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Material behaviour

Synergistic effect of maleimido phenyl urea derivatives mixed with some commercial stabilizers on the efficiency of thermal stabilization of PVC

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ABSTRACT

Four novel antimicrobial maleimido phenyl urea stabilizers **1**–**4** were synthesized from N-[4-(chlorocarbonyl) phenyl] maleimide with phenyl urea and its derivatives (p-methyl, o-chloro and p-carboxy). The effect of mixing maleimido phenyl urea stabilizer **2** with each of the reference stabilizers, dibasic lead carbonate (DBLC), cadmium-barium-zinc stearate (Cd-Ba-Zn stearate) or n-octyltin mercaptide (n-OTM), on the stabilization efficiency in thermal degradation of rigid PVC at 180 °C in air, has been investigated. Mixing was effected in the range of 0–100 wt% of stabilizer **2** relative to each of the reference stabilizers. The stabilizing efficiency was evaluated by measuring the length of the thermal stability period (Ts), the period during which no detectable amount of hydrogen chloride gas could be observed, and also from the rate of dehydrochlorination as measured by continuous potentiometric determination, and by the extent of discoloration of the degraded polymer samples. The results show a true synergistic effect from the combination of stabilizer **2** with any of the reference stabilizers. Mixing of the stabilizers improves the Ts values, decreases the rate of dehydrochlorination and lowers the extent of discoloration of the polymer. The maximum synergism was attained when stabilizer **2** is mixed with either of the three reference stabilizers in equivalent weight ratio (50%/50%). The observed synergism may be attributed to the different mechanisms by which the investigated and the reference stabilizers work.

1. Introduction

Poly(vinyl chloride), PVC, is a material of enormous technical and economic importance. It stands second in the world after polyethylene as regards the production and consumption of a synthetic material. Its extensive autocatalytic dehydrochlorination, with the subsequent formation of conjugated double bonds, on exposure to high temperature during its molding or use still remains one of its main problems [1]. This results in an unacceptable discoloration of the polymer and a drastic change in its physical and mechanical properties, together with a decrease or increase in molecular weight as a result of chain scission or cross linking, respectively, which can reduce the useful life of the product [2–4]. It is assumed that various defect sites in the polymer chains are responsible for this instability. Possible defect structures in PVC are branching, chloroallyl groups, end groups, oxygen containing groups, head to-head structures and the stereo order of the monomer units (tacticity) [5–10].

In general, the great commercial importance of PVC can be attributed to the development of effective means of

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stabilization. The thermal stabilizers commonly in use for the stabilization of PVC are either basic salts [11] which can react with the evolved hydrogen chloride gas, thus retarding the deleterious catalytic action of the eliminated hydrogen chloride [12], metallic soaps [13] and esters, or mercaptides of dialkyltin [14] that can exchange the labile chlorine in the backbone for other more stable ester or mercaptide group derived from the stabilizer. Moreover, stabilizers of an organic nature have also been developed to avoid the deleterious effect of the metal chlorides, by-products of metallic stabilizers, accumulated during the reaction of organometallic stabilizers with the PVC [15–18]. These metal chlorides are considered as strong catalysts for the subsequent dehydrochlorination process, are responsible for sudden blackening of certain formulations and may present a serious environmental problem [19,20].

On the other hand, PVC products for certain applications in the fields of construction, food package, decoration, medicine (e.g. for the fabrication of indwelling catheters in hospital care) and commodities such as construction tubing, films, toys, wallpaper, etc, cannot avoid contamination with microbes during their daily usage. For such applications, a new trend has been established recently based on the use of fully organic stabilizers of antimicrobial nature to obtain thermally stable antimicrobial PVC composites [21–23].

In our previous work [23], we have suggested that the stabilizing action of various antimicrobial maleimido phenyl urea stabilizers is due to a radical mechanism which disrupts the radical chain degradation process of the polymer through blocking the odd electron sites created on the PVC chains. However, almost all the commonly known stabilizers chosen in this study as references function through either neutralization of the evolved hydrogen chloride gas (the case of basic salts such as dibasic lead carbonate, DBLC), or through replacing the weakly bonded chlorine atoms by substitutes that have greater stability (the case of both soap and organotin stabilizer such as cadmium-barium-zinc stearate complex, Cd-Ba-Zn stearate, and n-octyltin mercaptide, n-OTM, respectively). Accordingly, it became of interest to investigate the effect of mixing maleimido phenyl urea stabilizer **2** (which seems to have a relatively higher stabilizing efficiency than other maleimido phenyl urea stabilizers **1**, **3** and **4**) together with those used in industry on the efficiency of thermal stabilization of PVC.

2. Experimental

2.1. Materials

The PVC (suspension) used in this study was additive free, with a K-value of 70 and supplied by Hüls Co. (Frankfurt, Germany). Cadmium-barium-zinc stearate complex (Cd-Ba-Zn stearate) obtained from G. Siegle and Co. (Stuttgart, Germany), n-octyltin mercaptide (n-OTM) obtained from America Company for PVC manufacturing (Alexandria, Egypt) and dibasic lead carbonate (DBLC) obtained from the National lead Co. (Darmstadt, Germany) were used in this study. P-Amino benzoic acid obtained from Oxford, p-toluidine obtained from Merck, and o-choloro aniline obtained from Schuchard–München were also used. N-[4-(chlorocarbonyl) phenyl] maleimide was synthesized according to the method described by Oishi and Fujimoto [24].

2.2. Preparation of maleimido phenyl urea and its derivatives

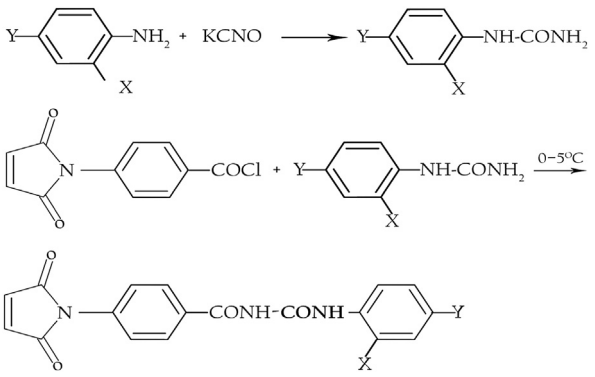
Four maleimido phenyl urea stabilizers **1**–**4** were prepared according to the method described in our previous work [23], as shown in Scheme 1. Briefly, 0.1 mol of potassium cyanate dissolved in 50 ml of warm water was added gradually with continuous stirring to 0.01 mol of the aromatic amine dissolved in 100 ml of 10% acetic acid solution. The reaction mixture was allowed to stand for 30 min, and cooled in ice for another 30 min. The crude (phenyl urea or its derivatives) was filtered, washed with water, recrystallized from boiling water and dried in an oven [25]. 9.42 g (0.04 mol) of N-(4-chloro carbonyl phenyl) maleimide was added gradually to the phenyl urea or its derivatives (0.04 mol) dissolved in least amount of dry cooled acetone, kept stirred for 1 h and poured onto crushed ice to separate the stabilizer which recrystallized from dry benzene.

The purity of the prepared stabilizers was checked by elemental analyses, melting point, IR, NMR and mass spectra. All the results are in good agreement with those previously reported [23] and are shown in Table 1. The prepared maleimido phenyl urea stabilizers are efficient antimicrobial agents against *B. subtilis* and *S. pneumoniae* as Gram positive bacteria and against *E. coli* as Gram negative bacteria and against *A. fumigatus*, *S. racemosum* and *G. candidum* fungi [23].

2.3. Measurements

FTIR spectra were recorded on a Shimadzu FTIR 8201 PC spectrophotometer using KBr pellets.

^{1}H-NMR spectra were recorded with a JOEL 270 MHz (Tokyo, Japan) spectrophotometer in DMSO-d_6 as a solvent



Scheme 1. Synthesis of maleimido phenyl urea derivatives.

Derivative Code	1	2	3	4
X	H	H	Cl	H
Y	H	CH_3	H	COOH