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Organic thermal stabilizers for rigid poly(vinyl chloride). Part XII: *N*-phenyl-3-substituted-5-pyrazolone derivatives

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Abstract

N-phenyl-3-substituted-5-pyrazolone derivatives have been examined as thermal stabilizers or co-stabilizers for rigid PVC in air, at 180 °C. Their high stabilizing efficiency is detected by their high induction period values (T_s) when compared with some of the common reference stabilizers used industrially, such as dibasic lead carbonate, calcium–zinc soap and *n*-octyl tin mercaptide. Blending these derivatives with some of the reference stabilizers in different ratios had a synergistic effect on both the induction period and the dehydrochlorination rate.

A probable mechanism for the stabilizing mode of *N*-phenyl-3-substituted-5-pyrazolone derivatives has been proposed. The stabilizing efficiency is attributed at least partially to the ability of the organic stabilizer to be incorporated in the polymeric chains, thus disrupting the chain degradation.

Keywords: Poly(vinyl chloride) (PVC); Stabilizer; Induction period (T_s); Degradation; Dehydrochlorination rate

1. Introduction

Poly(vinyl chloride) (PVC) is one of the most important commercial thermoplastic polymers used in our daily life, as it has a great technical and economic importance. But it still has some problems due to its poor thermal stability leading to its degradation by a dehydrochlorination reaction initiated at the labile sites present on the polymeric chains, such as branching, chloroallyl groups, end groups, oxygen-containing groups and head-to-head structures [1], in addition to the tacticity [2]. This leads to a great discoloration of the polymer and a deterioration of its physical and mechanical properties. For thermal stabilization of the polymer, highly effective additives such as metallic soaps [3–7], basic compounds [8] and organotin compounds [9] have been commercially used.

However, some of them are toxic and cause environmental problems, as most of them leave toxic residues during the degradation process. This has recently directed attention towards the use of organic stabilizers [10–32]. The present work was aimed to investigate a class of well-known compounds, *N*-phenyl-pyrazolone derivatives, as thermal stabilizers for rigid PVC. These compounds are available, easily prepared and possess a variety of functional groups, which can act as radical scavengers for the radicals resulting from the degradation process of PVC.

N-phenyl-3-substituted-5-pyrazolone derivatives have been known since 1883 as important intermediates for pharmaceuticals [33], agrochemicals and dyestuffs [34].

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They were also known as anti-inflammatory agents and allergy inhibitors, and also have bactericidal, fungicidal and herbicidal activities.

2. Experimental procedures

2.1. Materials

The commercial PVC (suspension) used in this study was additive free, with a *K*-value 70 and supplied by Hüls Co., dibasic lead carbonate (DBLC) (Rolite lead) from the National Lead Co., West Germany was also used. Basic lead stearate was obtained from "Linkers" – Far East Pte Ltd. – Singapore, *n*-octyl tin mercaptide was obtained from the "Witco Vinyl Additives GmbH" Co., Germany and Ca–Zn soap was obtained from "Lagor – S.P.A." Co. – Italy.

2.2. Experimental techniques

N-phenyl-3-substituted-5-pyrazolone derivatives were prepared according to a conventional method [35]. These derivative structures were proved by IR, elemental analysis and ^{1}H NMR.

Code names, melting points and elemental analyses of the prepared organic materials are tabulated in Table 1.

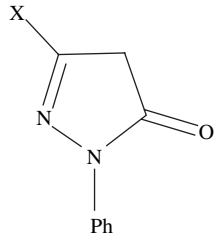
It is important to notice here that the ^{1}H NMR spectra have proved that in case of the amino derivative, the salicyloyl and acryloyl groups are attached to the amino group of the parent pyrazolone, whereas condensation of the crotonal, benzal and cinnamal is on the methylene group at position (4) of the pyrazolone ring irrespective to the derivative at position (3). This is due to the fact that the condensation reaction is done in alkaline medium (pyridine) which favours the attack on the active methylene group.

2.2.1. Preparation of PVC samples

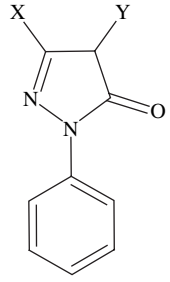
Samples of PVC for heat degradation were prepared by thoroughly mixing 1 g of PVC powder with 2 wt.% of the stabilizer (or a mixed stabilizer) in a mortar and 0.2 g of the resulting fine powder was used in the investigation.

2.2.2. Method of evaluation of the stabilizing efficiency

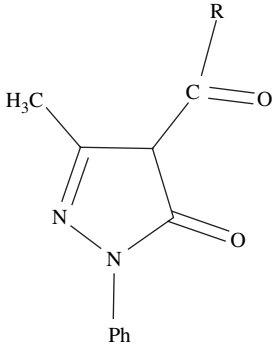
Evaluation of the stabilizing efficiency of PVC in the presence of various thermal stabilizers was carried out by measuring both the T_s (thermal stability) and the dehydrochlorination rate using a continuous potentiometric determination of the evolved HCl gas at 180 °C in air. A detailed description of this method was given elsewhere [36].

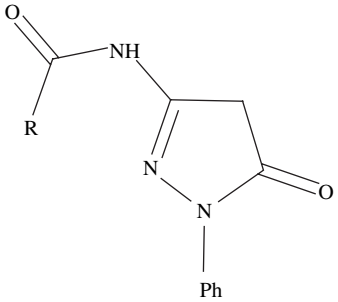


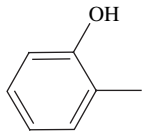
(Where X = -CH_3 or -NH_2)
3-Substituted-1-phenyl-2-pyrazolin-5-one



(Where Y= Benzal, Crotonal, Cinnamal
X= -CH_3 or -NH_2)





(Where R = CH_2=CH- or 

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