Effect of Stabilizer Type on the Physicochemical Properties Of Rigid PVC. III

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Synopsis

The crystallinity of rigid PVC specimens, stabilized by a tin mercaptide or a lead stabilizer, has been studied. It is found that the crystallinity of rigid PVC is greatly influenced by the type of stabilizer added, and that the response of the PVC toward subsequent UV exposure was also different. The effects of unstable structures and crystallinity, after UV irradiation, on the mechanical properties of rigid PVC have been investigated.

INTRODUCTION

The X-ray structure analysis is based on the phenomenon of diffraction of X-rays by a substance. The X-rays diffracting from crystallite regions give distinct reflections, while amorphous regions in the polymer give diffuse halos.

The crystallites which grow in the melt are not definite entities with sharp boundaries or crystal faces separating them fıom the surrounding amorphous material. Poly(vinyl chloride) may be generally described as amorphous. Different values of percentage crystallinity have been claimed. This discrepancy can be attributed to the method of polymerization, but a range of 5–15% crystallites is reasonable.

The present work studies the effect of using a lead stabilizer and a tin mercaptide stabilizer on the crystallinity of rigid PVC and its behavior after artificial weathering.

EXPERIMENTAL

Materials. PVC used is a commercial suspension polymer of K value 65 (Vinnol H65), from Wacker. The tin stabilizer was a tin mercaptide stabilizer MT, (Irgastab T65) from CibaGeigy. The lead system stabilizer PB was supplied by Al Sharif Plastics Co., Egypt.

Procedure. PVC formulations were compounded so as to contain different concentrations of Pb or MT, and these batches were then injection-molded. A detailed description was previously presented.[1] A part of these batches was then exposed to intensive UV degradation in a QUV fluorescent sun lamp apparatus for different durations, namely 173 h, 310 h, and 457 h.

A Siemens X-Ray diffractometer, Model D 500, was employed for studying

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crystallinity in the specimens. Crystallinity is estimated by measuring the peak areas of crystallites in the resulting X-ray patterns.

RESULTS

The different mechanical properties of rigid PVC are influenced by its relative crystallinity, as well as the structures initiating through stabilization and degradation reactions. In order to evaluate and compare the results obtained from X-ray diffraction patterns, a factor for determining crystallinity was employed:

$$R_{\text{cryst}} = \frac{\text{peak area of crystallites in specimens}}{\text{peak area of crystallites in PVC resin}}$$

where R_{cryst} = relative crystallinity.

Figure 1 displays the relation between R_{cryst} and stabilizer concentration. It could be noticed that the MT lines show continuous increases in crystallinity with increased stabilizer concentration; as for the Pb lines they show a continuous

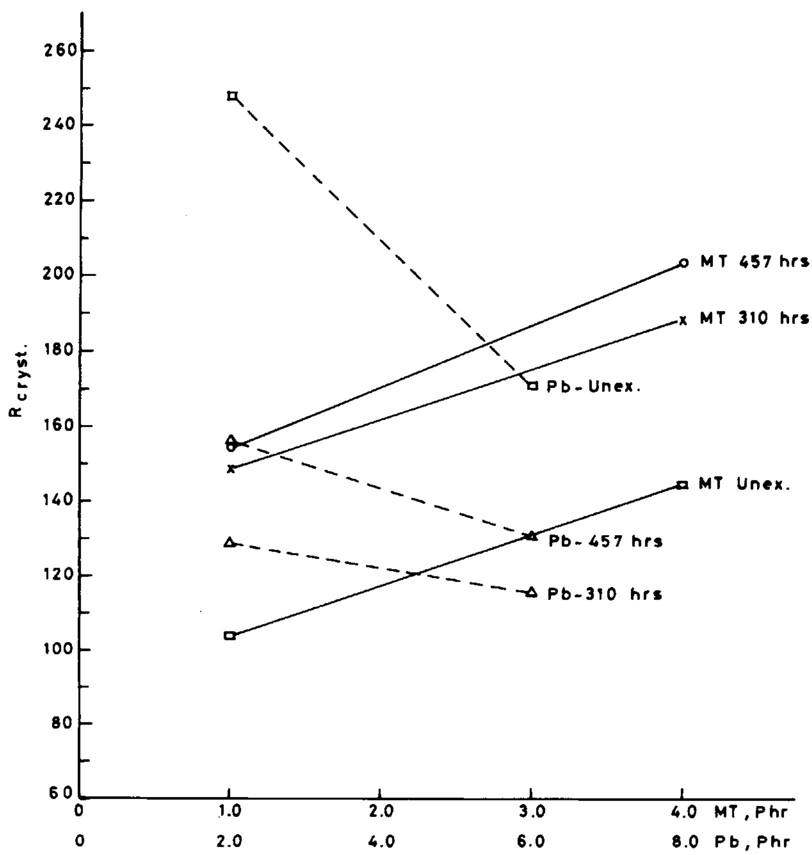

Fig. 1. Relative crystallinity vs. stabilizer concentration.

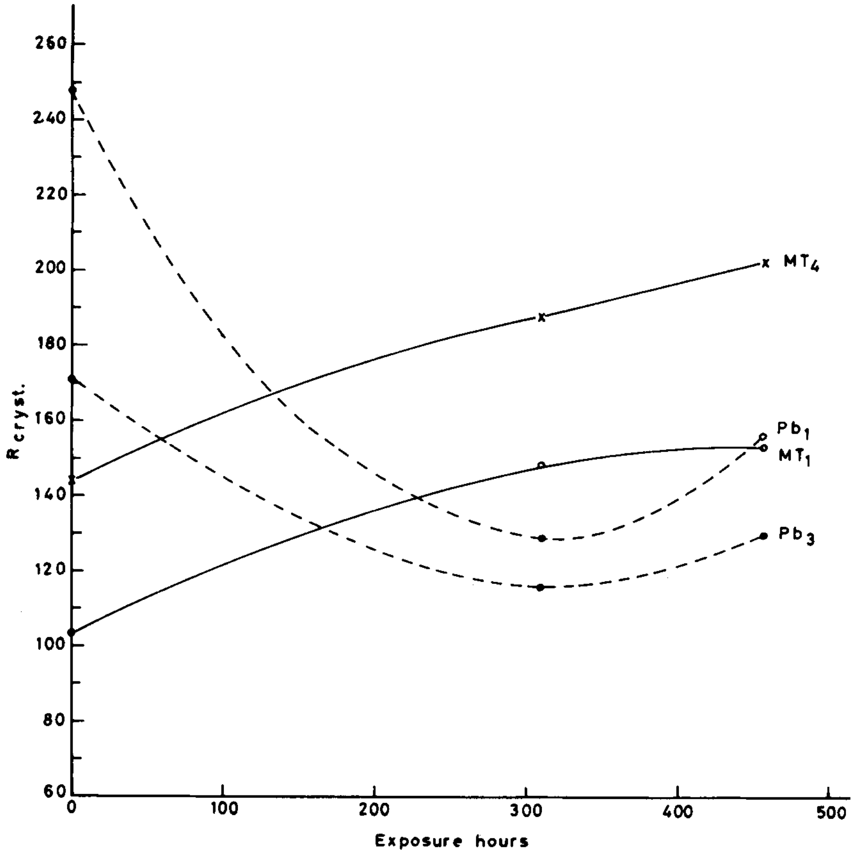

Fig. 2. Relative crystallinity vs. exposure (h) for MT and PB specimens.

decrease in crystallinity with increased stabilizer concentration. Hence MT enhances crystallinity, while higher concentrations of Pb inhibit crystallinity.

Figure 2 depicts the relation between the relative crystallinity and exposure hours, for MT 1, MT 4 (1 phr and 4 phr) and Pb 1, Pb 3 (2 phr and 6 phr). The two curves representing Pb 1 and Pb 3 show that, at zero exposure, Unex Pb 1 has higher crystallinity than Pb 3, and that, at 310 h, there is a sharp decrease in crystallinity where the difference in R_{cryst} between the two curves is a minimum. Surprisingly, after 457 h, both types of Pb have gained some additional crystallinity due to UV irradiation.

The MT 1 and MT 4 curves show continuous increases in crystallinity with prolonged exposure. These unexpected findings throw light on the behavior of rigid PVC during mechanical testing.[1,2]

Figure 3 shows that the impact strength and fracture toughness of unexposed Pb increases, as R_{cryst} decreases. This may be attributed to the fact that the growth in amorphous regions increases the toughness and resistance to brittle fractures. These amorphous regions which are less dense and less compact than the crystallites act as shock absorbers that minimize the effects of blows or brittle modes of fracture. As for MT, the increased crystallinity helps in reducing the

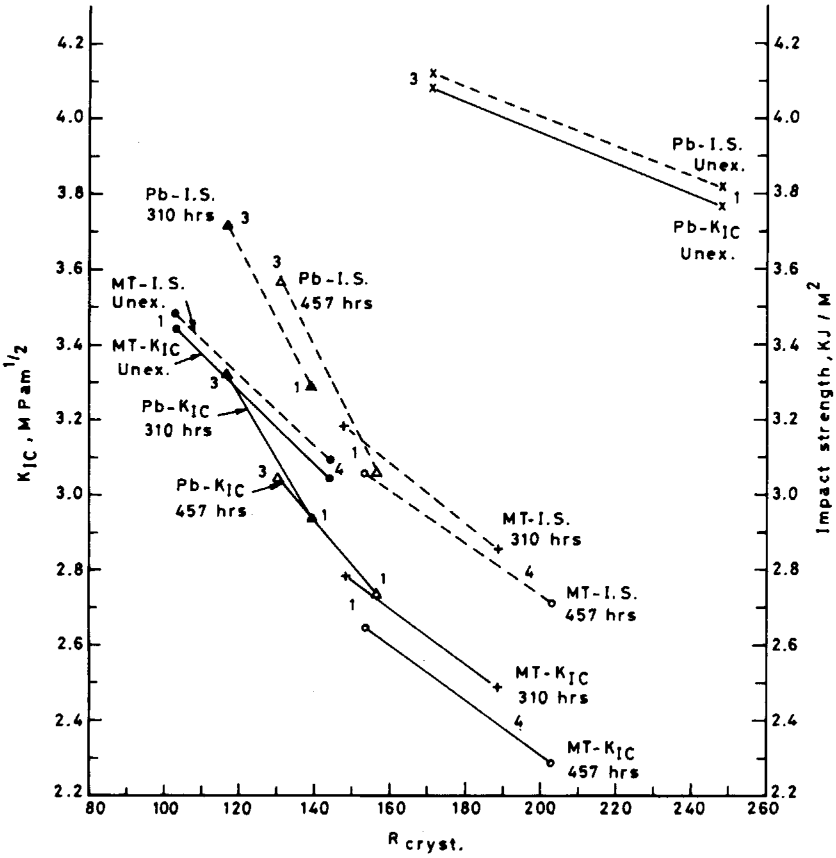

Fig. 3. K_{IC} and IS vs. relative crystallinity of MT and Pb specimens.

impact strength and fracture toughness values. Crystallites behave in this respect as flaws,[3] in spite of the fact that their general effect is to increase the tensile strength and stiffness of rigid PVC. This may be evidenced from Figures 4–6, which show that E_B and σ_y increase as the crystallinity of MT increases. As for ϵ_{max} for MT it suffers a reduction with longer UV durations and increased crystallinity; also ϵ_{max} for Pb drops with longer exposure, but with the diminution of crystallinity. The increase of E_B and σ_y for Pb is accompanied by a drop in R_{cryst} with increased Pb concentration. At 6 phr R_{cryst} is a minimum, while E_B or σ_y are at their peak values. Hence crystallinity alone cannot elucidate the behavior of E_B or σ_y for Pb specimens. This behavior has been related to the effects of $(C_{17}H_{35}COO)_2Pb$, at its lower and higher concentrations in the Pb stabilizer system.[2]

Other factors that influence the mechanical performance include carbonyl group concentration, carbon–carbon double bonds, and the extent of dehydrochlorination.

Figure 7 gives the relation between carbonyl group concentration and stabilizer concentration. It is evident that, as the stabilizer concentration increases, the

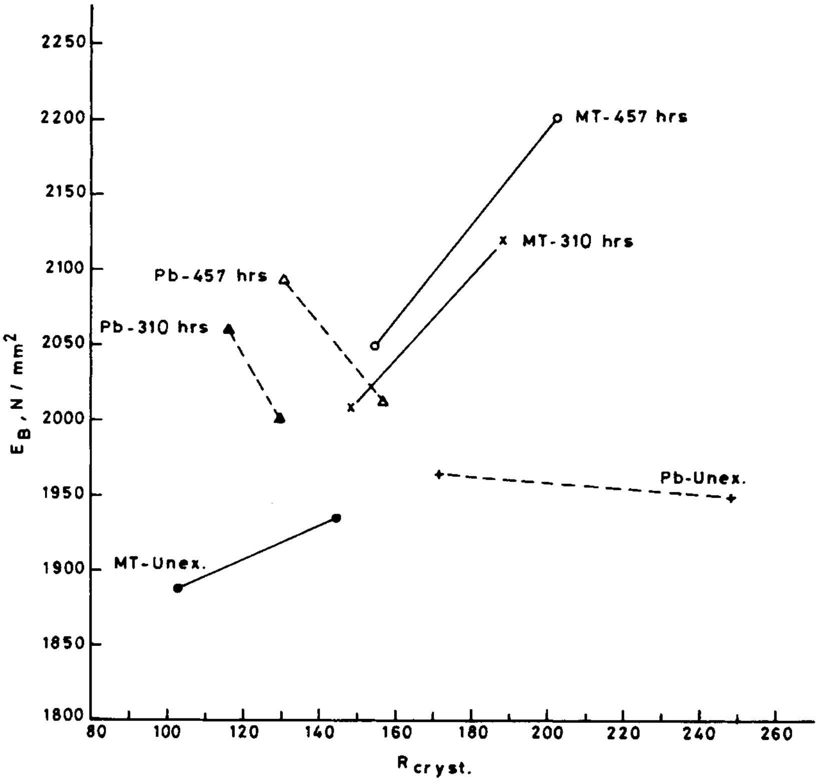

Fig. 4. E_B vs. relative crystallinity of MT and Pb specimens.

efficiency of stabilization improves, and —CO— concentration decreases. MT shows better resistance to —CO— formation than Pb. Also, with longer UV exposure, there is an increase in —CO— formation in both MT and Pb stabilized specimens, but Pb still maintains a higher concentration of —CO— than MT specimens.

Figure 8 shows that the content of conjugated double bonds in MT is lower than in Pb, even with increased UV exposure.

Figure 9 shows that the extent of dehydrochlorination in MT is less than that of Pb, before and after UV exposure, as determined by thermogravimetric analysis TGA.

Hence MT has better stabilizing efficiencies than Pb, but the mechanical performance of Pb or MT stabilized specimens is clearly the sum of the effects of crystallinity, unsaturation, and dehydrochlorination as well as the chemical and physical effects conferred by antiplasticization in the MT stabilizer, and PbO and dibasic lead stearate in the Pb stabilizer system.[1,2]

DISCUSSION

According to Tager,[4] antiplasticizer molecules increase the mobility of supermolecular structures, thus favoring their mutual orientation, which always

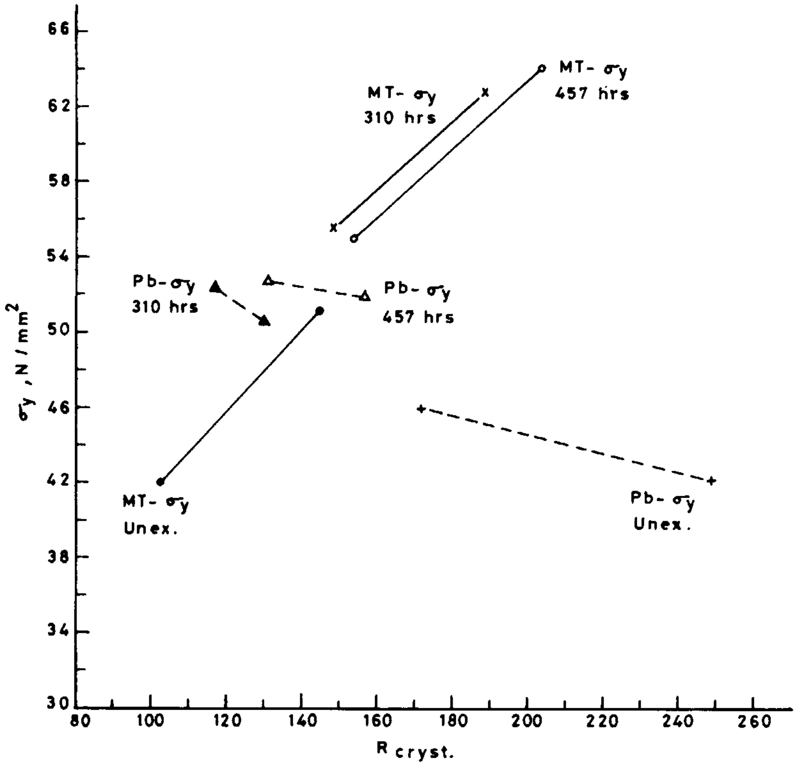

Fig. 5. σ_y vs. relative crystallinity of MT and Pb specimens.

increases the mechanical strength by enhancing recrystallization. The excess of MT stabilizer molecules which do not enter into chemical reactions act as a boundary lubricant which facilitates the orientation of the supermolecular structures, thus aiding the growth of existing crystallites and consequently the reduction in toughness. There is an intrinsic relation between antiplasticization, crystallinity, strength, and brittleness.

One of the direct effects of UV is to strengthen antiplasticization, which consists of forming chemical bonds with sulfur and adjacent polymer chains, and the introduction of additional hydrogen bonds through the formed carbonyl groups. Crystallinity also is increased as a result of enhancing orientation of supermolecular structures. Thus there is a direct link between crystallinity and antiplasticization. It is possible now to conclude that mercaptotin stabilizers enhance crystallinity while higher concentrations of Pb stabilizers inhibit crystallinity.

The matrix of MT-stabilized PVC, with an increased crystallinity, increased conjugation, increased carbonyl concentration, and increased dehydrochlorination attains, unfortunately, a brittle structure, and a significant drop in impact strength and fracture roughness occurs with increased UV exposure.

It is logic to expect that a rigid compact system will give an increase in σ_u, σ_y and E_B, since additional traverse ties and unsaturation impede lateral and lon-

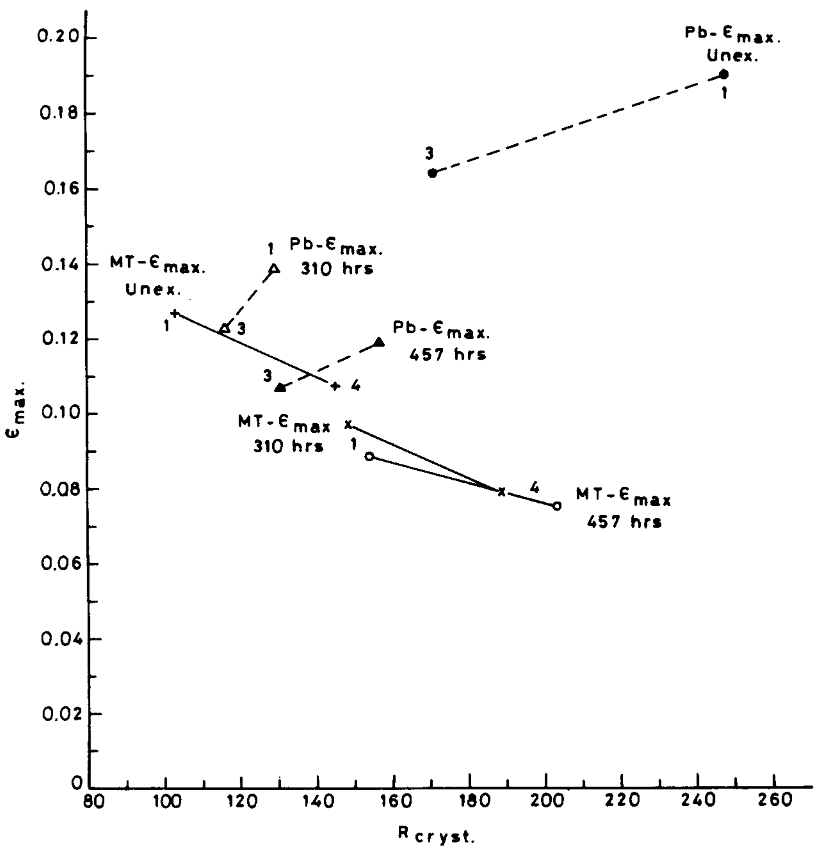

Fig. 6. ϵ_{max} vs. relative crystallinity of MT and Pb specimens.

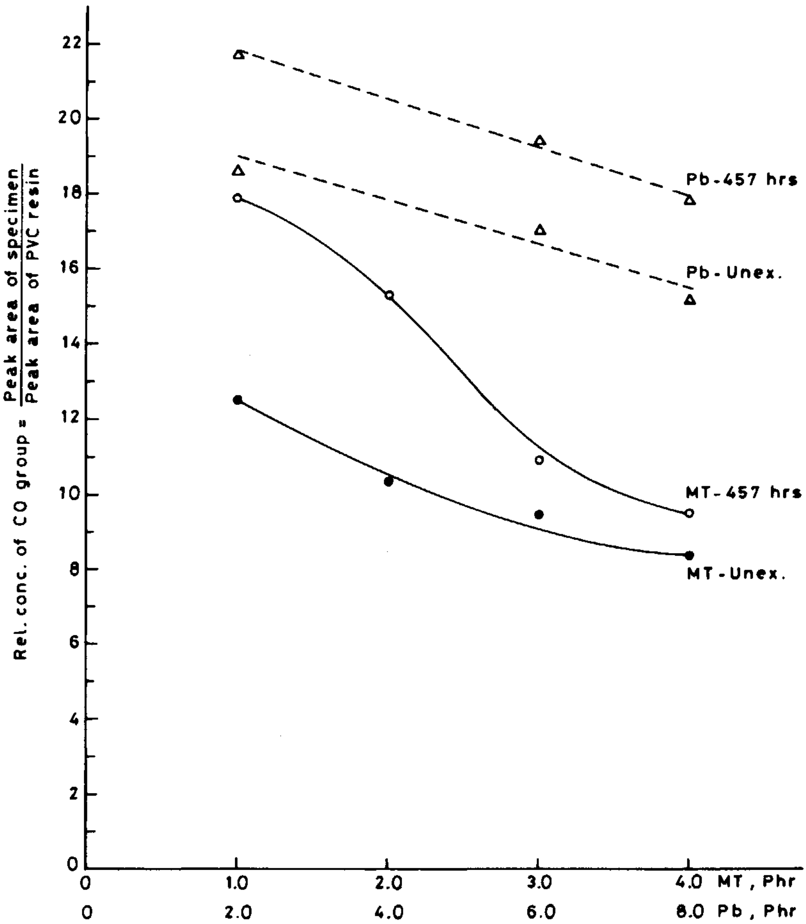

Fig. 7. Relative concentration of CO vs. stabilizer concentration of MT and Pb.

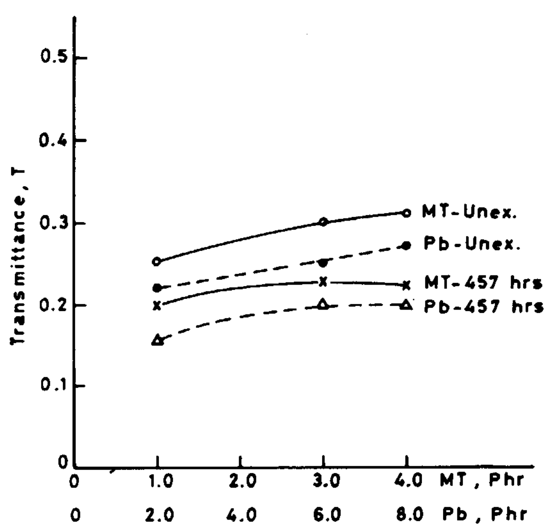

Fig. 8. Transmittance vs. stabilizer concentration for exposed MT and Pb (λ = 290 nm).

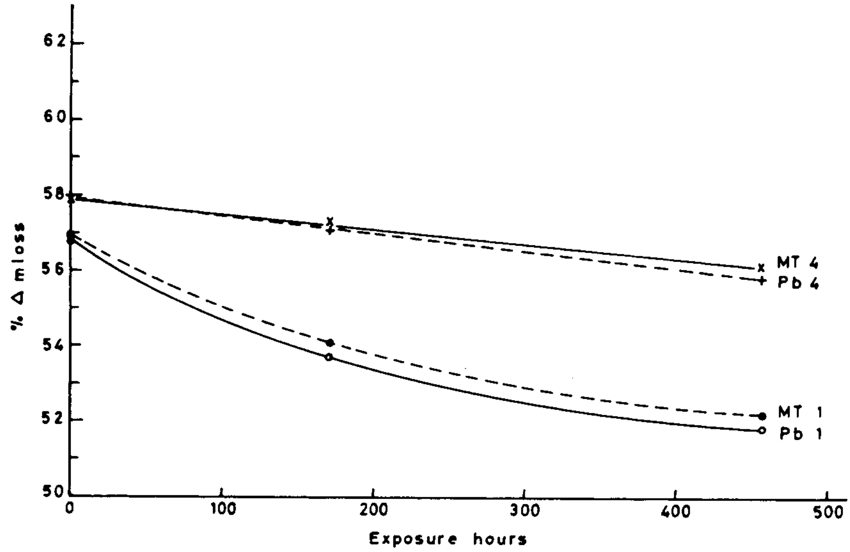

Fig. 9. % Δm loss vs. exposure (h) for Pb and MT.

gitudinal flexibility of the polymer chains, and thus the percentage elongation at break is reduced and brittle modes of fracture are possible.

As for Pb specimens, their crystallinity which has decreased after exposure, has helped to prevent sharp changes in impact strength, fracture toughness, elongation, and stiffness. This shows that amorphous regions are less amenable to changes in the mechanical properties than regions of crystallites.

PbO is thought to be responsible for hindering or retarding crystallinity, and thus, as its concentration after 457 h of UV exposure was decreased, crystallinity increased. It is worth to mention that the crystallite peaks of Pb were small and uniformly spread over the whole matrix, while those of MT specimens lacked such uniformity, and were bigger and sharper. These effects can possibly explain the better toughness and resistance to brittle fractures of Pb specimens, which are contrary to MT specimens (see Figs. 10 and 11). Finally, it could be said that the increase of crystallinity in PVC due to UV exposure is not surprising. Lately Raad and coworkers[5] have noticed an increase in the crystallinity of PP film with the increase of exposure time to UV radiation.

CONCLUSION

Crystallinity in rigid PVC is influenced by the type of stabilizer added. Increased amounts of MT stabilizer enhance crystallinity, while the opposite is true with respect to the Pb stabilizer.

Crystallinity and antiplasticization, which are caused mainly by the presence of sulfur in mercaptotin stabilizers are closely related to each other and influence the mechanical performance of MT stabilizers, are closely related to each other. Crystallites in MT show sharper and bigger peak areas, unlike Pb. In Pb they are spread uniformly along the whole specimen, unlike MT.

Crystallinity influences greatly the mechanical characteristics of MT specimens, while in Pb specimens it does not share the same degree of influence.

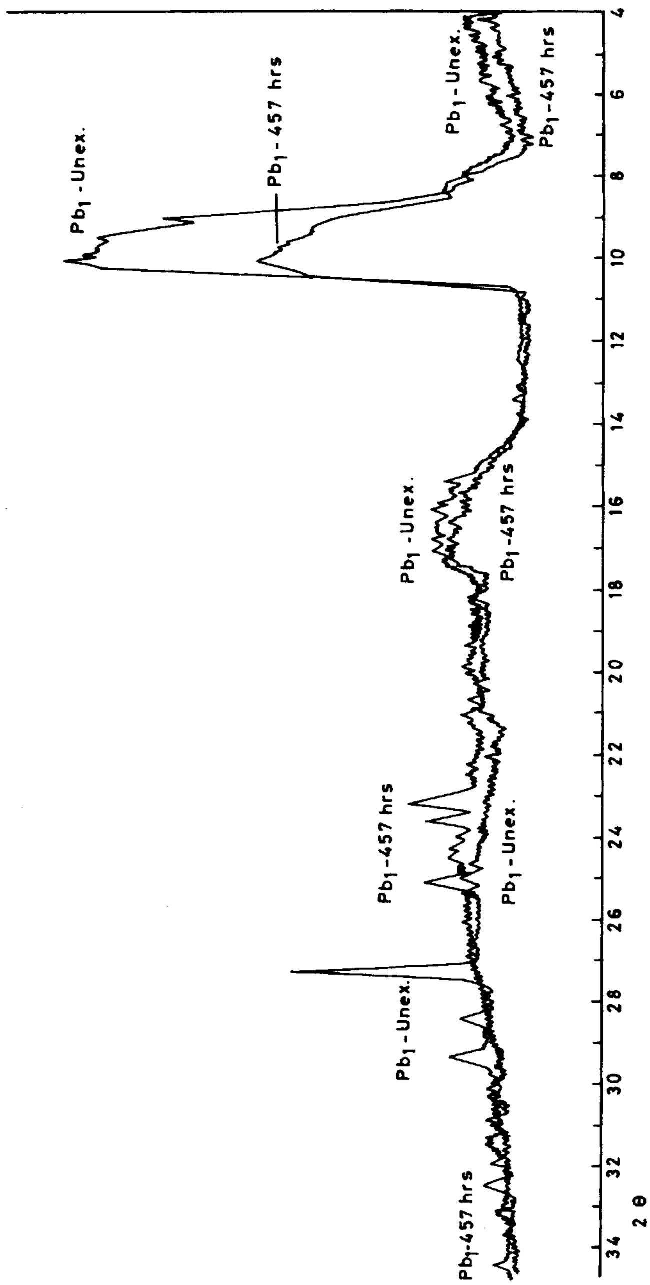

Fig. 10. X-ray diffraction patterns of unexposed and exposed Pb_1.

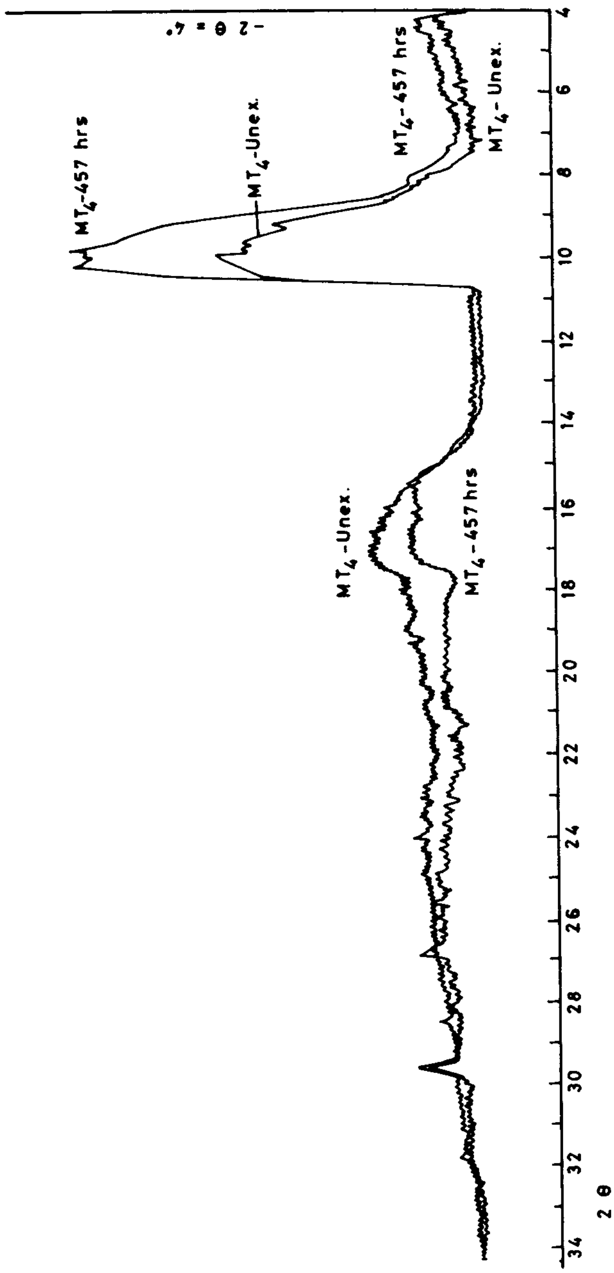

Fig. 11. X-ray diffraction patterns of unexposed and exposed MT_4.

Conjugated unsaturation, degree of dehydrochlorination, carbonyl group formation, and the chemical structure of the stabilizer system play an important role in the mechanical behavior of rigid PVC.

On the other hand, exposure to UV enhances crystallinity in MT specimens and retards crystallinity in Pb specimens. It is also concluded that, during tensile strength tests, amorphous regions represent zones of failure and fracture, while in impact strength tests or fracture toughness tests crystallites act as fields of failure and brittle fractures.

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