

Effect of Stabilizer Type on Artificial Weathering of Rigid PVC. II

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Synopsis

The determination of the effectiveness of lead (Pb) and mercaptotin (MT) stabilizers on the useful service life of poly(vinyl chloride) PVC in outdoor applications, necessitates testing the mechanical properties of the polymer before and after weathering, to learn its behavior in the outdoor environment. Artificial weathering was used, and four mechanical tests were carried out, namely tensile, flexure, impact, and fracture toughness tests. The Pb stabilizer system used gave better fracture toughness and impact strength after exposure. The tensile strength and modulus of elasticity of MT-stabilized specimens increased significantly after exposure, unlike Pb-stabilized specimens. Brittleness in unplasticized PVC can be attributed to a number of factors, such as unsaturation, carbonyl group concentration, stabilizer concentration, crystallinity, and extent of dehydrochlorination. The tensile strength and modulus of elasticity increase in tin mercaptide stabilizers significantly with increased UV exposure, while the increase in Pb specimens is less significant. There is a continuous diminution of the percent of elongation at break in both types of Pb or MT specimens, with increased exposure. The ductility of Pb may be accounted for by PbO and Pb stearate ($C_{17}H_{35}COO$)₂Pb. One of the possible causes for the brittleness of tin mercaptide stabilized specimens is antiplasticization.

INTRODUCTION

The absorption of UV light in the presence of oxygen, causes a set of complex reactions leading to the degradation of poly(vinyl chloride). Wavelengths shorter than 300 nm are filtered out by the atmosphere and those longer than 400 nm are ineffective in bond-cleavage processes, hence the 300–400-nm range is the cause of deleterious effects of sunlight.

The previous thermal history of a PVC specimen is shown to influence its photo-oxidation and weathering characteristics.¹

The mechanism for photo-oxidation is based on a free radical mechanism, induced by bond cleavage. These radicals attack PVC, causing dehydrochlorination with the formation of polyene sequences, which at a sufficient length are able to absorb visible light. Then oxidation follows giving rise to hydroperoxides and finally carbonyl groups. The combination of peroxides and unsaturations produced during processing has a strong photoactivating effect on PVC.

Stabilization of PVC against heat and light is vital to ensure maintaining the desired optimum end properties and characteristics.

ACCELERATED WEATHERING

Polymers being sensitive to the elements of the environment, which include sunlight and rain, have to be tested after long periods of outdoor exposure which in some cases are a few years. Instead, accelerated weathering can give reliable data, in a matter of days or weeks, provided the correct conditions and appropriate apparatus are used. The keys to successful accelerated weathering are the following: (1) Simulate the UV wavelength of sunlight that has a harmful effect and not the entire spectrum. (2) Simulate outdoor wetness attack by hot condensation, but not immersion. (3) Elevate the temperature to accelerate the effects of UV and condensation.

Temperature, water, and UV interact to increase the rate of degradation of polymers.

Rain or dew condensed from an air-water vapor mixture are electrolytes bearing dissolved oxygen. The pH of rain or dew is slightly acidic, which, combined with hot weather, provides a strong effect. For this reason, some of the apparatus for accelerated weathering combine the effects of temperature, water, and UV for a close analogy with the natural environment, but using more stringent conditions.

The types of apparatus used for this purpose are classified according to the type of UV source used.

Xenon arcs

These give the closest analogy to the full solar spectrum. Their main drawback is the loss of intensity because of a decrease in transmission of the envelope and filters.

Carbon Arcs

These arcs are deficient in the 300–350 nm, which is critical for PVC and several other polymers that absorb damaging light at this spectrum. Filters have been used to absorb the radiation above 350 nm.

Fluorescent Sun Lamps

The fluorescent sun lamp, with peak emission at 313 nm, and a low cutoff at 280 nm, is an excellent source of UV irradiation. These lamps are a diffuse light source producing UV from a wide area and providing a uniform intensity. The intensity of radiation of tubes in the near-UV spectrum is poor compared with the sun. This drawback may be compensated for by using fluorescent black lamps.

Mercury Arcs

These arcs do not give accurate reproduction of the solar spectrum and show a deficiency at the 300–400-nm region. High-pressure arcs, with appropriate filters, gave better results.

EXPERIMENTAL

Effect of Weathering on the Mechanical Properties of PVC

Determination of the effectiveness of stabilizers and the useful service life of PVC in outdoor applications necessitate testing the properties of the polymer before and after exposure to understand its behavior after weathering.

Failure or deterioration may be detected by determining the change in a selected property.

It is worthy to add that a criterion for failure of the property under consideration has to be established, since the different properties studied may have different rates of deterioration and resistance to weathering. Measurement of the chemical changes that occur after accelerated weathering, such as carbonyl group formation, and determining their concentration by analysis, or the loss in chlorine content in the polymer chain, or following the increase in double-bond formation, have always been utilized to determine the changes in the polymer structure and the stabilizer effectiveness after exposure.

Materials

Unplasticized PVC (K 65), tin mercaptide stabilizer MT, and lead system stabilizer Pb, were used. Formulations containing 1, 2, 3, and 4 phr MT, and 2, 4, 6, and 8 phr Pb were prepared. Other details of the formulations are found in ref 2.

Methods

The injection-molded specimens which were processed such that a state of well-fused PVC was reached by applying the following conditions: screw forward speed, 9 mm/s; screw speed, 10 rpm; injection pressure, 110–120 kp/cm²; injection time, 8 s; mold closed time, 27 ± 1 s; mold temperature, 50–55°C; molding temperature (metering zone) for MT specimens was 180 and 185°C for Pb specimens. The dimensions of the specimens were 6.5 × 13 × 130 mm. The injection molded specimens were exposed in a fluorescent sun lamps apparatus, type QUV. Mechanical tests were carried out on an Instron universal testing machine model 1128 (capacity 100,000 lb). Specimens were conditioned according to ASTM D618 for 40 h at 23 ± 2°C and 50% relative humidity. Testing was performed at the same conditions of temperature and humidity.

Impact Strength

The impact strength of the lead-stabilized specimens and the mercaptotinstabilized specimens has been determined according to ASTM D256 for plastics and electrical insulating materials. Izod type method A was performed.

Plane Strain Fracture Toughness

The method adopted was the recommended practice ASTM E399-74. Though this test is established for metals, it has been successfully applied to plastics.³

Flexural Strength

The method used was ASTM D790, Method I, Procedure B, which utilizes a three-point loading system with central loading.

Tensile Strength

The ASTM D638 method has been used.

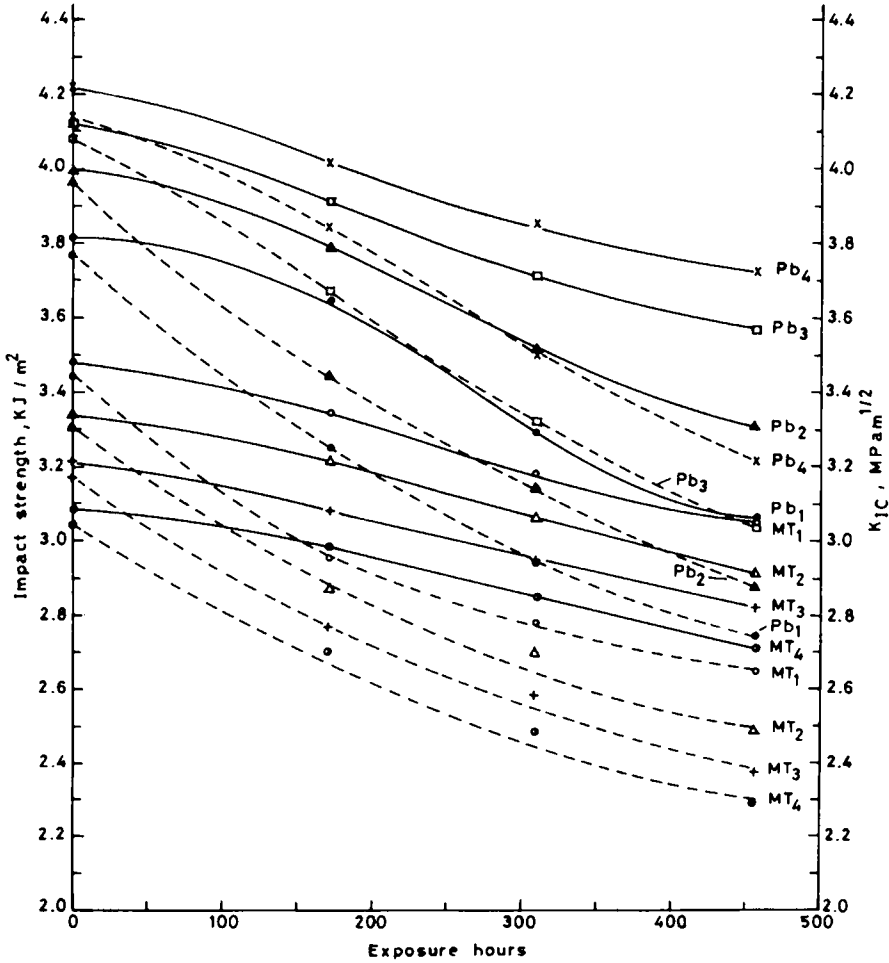


Fig. 1. Impact strength (—) and K_{1C} (- - -) versus exposure hours.

RESULTS

Impact Strength

Figure 1 shows the impact strength, kJ/m^2 versus exposure hours, for MT and Pb specimens. It is evident that there is a steady and slow decrease of impact strength, as the exposure time in the QUV apparatus increases. Pb-stabilized specimens show an improvement in impact strength, as the percent of stabilizer increases, contrary to MT specimens. At zero exposure, MT4 has a lower value than MT1, but the rate of decrease of impact strength is almost constant with respect to MT1 and MT4. This shows that the Pb-stabilized specimens have better impact resistance than the MT-stabilized specimens.

Plane Strain Fracture Toughness

Figure 1 depicts the strong resemblance between the behavior of MT- and Pb-stabilized specimens toward plane strain fracture toughness and impact strength. The only difference is that the rate of decrease is higher in fracture toughness than in impact. The plane strain fracture toughness test may be taken as another form of impact tests, but with a much slower crosshead speed—50 cm/min compared with 340 cm/min—and a sharper crack—0.45–0.55 of the depth compared with a notch of 0.2 of the depth.

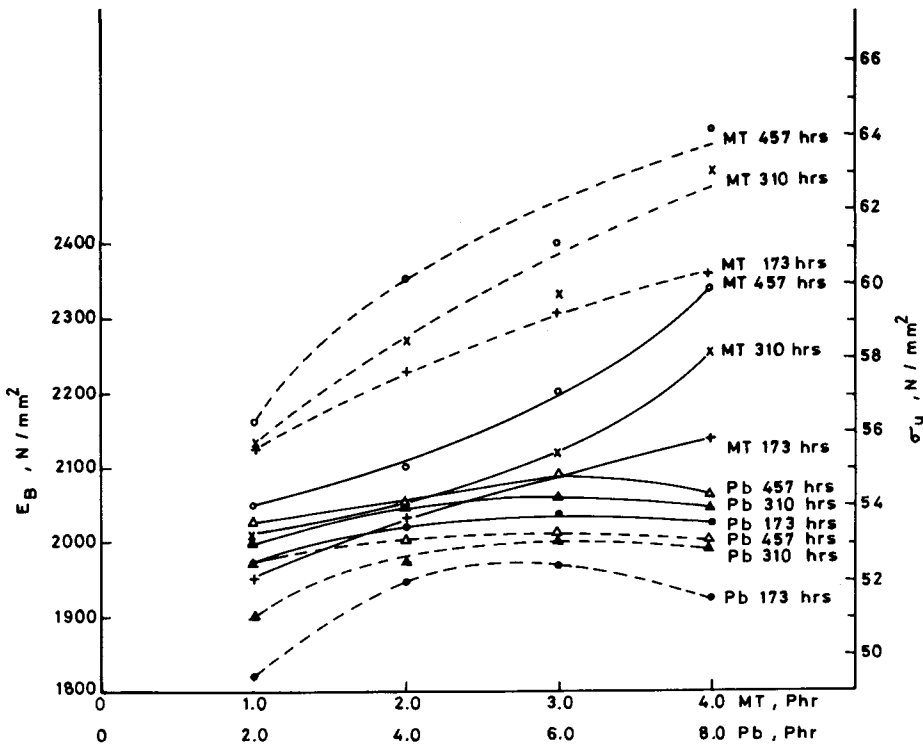


Fig. 2. E_B (—) and σ_U (---) versus stabilizer concentration.

Pb-stabilized specimens are better than MT-stabilized specimens with respect to their resistance to crack growth and brittle fracture.

Flexural Strength

Figure 2 shows the relationship between the modulus of elasticity, E_B , and Pb and MT concentration. The flexural strength for MT specimens is directly proportional to the time of exposure. The slope of the curves for the specimens exposed for 173 h is less steep than for specimens exposed for 457 h.

Pb-stabilized specimens show a tendency toward an increase in the flexural strength against percent of Pb stabilizer added until 6.0%, which represents a point of maximum for the curves, then the flexural strength decreases at higher levels of Pb stabilizer.

Figure 3 displays the relationship between E_B and exposure duration. The figure shows that the changes in E_B with respect to exposure durations for Pb specimens are gentle compared with the rapid increase in E_B for MT specimens.

Tensile Strength

Figure 3 shows that strain decreases with longer exposure hours and higher percent of stabilizers. MT specimens are less ductile than Pb specimens. The rate of decrease for MT is lower than for Pb, but the initial values are considerably lower than those of Pb.

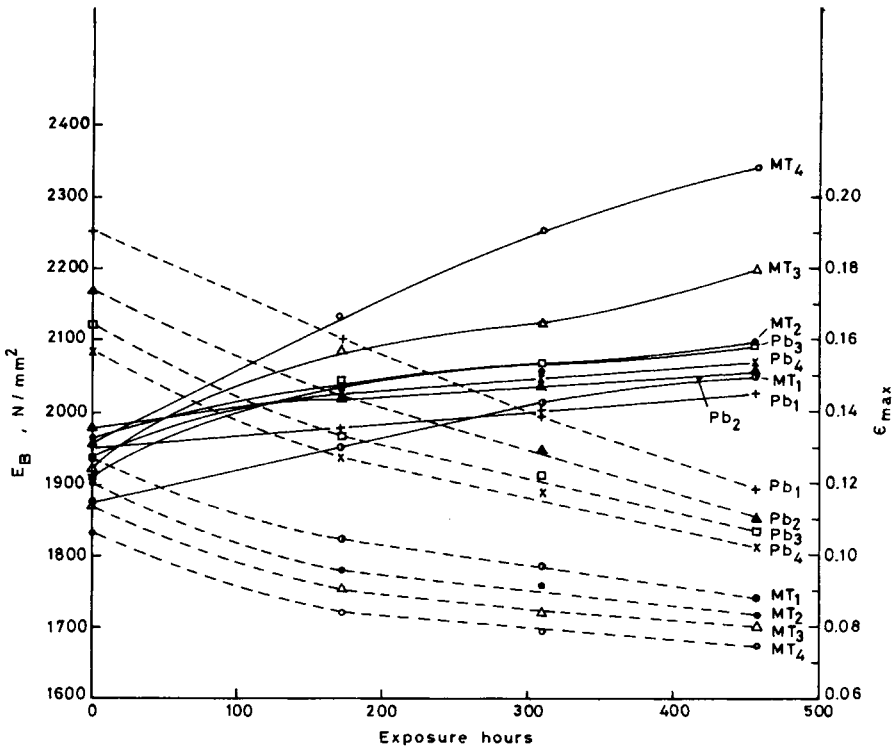


Fig. 3. E_B (—) and E_{max} (- -) versus exposure hours.

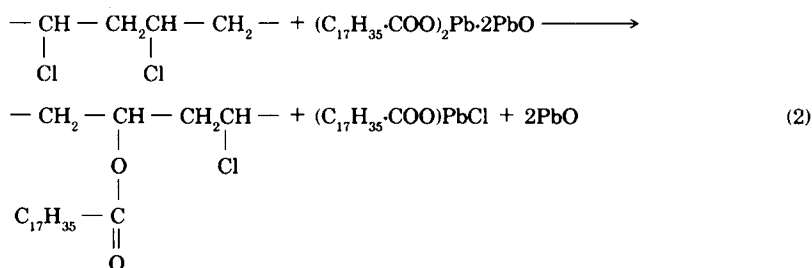
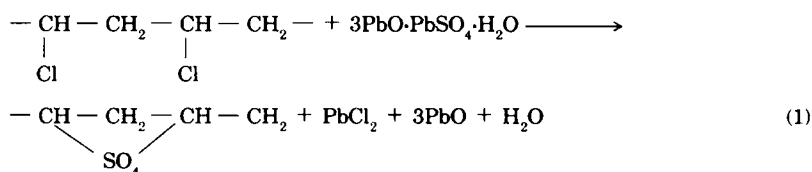
Figure 2 gives the relationship between the ultimate tensile strength and stabilizer concentration, and shows that MT specimens have gained additional tensile strength due to irradiation of intensive UV and this is proportional to the time of exposure and percent of MT. On the other hand, Pb curves show a very slight gain in strength at the beginning, followed by a decrease in tensile strength at higher percent of Pb for 173 h, and 310 h of exposure. As for the curve representing 457 h of exposure, the gain and loss are smaller than the other curves. The resemblance between the shapes of the curves in Figure 2, i.e. between E_B and σ_u should be noted.

Figure 4 depicts the effects of UV exposure on σ_y for Pb and MT. The figure shows that there is an abrupt change in σ_y for MT up to the first interval of exposure which is 173 h, and then the increase slows down up to 457 h. As for the Pb specimens, the increase in σ_y up to 173 h is more gentle than MT, and continues so up to 457 h.

DISCUSSION

Pb Stabilizer System

The lead stabilizer system used is composed of tri-basic lead sulphate monohydrate $3\text{Pb} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$, and dibasic lead stearate $(\text{C}_{17}\text{H}_{35}\text{COO})_2\text{Pb} \cdot 2\text{PbO}$. Its stabilization action may be illustrated as follows:



$(\text{C}_{17}\text{H}_{35} \cdot \text{COO})\text{PbCl}$ can further react as a stabilizer to give PbCl_2 . PbO being amphoteric reacts with HCl to give PbCl_2 , which is harmless compared with CdCl_2 or ZnCl_2 . Dibasic lead stearate as shown from reaction (2) tends to replace labile chlorine, with the more stable $\text{C}_{17}\text{H}_{35}\text{COO}$ —group, which can form hydrogen bonds with adjacent polymer chains.

Artificial weathering induces carbonyl groups, hydroperoxides, unsaturation, conjugated double bonds, affects the glass transition temperature T_g , and the rate of dehydrochlorination.⁴

The fracture toughness-impact strength relationship, and tensile strength-elongation and stiffness relationships, are greatly influenced by such structural and chemical changes in PVC.

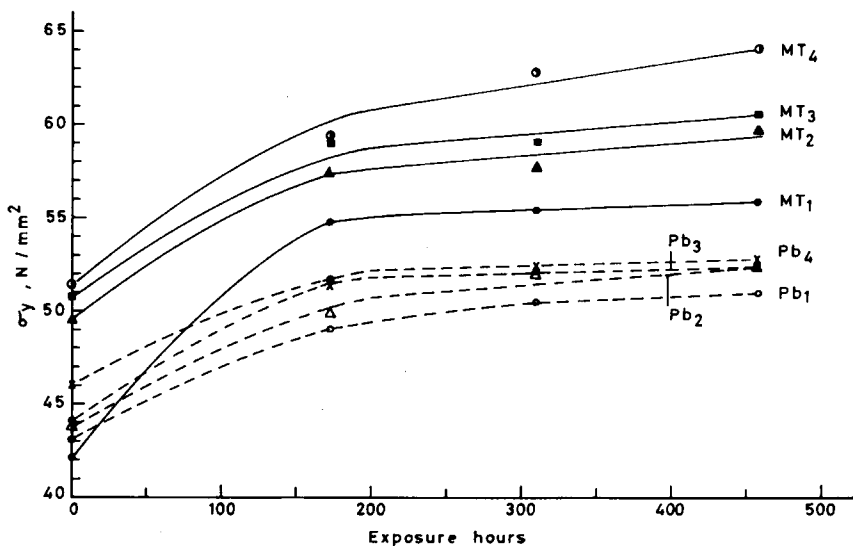


Fig. 4. σ_y versus exposure hours.

The polymer is under the influence of two effects which are responsible for the maximum points on the curves representing E_B and σ_u at Pb 173 h (Fig. 2). At 2 phr Pb, all the $(C_{17}H_{35}COO)_2Pb$, $PbSO_4$, and PbO are consumed, and they are insufficient, such that there is a high concentration of carbonyl groups, unsaturation, and conjugated double bonds. The sulfate and stearate residues are capable of forming hydrogen bridges with adjacent chains, thus at 4 phr Pb, the strength and stiffness improve and elongation decreases, as a result of the increased intermolecular forces. At 6 phr Pb, the stabilization requirements with respect to HCl elimination are satisfied completely and additional hydrogen bonds are formed, increasing strength and stiffness.

The impact strength and fracture toughness have their lowest values at 2 phr, due to the higher concentration of $-CO-$, conjugation, and higher loss of HCl. These factors increase the rigidity of the chains and hence lower the values of impact strength or fracture toughness. As the concentration of the Pb stabilizer system increases, the rigidity of the chains decreases, and the fracture toughness and impact strength improve. But at 8 phr the molecules of $(C_{17}H_{35}COO)_2Pb$, become in excess of the requirements of degradation reactions, so that they are adsorbed by the hydrogen atoms of the polymer thus shielding their polarity and causing a slight reduction in the intermolecular forces between the polymer chains, increasing toughness and reducing strength and stiffness, and impeding the reduction in ϵ_{max} .

As the exposure durations increase to 310 h, and then to 457 h at 8 phr, the reduction in σ_u or E_B diminishes, since excess $(C_{17}H_{35}COO)_2Pb$ becomes depleted, and thus its tendency to reduce strength or stiffness decreases greatly. Thus, additional hydrogen bonds are formed as the stearates become bound to the polymer chains, causing the rise of E_B and σ_u . UV exposure impairs fracture toughness and impact strength significantly, since PbO , which has been in excess before UV exposure, is now depleted with the increased hydrogen chloride elimination resulting from the longer exposure

durations, to yield PbCl_2 . PbO is held responsible for the higher ductility and toughness which characterizes Pb-stabilized specimens. Thus, the lower its concentration, the lower the ductility and toughness values.

The increase in carbon-carbon double bonds makes the chains rigid and brittle due to the redistribution of charges in the polymer chains. This adds to the growth of E_B and σ_y and the reduction of ϵ_{\max} and toughness.

Tin-mercaptide Stabilizer

The tin-mercaptide stabilizer is characterized by strong chemical bonds formed by sulfur, which are responsible for the antiplasticization phenomenon. Exposure to intensive UV has resulted in the increase of unsaturation, carbonyl group concentration, antiplasticization, and crystallinity.⁴ The net result is shown by the reduction of ϵ_{\max} , K_{IC} and IS and the increase in σ_w , σ_y , and E_B .

Additional bonds are formed by S in MT that reacts to face the increasing degradation reactions, with longer exposure durations. The UPVC matrix with the aforementioned characteristics attains increasing rigidity with the reduction of the intermolecular distances between polymer chains, especially in crystallites. It is logical to expect that a rigid compact system will give an increase in σ_y , σ_w and E_B , since the traversals impede lateral flexibility of the polymer chains and impede elongation. Unfortunately, due to the increased excitation of molecules and the redistribution of charges in the matrix after UV exposure, the matrix becomes sensitive to whether the specimen contains a blunt notch or a notch with a sharp crack. The excited molecules will readily lead to chains that will readily rupture to release the excess absorbed energy at lower energies of rupture.

CONCLUSION

The Pb stabilizer system used showed better fracture toughness and impact strength after artificial weathering than the mercaptotin stabilizer used.

Brittleness in UPVC can be attributed to a number of factors such as unsaturation, carbonyl group concentration, stabilizer concentration, crystallinity, and extent of dehydrochlorination.

The tensile strength and modulus of elasticity increase in tin-mercaptide stabilizers significantly with increased UV exposure, while the increase in Pb specimens is less significant.

There is a continuous diminution of percent elongation at break in both types of Pb or MT specimens, with increased exposure. The ductility of Pb may be accounted for by PbO and Pb stearate $(\text{C}_{17}\text{H}_{35}\text{COO})_2\text{Pb}$.

One of the possible causes for the brittleness of tin-mercaptide-stabilized specimens is antiplasticization.

It would be much safer in hot countries to avoid storing UPVC pipes for any length of time in the open air. The use of Pb stabilizers or organotin stabilizers free of sulfur is recommended in rigid PVC pressure pipes to avoid brittle fractures due to mercaptotins.

Windows, profiles, and other particles exposed to the direct sun, especially in hot countries, could be made of PVC with stringent levels of stabilizers.

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NOMENCLATURE

UPVC	unplasticized polyvinyl chloride
I.S.	impact strength
σ_u	tensile ultimate strength
σ_y	yield strength
ϵ_{\max}	maximum strain
E_B	modulus of elasticity from bending

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