoor exposure.

Four different mechanical properties were chosen to characterize the original and degraded films: strain at break, yield stress, tensile modulus, and sonic modulus. As these properties show different sensitivity to the presence of structural defects, their

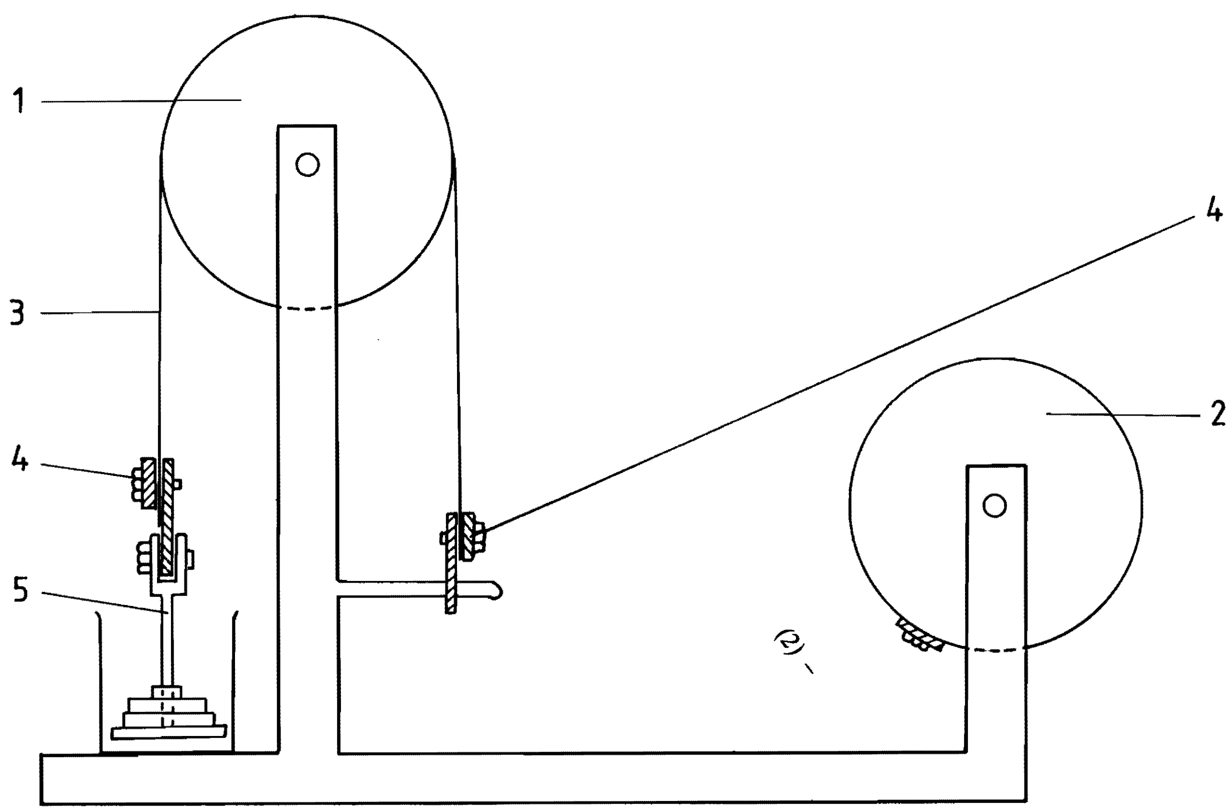

Figure 1. The Device for Weathering of Polymeric Films Under Mechanical Stress and Contact with a Solid Support.
(1) – Support cylinder for weathering of films under stress;
(2) – Reference cylinder, 3 – tested film, 4 – clamps;
(5) – dead weight.

comparison allows one to estimate the degree of heterogeneity and anisotropy of the degradation processes.

EXPERIMENTAL

Apparatus

The apparatus [6] employed for weathering tests in this study is depicted diagrammatically in Figure 1. During weathering the film specimens (3) were wrapped around cylinders (1) made from various materials and loaded. Reference cylinders (2) of the same materials were used in control tests without mechanical stress. The supporting cylinders were manufactured of the following materials: Duralumin (dural) *i.e.* an alloy based on aluminum, copper, manganese, and magnesium; carbon steel (class 11 according to Czechoslovak Standards); polyamide-6 and glass SIMAX.

The tested specimens had a rectangular shape (100 mm wide and about 400 mm long). The rubber coated clamps (4) ensured uniform stress distribution across the film specimens (3) during the weathering.

Material

To demonstrate the effect of stress and of solid support during outdoor aging a polyamide-6 blown extruded film was used. The film was prepared on a laboratory extruder from a commercial grade polyamide-6 (Spolamid, Spolana Neratovice, Czechoslovakia). The film was about 40 μm thick with an average density of $\rho = 1133\ \mathrm{kg\ m^{-3}}$ as determined at 23°C in toluene at 43 % relative humidity (R. H.).

Exposure

Films were exposed to outdoor conditions for two months (28 June through 30 August, 1986) in Prague–Petřiny (50° 06′ north latitude, 14° 21′ east longitude). During the exposure the axes of both testing and reference cylinders were oriented along the east–west line. The machine direction of the film coincided with the direction of applied stress. A stress of 4.8 MPa (approximately 10 % of the yield stress of the film) was employed for all the samples.

The variations of relative humidity and mean temperature during the exposure period are given in Figure 2. (A typical variable weather situation, sometimes prevailing in summer in central Europe, can be seen.) The total solar radiation during that period was $1.05 \times 10^9\ \mathrm{J\ m^{-2}}$ (457 h of sunshine) and the total rainfall was 162 mm.

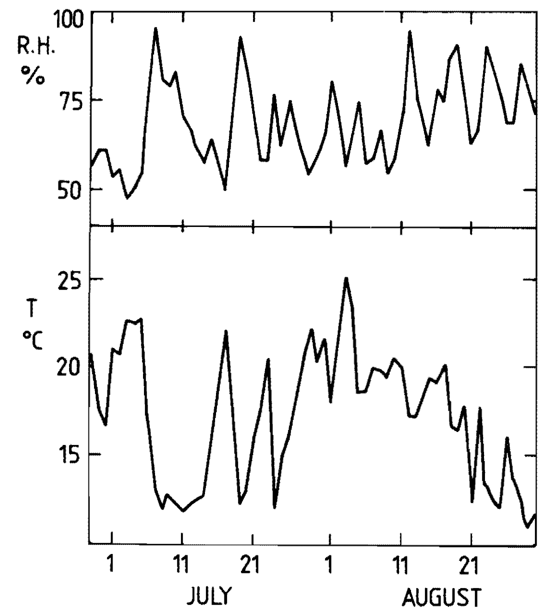

Figure 2. Variation of Relative Humidity (R. H.) and Mean Daily Temperature, T, *During July and August 1986 at Prague-Petřiny.*

Stress–Strain Tests

The specimens for mechanical testing were strips cut either along the machine direction (MD) or along the cross direction (CD). The specimen width was 5 mm and the gauge length was 20 mm. The stress–strain curves of both original and aged films were determined with an Instron TM tester at 25 ± 1°C, 65 ± 5 % R.H., test speed 5 cm min^{-1}. Three mechanical characteristics were determined from the curves: strain at break, ε_b, yield stress, σ_y, and tensile modulus, E, (as the slope of the linear part of the curve). At least five individual curves were used to calculate the final data.

Sonic Measurement

The velocity c of longitudinal acoustic waves at 23 ± 1°C, 43 ± 5 % R.H. in both machine and cross direction of the films were determined with a PPM 5 Tester (H.M. Morgan, Co., U.S.A.). The measuring frequency was 5 kHz. The sonic modulus E^s was calculated from the approximate equation $E^s = \rho c^2$, where ρ is the film density. The non-destructive sonic measurements were carried out before the stress–strains tests so that sonic and tensile properties of identical film sections could be compared.

RESULTS AND DISCUSSION

The mechanical properties of the original film are summarized in Table 1 and the corresponding properties of the same film weathered both under and without mechanical stress on various solid supports are shown in Table 2. (In that table only results for film sections facing south during exposure are reported.) It can be seen that the action of mechanical stress during weathering changes the anisotropy of degradation as manifested in strain-at-break values: The films weathered without mechanical stress show typically a higher strain at break along the machine direction in agreement with the results reported previously for UV−irradiated polyethylene films [7, 8]. However, the strain-at-break values of films weathered under stress are systematically lower in the machine direction than in the cross direction. (Note that in this experiment the machine direction coincided with the direction of stress applied during weathering.) In the case of the glass supporting cylinder the stressed film even broke shortly before the end of the two-months exposure period. Qualitatively, this could be expressed as zero strain-at-break value. (In this case not only the stress, but probably also the heating of the hollow glass cylinder due to the greenhouse effect accelerated the degradation.)

Table 1. Mechanical Properties of Original Polyamide-6 Film. (MD − Machine Direction, CD − Cross Direction)

Property	MD	CD
Strain at break, ε_b, %	400 ± 35	375 ± 25
Yield stress, σ_y, MPa	48 ± 2	49 ± 2
Tensile modulus, E, MPa	1300 ± 100	1400 ± 100
Sonic modulus, E^s, MPa	2850 ± 50	2750 ± 100

Table 2. Mechanical Properties of Polyamide-6 Film after Two Months of Outdoor Exposure.

Property	Contact with:		Glass		Polyamide-6		Dural		Steel		No contact	
	Experimental variation	Under stress[a]	MD	CD	MD	CD	MD	CD	MD	CD	MD	CD
ε_b, %	± 50 %	Yes	0[b]	13	14	17	11	11	14	85	6	3
		No	18	7	34	36	15	11	100	32	–	–
σ_y, **MPa**	± 5 %	Yes	53[b]	52	53	47	57	49	42	41	55[c]	52[c]
		No	51	48	55	50	49	50	55	53	–	–
E, MPa	± 10 %	Yes	1500[b]	1550	1600	1550	1750	1600	1050	1300	1700	1950
		No	1500	1450	1700	1450	1500	1600	1650	1750	–	–
E^s, MPa	± 5 %	Yes	2750[b]	2700	3250	2800	2850	2700	1950	2200	3000	2600
		No	2750	2800	3300	3100	2600	2900	3200	3100	–	–

Data corresponding to machine direction (MD) and cross direction (CD) are given for film sections exposed southwards on support cylinders. Direction of stress during the exposure coincided with the machine direction of the film. Meaning of symbols is the same as in Table 1.

[a] Stress of 4.8 MPa applied during the exposure

[b] Sample failed during the exposure. Data were determined for the material in the vicinity of the fracture path.

[c] Most of the specimens failed before reaching the yield point (9 out of 12 for MD, 10 out of 12 for CD).

The anisotropy in strain at break after weathering can be explained by a model based on anisometric structural defects (see Figure 3): It was recognized that the degradation of a polymer in the solid state is a heterogeneous process [7], initiated and concentrated predominantly around impurities or weak centres. On subsequent mechanical testing up to break, cracks develop from these sites, but they immediately interfere with intrinsic anisometric flaws aligned along the machine direction and acting as barriers to crack propagation. Consequently, the extensibility of irradiated polymer is larger along the machine direction than along the cross direction. However, the situation changes, when mechanical stress is applied simultaneously with outdoor exposure. The fracture process predominates and a new system of sharp cracks develops from degraded sites perpendicularly to the stress direction. (A developed system of sharp cracks observable even with the naked eye is shown

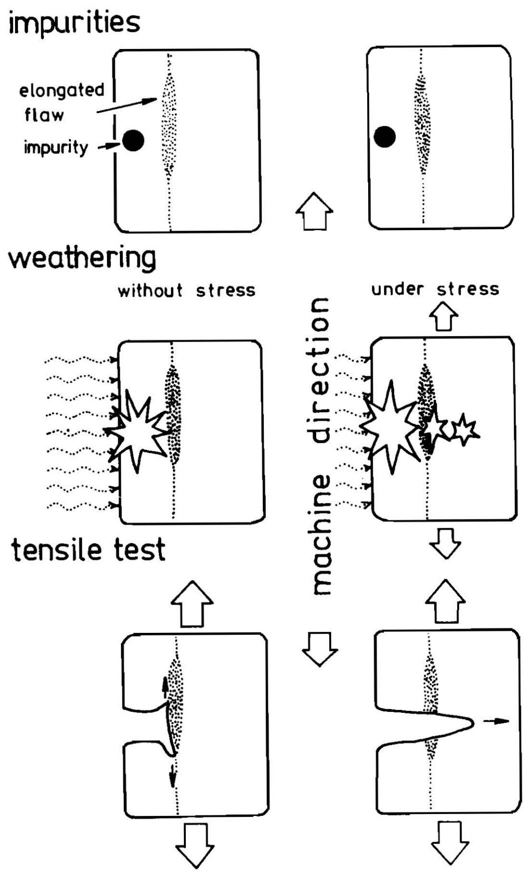

Figure 3. A Model of Crack Initiation on Weathering in an Oriented Polymeric Film Exposed to Environment and Mechanical Stress. The photooxidative degradation of the material is concentrated around intrinsic photosensitive impurities. On subsequent tensile test cracks grow from the weak centers, but elongated flaws and film orientation paralyze crack propagation across the machine direction. As a result, the macroscopic strain at break of weathered film is larger in the machine direction than in the cross direction (left). However, if mechanical stress is acting during the exposure period, formation of sharp cracks dominates and macroscopic strain at break along machine direction drops under the value corresponding to the cross direction (right).

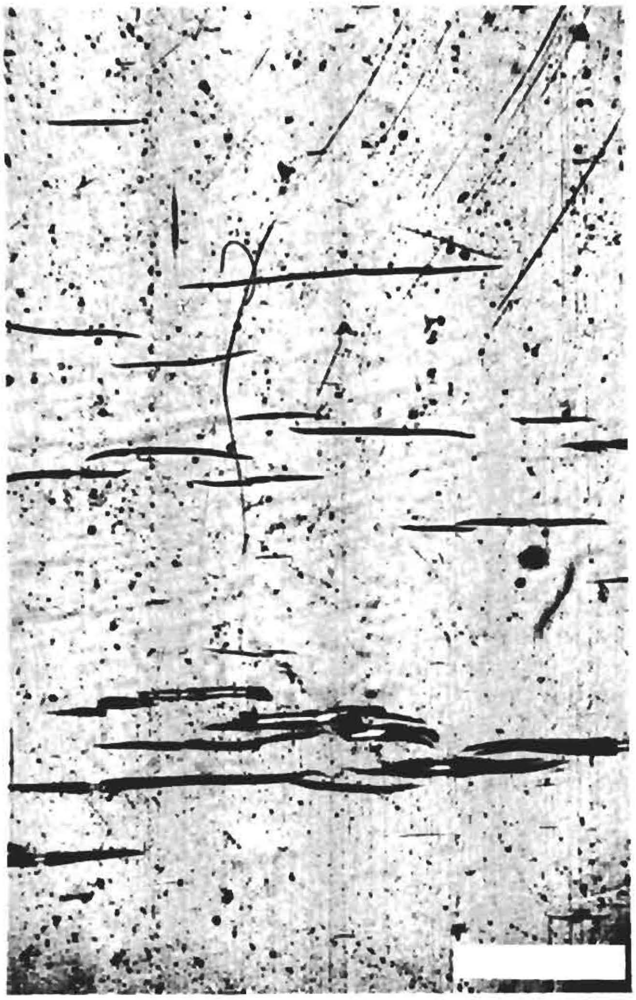

Figure 4. Photomicrograph of a Polyamide-6 Film After Two-Months Weathering Under Stress on Glass Cylinder. The cracks are aligned perpendicularly to the stress direction. Bar is 5 mm.

in Figure 4 for the sample weathered under stress on the glass support cylinder.) On subsequent tensile testing these cracks determine the ultimate behavior of the aged film. As a result, the macroscopic strain at break along the machine direction decreases distinctly.

Unlike the strain-at-break values, neither the tensile modulus, nor the sonic modulus showed any significant anisotropy. However, a systematic increase or decrease of moduli upon aging was found, depending on the support for both machine and cross directions. The action of mechanical stress during exposure did not produce any significant effect on the moduli, with the exception of the steel support.

From Table 2 it can be seen that for samples weathered under stress on a steel support a distinct plastification is manifested: yield stress σ_y, tensile modulus E, and sonic modulus E^s show a marked drop upon weathering. It seems likely that a synergistic action of metal ions, moisture, UV light and mechanical stress played an important role here [2]. (Synergistic effect of acid rain, SO_3, NO_x and ozone with mechanical stress on polyamide degradation has already been recognized [9]). The effect of solar radiation on the plastification is illustrated in Figure 5, where a detailed topography of local sonic moduli in machine direction for the sample weathered on the

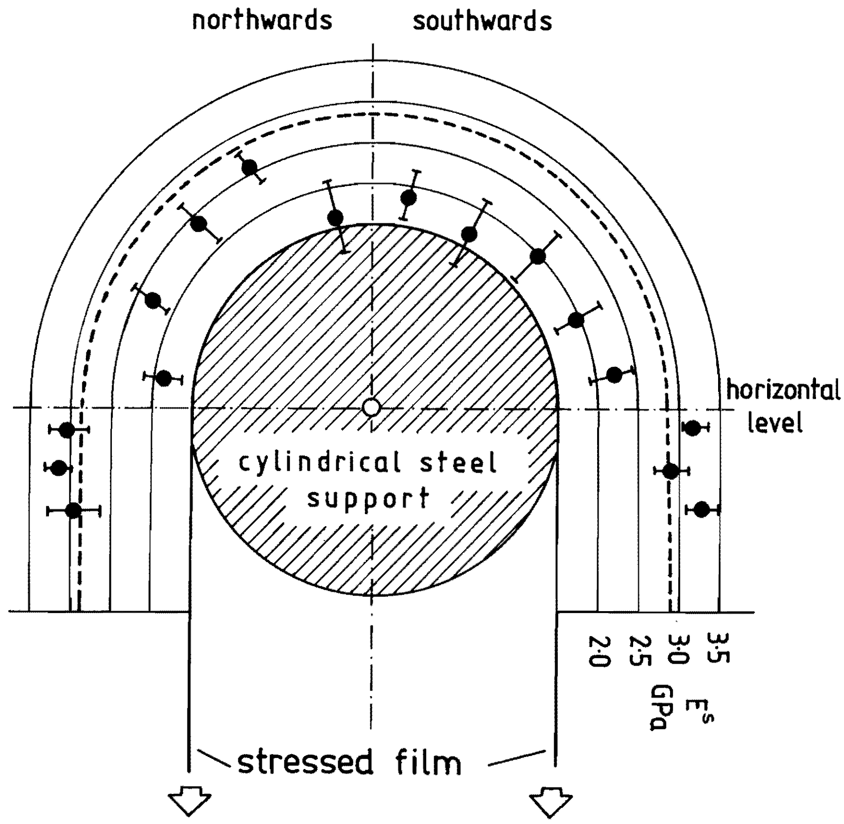

Figure 5. Representation of the Angular Dependence of Sonic Modulus E^s in Machine Direction of a Polyamide-6 Film After Two-Months Weathering Under Stress on Steel Cylinder. Note the distinct plastification in the southward section of the film. The dashed line corresponds to the modulus of the unaged film.

steel support is plotted. The decrease in modulus as compared to the original value (indicated by the dashed curve) was most distinct in the southward section of the film. In the northward section the decrease was less pronounced. In contrast to that the film sections weathered under stress but without contact with steel exhibited a significant increase in modulus.

The plastification by a steel support under stress as monitored by sonic modulus was virtually isotropic. However, strain-at-break values of films weathered under stress on steel show a distinct anisotropy. This behavior can be explained by simultaneous (and competitive) effects of plastification and formation of cracks aligned perpendicularly to the machine direction. (cf. Figure 4). Obviously, cracks lower the extensibility of the film, particularly in the direction perpendicular to the crack orientation. Due to plastification, however, the films aged on the steel support show higher strain-at-break values that the other samples weathered under stress. This is also shown in Figure 6, where the effects of steel and dural supports on the stress–strain traces of the exposed

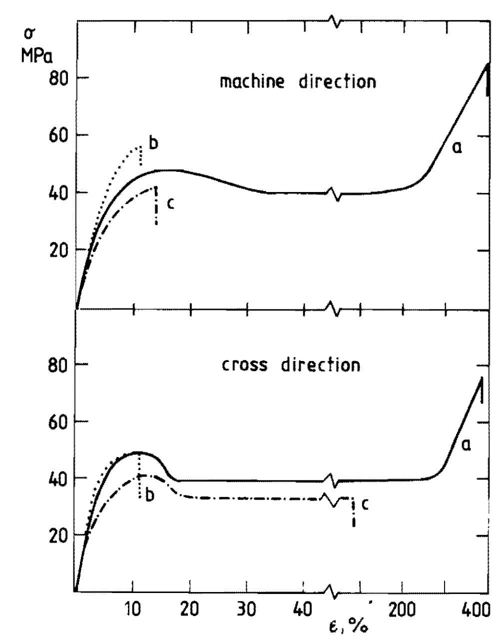

Figure 6. Stress–Strain Curves for the Polyamide-6 Films Before and after Two-Months Weathering Under Stress on Two Different Support Cylinders. (a) Original film; (b) dural support; (c) steel support.

films are compared. A lower modulus, a lower yield stress and a less pronounced decrease in extensibility for the case of the steel support are clearly manifested.

Although the experimental evidence of the plastification effect of the steel support on polyamide-6 films weathered under stress is clear, we cannot offer any plausible explanation of this behavior at present. With all other supporting materials employed in this study (glass, polyamide-6, dural), a systematic increase of the tensile moduli was observed, particularly in the case of dural. However, the sonic moduli of the corresponding films did not show any significant changes. This discrepancy seems to reflect the heterogeneous nature of the crosslinking reaction, and also possible effects of flaws on material compliance.

We conclude from the above results and considerations that the proposed method of weathering under stress on a solid support yields new information and may contribute to our understanding of polymeric film failure under real service conditions.

CONCLUSIONS

1. The presence and type of solid support during the weathering of stressed polyamide-6 films significantly affects the resulting mechanical characteristics: While Duralumin alloy enhances embrittlement, steel support of a stressed sample brings about a distinct plastification.

2. The strain at break of the exposed films shows significant differences between the machine and cross directions. No such anisotropy, however, was found in the moduli. This behavior reflects the presence of anisometric flaws which develop perpendicularly to the stress direction during weathering.

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