Effect of Stabilizer Type on the Mechanical Properties of Rigid Poly(vinyl Chloride). I

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Synopsis

The effect of stabilizers on the mechanical properties of UPVC and how these are affected by different formulations has been studied. Three stabilizers, tin mercaptide MT, lead system Pb, and Ba/Cd/Zn complex BCZ, were used. A high-intensity blender was used for dry blend compounding, and the blend was injection-molded on a Kuasy single Screw injection molding machine. A two-cavity mold was made for forming the specimens. The specimens were tested for their impact strength, fracture toughness, tensile strength, and flexural strength. Increasing MT stabilizer was shown to increase the tensile strength and to decrease fracture toughness, impact strength, and ductility; this was attributed to antiplasticization. Increasing the Pb stabilizer conferred ductility and improved fracture toughness and impact strength. It is concluded that stabilizers have a marked effect on the mechanical behavior of rigid PVC.

INTRODUCTION

During processing of poly(vinyl chloride), it is exposed to drastic conditions of heat and pressure; and during the lifetime of an article, it may be exposed to the dual effect of solar energy, i.e., heat and light.

Dehydrochlorination is the initial reaction in PVC degradation, and it has been related to the structural irregularities in the polymer chain. Such irregularities act as initiation sites for degradation.

Stabilizers are added to PVC resins, to utilize their preventive and curative functions, with respect to degradative reactions. The selection of a particular stabilizer system depends on some factors such as end use, product price, service life, and weatherability. Stabilizers are responsible for retaining the desired physical, chemical, and mechanical properties of PVC during and after processing. Stabilizers are classified into metallic salts, organometallic salts, and organic costabilizers.

SIGNIFICANCE OF MECHANICAL TESTS

Determination of the mechanical properties is vital, for the successful design of plastic components and pipes. Short-term strength tests serve as a very successful tool for quality control and evaluation of the performance of rigid PVC pipes. Such tests are tensile strength tests, flexural tests, and impact strength tests. A rigid PVC pipe is subjected to some factors that affect its long-term behavior. Thus, during fabrication of a pipe, impurities in the resin, bad pro-

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cessing conditions, or inadequate proportions of lubricants or stabilizers can lead to craze formation or local spots of degraded PVC. Plane strain fracture toughness test methods for metals (ASTM E399-74) were applied to rigid PVC. In this way it is possible to elucidate its fracture toughness behavior, under the effect of different stabilizers, at different concentrations.

The main purpose of the following study is to find out whether the different stabilizers have a profound effect on the mechanical properties of rigid PVC and how these are affected by different formulations.

MATERIALS AND EXPERIMENTAL METHODS

Materials

Formulations for PVC pressure pipes depend on many factors such as the type of extruder used, twin screw or single screw, and the degree of weather resistance required. High weather resistance implies the use of high concentrations of stabilizer.

For single screw extrusion or injection molding, the following formulations may be used.

Tin Mercaptide Stabilizer		
	S-PVC	100
	MT stabilizer	2.0
	Ca stearate	0.5
	PE (polyethylene) wax	0.3
	Stearic acid	0.2
	$CaCO_3$	1.0
Pb Stabilizer		
	S-PVC	100
	Tribasic lead sulfate	
	($3PbO{\cdot}PbSO_4{\cdot}H_2O$)	2.0
Pb system		
	Dibasic lead stearate	
	$(C_{17}H_{35}COO)_2{\cdot}2PbO$	2.0
	Calcium stearate	0.5
	PE wax	0.3
	Stearic acid	0.2
	$CaCO_3$	1.0
Ba/Cd/Zn Complex		
	S-PVC	100
	BCZ complex	4.0
	Ca stearate	0.5
	Stearic acid	0.2
	PE wax	0.5
	$CaCO_3$	1.0

Four batches of the MT formulation containing 1 phr, 2 phr, 3 phr, and 4 phr of MT were prepared. Similarly, four batches of Pb formulation containing 2 phr, 4 phr, 6 phr, and 8 phr of Pb system were prepared. Also three batches of BCZ formulation containing 2 phr, 3 phr, and 4 phr were prepared. Thus, the effect of stabilizer level may be investigated: (1) S-PVC resin (Vinnol H 65) was supplied by the Wacker Co.; it is suspension polymerized; stabilizers used: (2) liquid tin mercaptide (Irgastab T 65) was supplied by Ciba Geigy Co.; (3) liquid barium–cadmium–zinc complex (Irgastab BC 206) was supplied by Ciba Geigy Co.; (4) a powdered lead stabilizer system was supplied by Alsharif Plastic Company, Cairo, Egypt.

Methods

Dry Blend Compounding of Rigid PVC. A high intensity blender of capacity 4 kg, having propellor-type blades, was used. The propellor rotates at very high speeds up to 1500 rpm and causes a vortex mixing action, providing uniform mixing of all the compounds. The direct benefit of dry blending by this method is to get free-flowing blends, free of agglomerates, while the resin particles are uniformly coated with stabilizer, lubricant, and filler. This ensures homogeneous chemical and physical properties of the molding or extrudates.

All the ingredients are added except for the filler, and the blender is allowed to start, until the temperature reaches about 80°C; then it is stopped, and the filler is added. The blender is then put to work until the temperature of the blend reaches about 110–120°C, and then it is emptied and cooled[1]; otherwise, liquid stabilizers may vaporize due to the heat evolved. Higher output extrudates are obtained, if temperatures are within the range 105–125°C and tip speeds of 20–30 m/s are employed.[2] Much higher speeds cause slower rates of extrusion due to the greater compactness of the particles.

Procedure. Dry blending was accomplished according to the forementioned conditions. Injection molding followed on a Kuasy single screw injection molding machine, which was adjusted according to ASTM D 1897. A two-cavity mold conforming to ASTM D 647 was constructed. The specimens were molded as bars, with the dimensions 6.5 × 13 × 130 mm. All specimens were conditioned at 23 ± 2°C, and 50% RH, for 40 h. The apparatus used for testing tensile properties, flexure, and plane strain fracture toughness was the Instron Universal Testing Machine Model 1128 (capacity 100,000 lb).

Impact Strength. The method of testing employed was Izod Impact (ASTM D 256). The specimens were cut to be 6.5 × 13 × 65 mm and were notched by a notcher apparatus (Custom Scientific Instruments, U.S.A.).

Plane-Strain Fracture Toughness. This technique enables predicting the strength of brittle or semibrittle materials containing cracks or cracklike defects. The method for testing plane strain fracture toughness designed for metals ASTM E 399-74 has been applied to rigid PVC.[3,4] The notch was introduced by a form tool on a shaping machine with an average speed of 0.3 m/s. The form tool was shaped to have an edge angle of 30°. A razor blade with an edge angle of 10° was used instead of fatigue cracking[3,4] to make the initial precrack. This technique is convenient for precracking polymers and gives results similar to those obtained by fatigue cycling, through the slow and controlled insertion of the blade at the tip of the notch.[3,4] Single-edge bend specimens were prepared. The initial precrack and notch must be within the range $(0.45\text{–}0.55)W$, where W is the width of the specimen, whose dimensions were 6.5 × 13 × 53.5 mm, ($W/2$, W, $4.1W$). The crack lengths were measured by a traveling microscope. The specimens were tested at a high displacement rate of 500 mm/min.

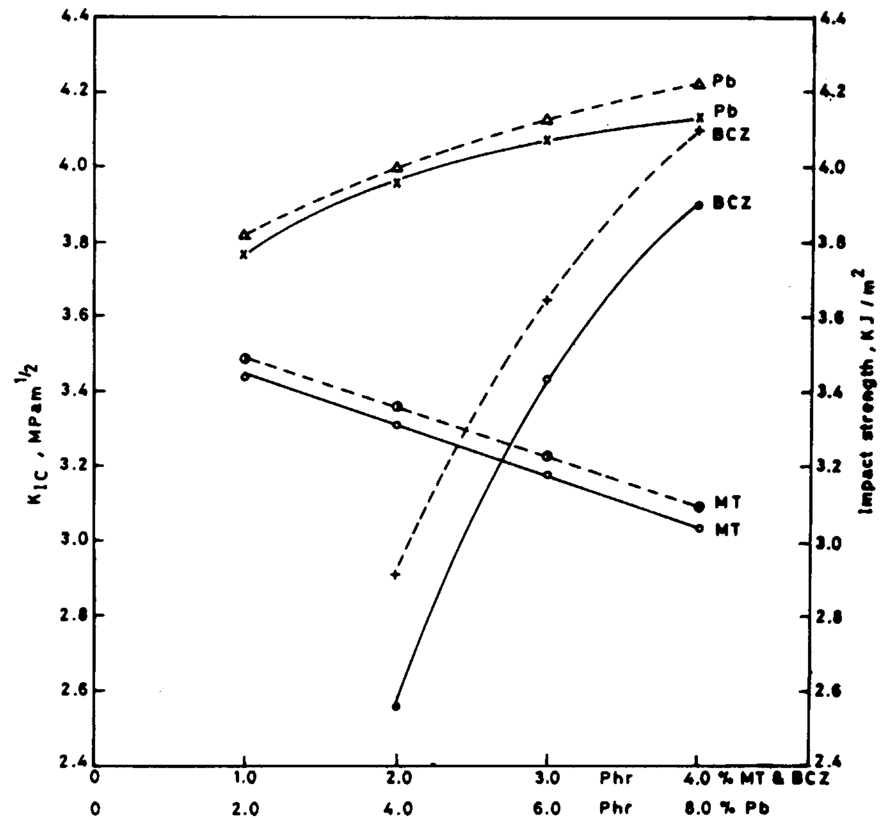

Fig. 1. Impact strength and K_{Ic} vs. % stabilizer: (---) impact; (—) fracture toughness.

Tensile Tests. These tests were performed according to ASTM D 638 standard method. The dimensions of the specimens were 6.5 × 13 × 130 mm. The gauge length was 80 mm and the crosshead speed was 5 mm/min.

Flexural Tests. Flexural tests, conformed to method I, procedure B, of ASTM D 790. The dimensions of the specimens were 6.5 × 13 × 130 mm, and they were tested flatwise, at a span of 100 mm and a crosshead rate of 28 mm/min. The rate of straining of the outer fibers being 0.1 mm/mm·min. The test is stopped by the time the maximum strain in the outer fibers reaches 0.05 mm/mm.

RESULTS

Impact Strength

These tests have shown that (Pb) lead stabilized specimens give the highest impact strength, compared to the other two stabilizers. Figure 1 shows that as the percentage of stabilizer increases, the impact strength increases for Pb specimens and BCZ specimens and decreases for MT specimens. This is due to the fact that the increase in stabilizer concentration is not always in favor of the mechanical properties. The increase in the impact strength with the increase

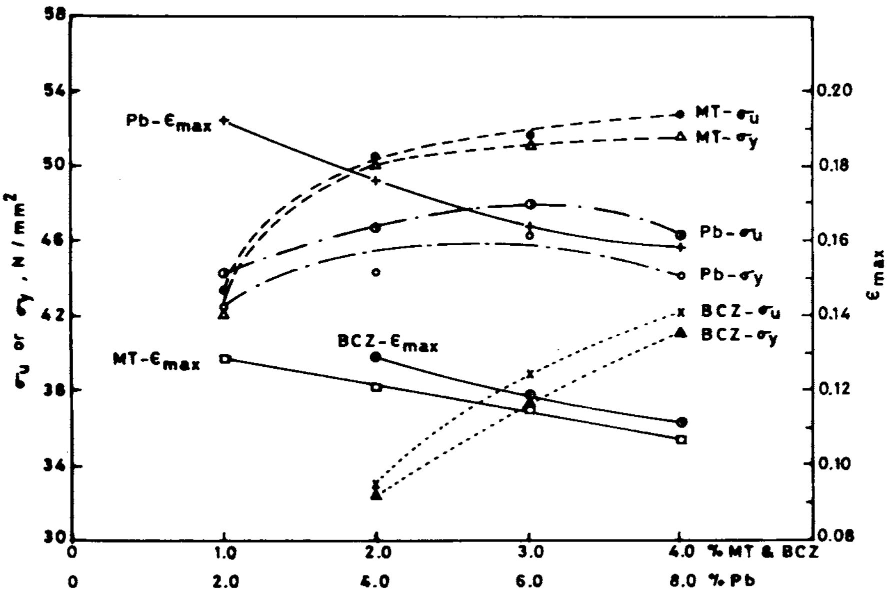

Fig. 2. Ultimate tensile strength and yield strength vs. % stabilizer. It represents also the ultimate strain vs. % stabilizer.

in stabilizer concentration for Pb or BCZ may be attributed to the increased stabilizer efficiency. Degradation during processing is therefore inversely proportional to the concentration of stabilizer present. The decrease in impact strength with the increase in MT stabilizer is related to the chemical structure of the MT. It is most probable that this sulfur-containing stabilizer causes antiplasticization, thereby increasing the tensile strength and stiffness, which occur at the expense of the impact resistance. At lower concentrations of some plasticizers, containing polar atoms, the antiplasticization effects are known to occur,[5] which resembles exactly the behavior of the MT stabilizer.

Fracture Toughness

Figure 1 gives the relation between K_{Ic}, the critical stress intensity factor, and stabilizer concentration. It is evident that there is a close resemblance between the behavior of the specimens under plane strain fracture toughness conditions and under impact loading conditions.

At 500 mm/min which is the displacement rate used, specimens failed in a brittle mode. On trying to reduce this rate to 200 mm/min or to 400 mm/min, ductile fractures prevailed.

Tensile Strength

The stress–strain curve of UPVC is one that shows necking rupture. The yield point is not pronounced, and is defined by the stress, at which the permanent set is 0.2%. The duration of loading, the rate of loading, and temperature have a great effect on ductility and brittleness. Under rapid loading, brittleness results, while, under prolonged loading, ductility results.

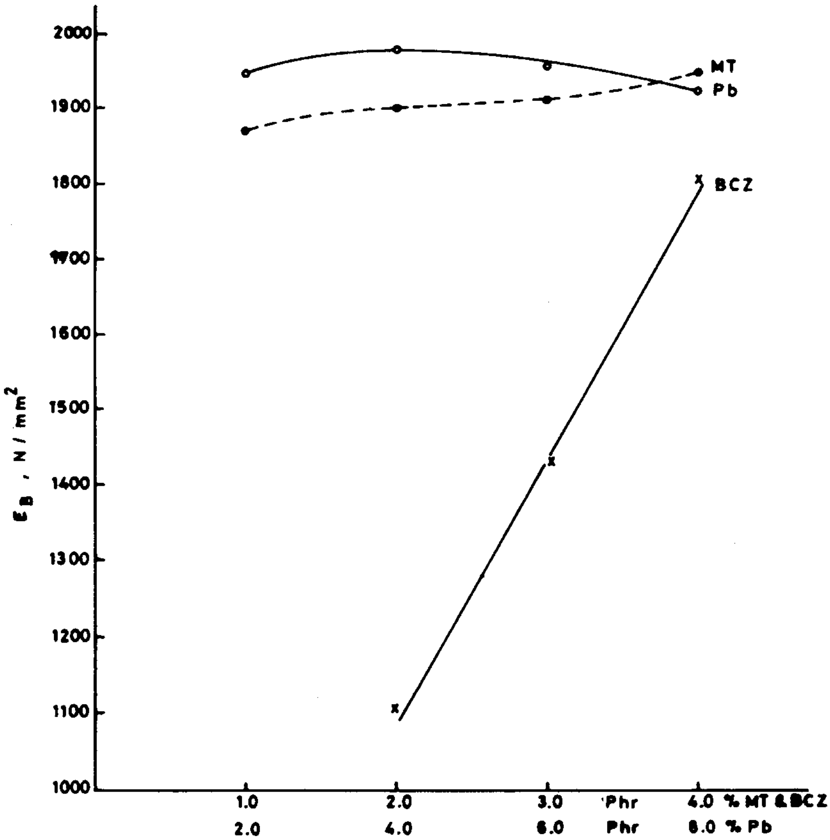

Fig. 3. The modulus of elasticity from bending vs. % stabilizer.

From Figure 2, it can be shown that σ_u and σ_y for MT-stabilized specimens are higher than those of Pb or BCZ. Figure 2 shows also the ultimate strain vs. percentage stabilizer. t_{max} for Pb is much higher than t_{max} for MT or BCZ. This gives an indication of the brittleness of MT-stabilized UPVC and the ductility of Pb-stabilized specimens. At lower concentrations of BCZ, its stabilizing power becomes weaker, which reduces the impact strength, tensile strength, and ductility of UPVC.

Flexural Strength

Figure 3 shows that the modulus of elasticity from bending, E_B, for MT is higher than that for BCZ or Pb, at 4% MT. But is becomes less than E_B for Pb at lower concentrations. E_B for BCZ is lower than for MT and Pb, and shows a steep slope, meaning that, at lower concentrations of BCZ, E_B is very poor, but at 4% BCZ, it has reasonably good values. Hence a high percentage of BCZ is recommended in formulations.

Higher stress values are needed to attain 0.05 mm/mm strain at the outer fibers of the 4% MT specimens than for the Pb or BCZ, showing that they are more stiff, which is a direct effect of the stabilizer. The behavior, however, is slightly reversed at lower concentrations of MT.

CONCLUSIONS

1. The impact strength and fracture toughness tests show that Pb stabilizers confer better impact resistance and fracture toughness. They are more resistant to brittle fractures, which are undesirable in rigid PVC pressure pipes. These properties are proabably caused by PbO, found in the Pb system. The sulfur in the tin mercaptide stabilizer causes antiplasticization, which explains the unexpected behavior of MT specimens. These tests uncover the reasons for the premature brittle fractures, which were encountered frequently during testing American rigid PVC pressure pipes,[6] without an apparent reason. American UPVC pressure pipes are stabilized by mercapto tin stabilizers, since Pb stabilizers are forbidden in the United States.

2. Tensile tests show that Pb confers ductility to UPVC, while BCZ or MT confer brittleness.

3. Flexural tests show that at higher levels of MT, it becomes stiffer than BCZ or Pb specimens.

NOMENCLATURE

UPVC unplasticized poly(vinyl chloride)
σ_u tensile ultimate strength
σ_y yield strength
ϵ_{max} maximum strain

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