PÔSTER - RESUMO - MATERIAIS E BIOMATERIAIS

AGEING OF FLEXIBLE PVC IN CONSUMER GOODS: COMPOSITIONAL EFFECTS ON PLASTICIZER MIGRATION AND DEHYDROCHLORINATION

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Introduction

Poly(vinyl chloride) (PVC) has been one of the most widely produced and utilized plastics globally since the 1950s, due to its technical versatility and economic viability. This adaptability largely stems from the incorporation of additives. Among these, plasticizers are used for enhancing flexibility, often reaching concentrations of up to 50 phr. Historically, phthalates—specifically di(2-ethylhexyl) phthalate (DEHP)—dominated the market until the early 2000s. However, the discovery of toxic effects, including reproductive toxicity, carcinogenesis, cardiotoxicity, hepatotoxicity, and nephrotoxicity, led to global health concerns. Consequently, many governments have adopted regulations and bans on phthalates, driving the development and use of non-phthalate plasticizers as sustainable alternatives to mitigate these toxicological risks.

The degradation of PVC plasticized with phthalates, is characterized by the dehydrochlorination of the polymeric matrix, followed by plasticizer diffusion through the polymer and subsequent release into the environment. These phenomena result in surface stickiness, loss of ductility and discoloration, directly affecting the service life of consumer goods. In this context, this study investigates the ageing behavior of four flexible PVC formulations containing

alternative plasticizers compared to a DEHP reference. The objective is to elucidate the specific chemical and physical degradation mechanisms and evaluate their implications for the structural stability and longevity of soft PVC products.

Experimental Results

Flexible PVC samples, stabilized with 2 phr of calcium stearate and containing 40 phr of plasticizer— DEHP, di(2-ethylhexyl) adipate, (DEHA), di(2-ethylhexyl) terephthalate (DEHT), acetyl tributyl citrate (ATBC), trioctyl trimellitate (TOTM) - underwent 70 days of accelerated ageing (70 °C, 50% RH). Degradation was monitored via gravimetry, colorimetry (CIELab), and spectroscopic monitoring and spectroscopy (UV-Vis and micro-FTIR), with the later one mapping chemical changes along the film thickness.

Gravimetric data indicated that TOTM formulation exhibited the highest stability, with negligible mass loss throughout ageing. In contrast, DEHA- and ATBC plasticized samples showed the highest mass-loss rates, following diffusion-controlled kinetics (linear relationship with $t^{1}?^{2}$). Samples containing DEHP and DEHT displayed surface evaporation limited behavior, characterized by a linear mass loss with time. Micro-FTIR analysis revealed the formation of a surface layer composed of residual plasticizer and acidic hydrolysis products, evidenced by a decrease in the ester carbonyl band (~1721 $cm?^{1}$) and the emergence of a new band around ~1680 $cm?^{1}$ during ageing. While surface layer formation suggests evaporation control, the diffusion kinetics of DEHA and ATBC contradict this. This inconsistency suggest a hybrid plasticizer migration mechanism involving diffusion, evaporation, and concurrent chemical transformations.

Simultaneously, a progressive yellowing of the samples was observed, quantified by an increase in the b* parameter of the CIELab color space, with ATBC formulation being the most susceptible to chromatic alteration. UV-Vis spectroscopy showed an increase in absorption bands at 366 nm and 450 nm, attributed to conjugated dienes, establishing a direct relationship between polyene formation, as result of the PVC dehydrochloration, and the intensification of yellow coloration.

Conclusions

The thermo-oxidative degradation of flexible PVC involves complex, interrelated processes, primarily dehydrochlorination of the polymer matrix and plasticizer migration. Among the systems evaluated, ATBC exhibited the highest degree of yellowing, despite its low toxicity and biodegradability. DEHA, although partially derived from renewable sources and biodegradable, also showed significant migration and intense yellowing. In contrast, formulations containing TOTM and DEHT demonstrated superior stability, characterized by lower mass loss and superior color retention, emerging as the most viable alternatives to DEHP.

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Palavras-chave: soft-pvc; consumer goods; degradation; alternative plasticizers.