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Thermal energy storage systems based on poly(vinyl chloride) blends

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Abstract

A series of blends of poly(vinyl chloride) (PVC) with: (i) poly(methyl methacrylate) (PMMA), or (ii) polyoxymethylene (POM), with poly(ethylene glycol) (PEG) as a thermal energy storage material, has been investigated by differential scanning calorimetry (DSC), scanning electron microscopy (SEM), thermogravimetric analysis (TGA) alone, or coupled with Fourier transform infrared spectroscopy (FTIR). For the blends under investigation it was found that PEG has a significant effect on their thermal properties. It causes the initial decomposition temperatures to increase by about 70°C for PVC/POM blends, a substantial suppression of the volatile products evolution for PVC/PMMA blends, and for both polymer systems an improvement in the surface morphology in terms of uniformity. Based on the radical decomposition schemes of PEG and PVC a possible radical scavenger action was discussed as a reason for greater thermal stability. © 1998 Elsevier Science Ltd. All rights reserved.

1. Introduction

The blending of polymers is one of the ways of modifying the physical properties of a polymer in a desired way. For poly(vinyl chloride) (PVC), which was the component of the first thermoplastic polymer blend patented as early as 1942 [1], this is particularly true in terms of improving its thermal properties since the thermal degradation of poly(vinyl chloride) (PVC) is a complicated phenomena consisting of several partial reactions [2, 3]. It is generally agreed that the process starts from labile centres, e.g. head-to-head structures, sites of unsaturation or tertiary chlorine atoms [4]. Primary evolution of hydrogen chloride leads to the formation of polyene sequences, which are, in turn, facilitated by double bonds formed in the initiation step. Structural changes make the polymer chain more liable to degradation, and morphological changes affect the diffusion of HCl from the reaction site [5]. Having in mind such a unique material's behaviour it seems extremely interesting to analyse polymer systems comprising of other polymers. For this study, two polymer blends of PVC were used: poly(methyl methacrylate) (PMMA) or polyoxymethylene (POM). The first one is well known to be miscible with PVC [6–9], the latter is believed to exhibit partial miscibility only [10]. Both polymeric systems were modified by the introduction of polyethylene glycol (PEG), to ascertain the influence of this promising thermal energy storage material on the thermal behaviour of blends under investigation. PEG is a white, free flowing powder, or creamy white flakes, and is used as a water-soluble lubricant for rubber moulds, textile fibres, and metal forming operations [11]. It is also used in water paints, paper coatings, polishes, and in the ceramic industry, as well as for chromatographic stationary phases. PEG has been considered a thermal energy storage material, because of its relatively large heat of fusion, congruent melting behaviour, non-corrosiveness, and wide melting point range as a phase change material (PCM) [12–15]. Thermal energy storage using the latent heat of PCM has been studied actively since the 1930 s. Latent

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heat storage using PCM is particularly attractive due to its high energy storage density and isothermal storage. Some problems arise at elevated temperatures since PEG is susceptible to free-radical attack, because the high strains present at the chain folds of the lamellar structure lower the activation energy for hydrogen abstraction [16]. The formation of low molecular weight products causes a decrease of melting point and heat of fusion, so the performance of the thermal energy storage system declines as the degradation proceeds.

The aim of the present work is to analyse thermal behaviour of PVC blends containing PEG as potential candidates for modern thermal energy storage materials.

2. Experimental

2.1. Materials

The samples were prepared by dilution of PVC-S (Zaklady Azotowe Tarnów-Moscice S.A., $M_w = 154200$) with PMMA (ICI, Runcorn, UK, $M_w = 108000$) or POM (a copolymer of trioxane and dioxolane from Zaklady Chemiczne Tarnów-Moscice S.A.) in dimethylformamide.

PEG ($M_w = 3400$) was a product of Polysciences Co (Warrington, PA, USA). Polymer films were dried in vacuo for several days and were then stored in closed containers. A description of the samples is given in Table 1.

2.2. Techniques

2.2.1. Differential scanning calorimetry

For the DSC measurements a Netzsch DSC 200, operating in a dynamic mode, was employed. A sample of ~5 mg weight was placed in a sealed aluminium pan. The heating rate of 10 K/min was applied, as the best choice to ensure high resolution of the DSC curves. Prior to use the calorimeter was carefully calibrated with an indium standard; an empty aluminium pan was used as a reference.

2.2.2. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed on a TG-209 (Netzsch) thermogravimetric analyser, operating in a dynamic mode at a heating rate of 10 K/min. The conditions were: sample weight ~5 mg, atmosphere—argon, flow rate—30 cm^3/min, temperature range: 30–450°C.

2.2.3. Thermogravimetric analysis coupled with Fourier Transform infrared spectroscopy

Thermogravimetric analysis coupled with Fourier transform infrared spectroscopy was carried out using a Perkin–Elmer 7 thermogravimetric analyser (heating rate = 50 K min, sample weight ~5 mg, nitrogen flow = 50 cm^3/min) and a Perkin–Elmer 1725X FTIR spectrometer. The thermogravimetric analyser and spectrometer were suitably coupled to enable the passage of evolved products from the furnace to the gas cell over a short path, to minimize secondary reaction or condensation on cell walls.

2.2.4. Electron microscopy investigation

A variable-pressure scanning electron microscopy (LEO 435 VP, Germany) was used to investigate the surface morphology of the blends. The samples were used directly for examination, and the apparatus operated in the variable pressure mode. The pressure in the specimen chamber was adjusted to 36 Pa, while maintaining a high vacuum in the region of the gun. The energy of the electron beam was 20 kV, the electron probe current was aproximately 300 pA, and a four-quadrant backscattered detector was used for analysis.

Table 1. Characteristics of the samples used in this work

Sample no.	PVC/PMMA (1:1) + PEG [wt.%]	PVC/POM (1:1) + PEG [wt.%]
1	0	
2	0.5	
3	2.0	
4	5.0	
5	10.0	
6		0
7		0.5
8		2.0
9		5.0
10		10.0

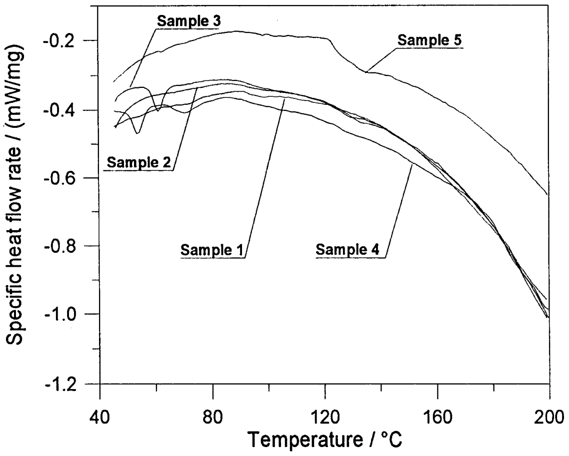


Fig. 1. DSC scans of samples 1–5.

3. Results and Discussion

3.1. PVC/PMMA blends

DSC results of PVC/PMMA blends modificated with PEG are presented in Fig. 1 It can be seen that the T_m of PEG is located in the temperature range of 55–60°C; T_gs of PVC and PMMA are approximately 85 and 110°C, respectively.

An SEM microphotograph shows lamellar arrangements of the microcrystallites - Fig. 2. Such highly

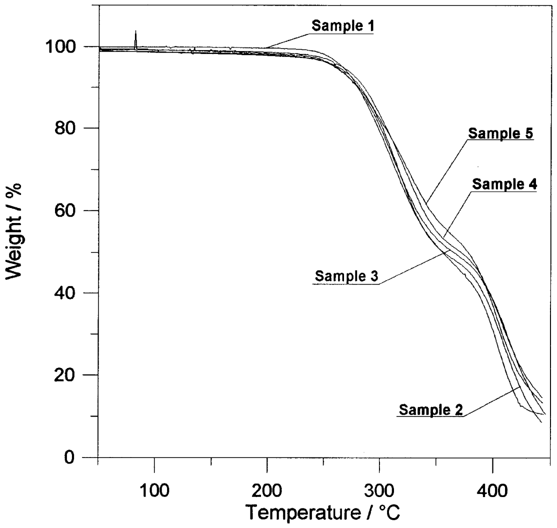


Fig. 3. TG curves of samples 1–5.

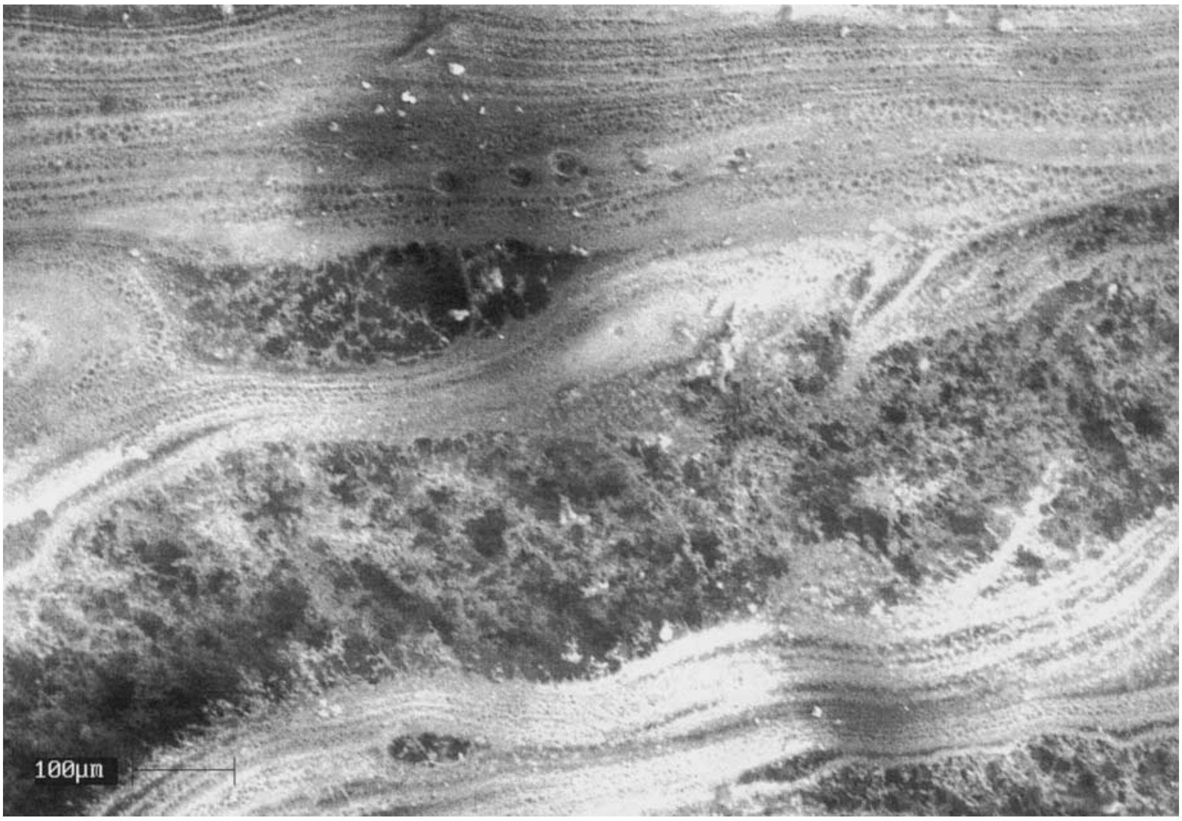


Fig. 2. SEM microphotograph of sample 3.

developed folded surface morphology is more stable against the degradation process than completely disordered parts. A similar effect is often observed in the case of photodegradation, which is believed to start preferentially in the amorphous part, and then the crystalline region is ultimately degraded [17].

Thermal stability studies performed on the basis of TG measurements show that the initial decomposition temperature is approximately 250°C, and the degradation profiles are generally of a similar, two-step type—Fig. 3.

A volatile products emission profile, obtained by the Gram–Schmidt orthogonalization, indicates a single maximum after 7.93 min (Fig. 4a), and the composition of the vapour phase can be identified by FTIR analysis (Fig. 4b). The intensity of volatile products evolution is lower than for pure PVC/PMMA blends [18]. Absorption bands at ~2960, 2470, 1750, 1200 and 920 cm^{-1} can be attributed to the vibration frequencies of HCl, CO_2, C═O, C—O and CH groups, respectively.

Structural hierarchy of PVC, which consists of agglomerates, primary particles, domains and

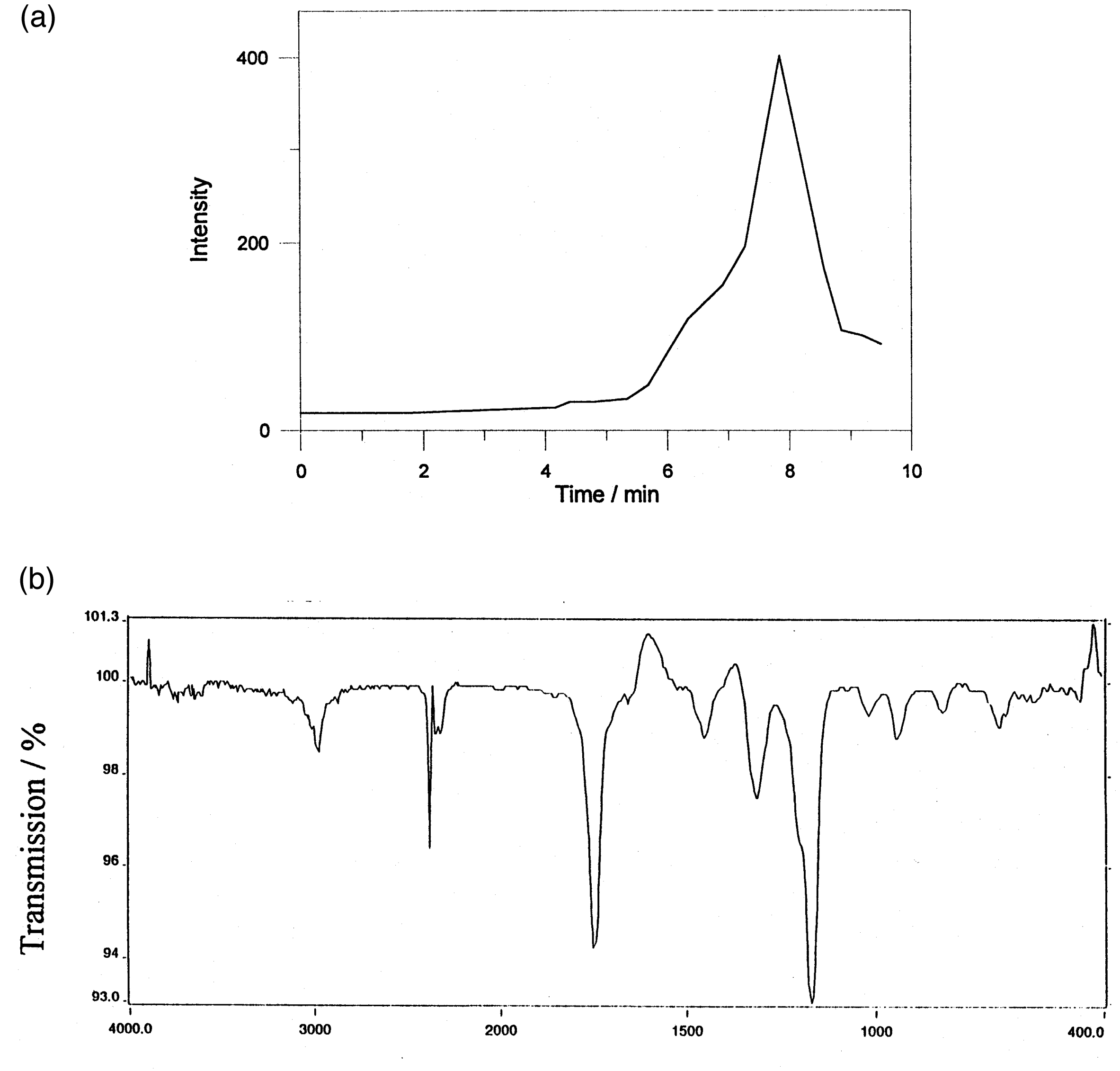


Fig. 4. A Gram–Schmidt chromatogram of sample 4. (b) FTIR spectrum of sample 4 after 7.93 min.

microdomains [19, 20], governs the phase structure of PVC blends, since it forms a usually dispersed crystalline phase, thus influencing the system properties on different microstructural levels. Crystalline populations of PVC have been studied by X-ray techniques for both solvent-cast and commercial materials [21, 22]. The model derived from the X-ray analyses elucidates the morphology to some extent, although considerable uncertainty still remains. The presence of crystallinity is accepted by almost all authors, but some have questioned the crystalline percentages as being too high for such an atactic polymer. The crystalline percentages are higher than can be accounted for in terms of crystallization from syndiotactic sequences only. This is the so-called "crystallinity enigma" of PVC, as discussed by Hobson and Windle [23]. The inclusion of isotactic chains that can emulate the syndiotactic conformation in otherwise syndiotactic crystals, has been proposed as an explanation for the higher than calculated crystallinities obtained for PVC. The pseudosyndiotactic conformation closely resembles the planar zig-zag of the normal syndiotactic chains and has an axial repeat distance within 0.3% of the syndiotactic repeat distance. Recent developments in high resolution transmission electron microscopy (HRTEM) with digital image analysis, has confirmed the microdomain model of crystallinity in PVC, with both fringed micelle and folded-chain crystals similar to those found in stretched PVC gels [24].

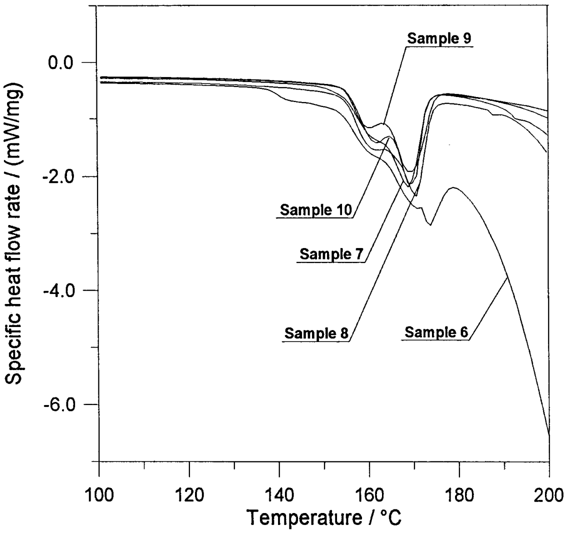


Fig. 5. DSC scans of samples 6–10.

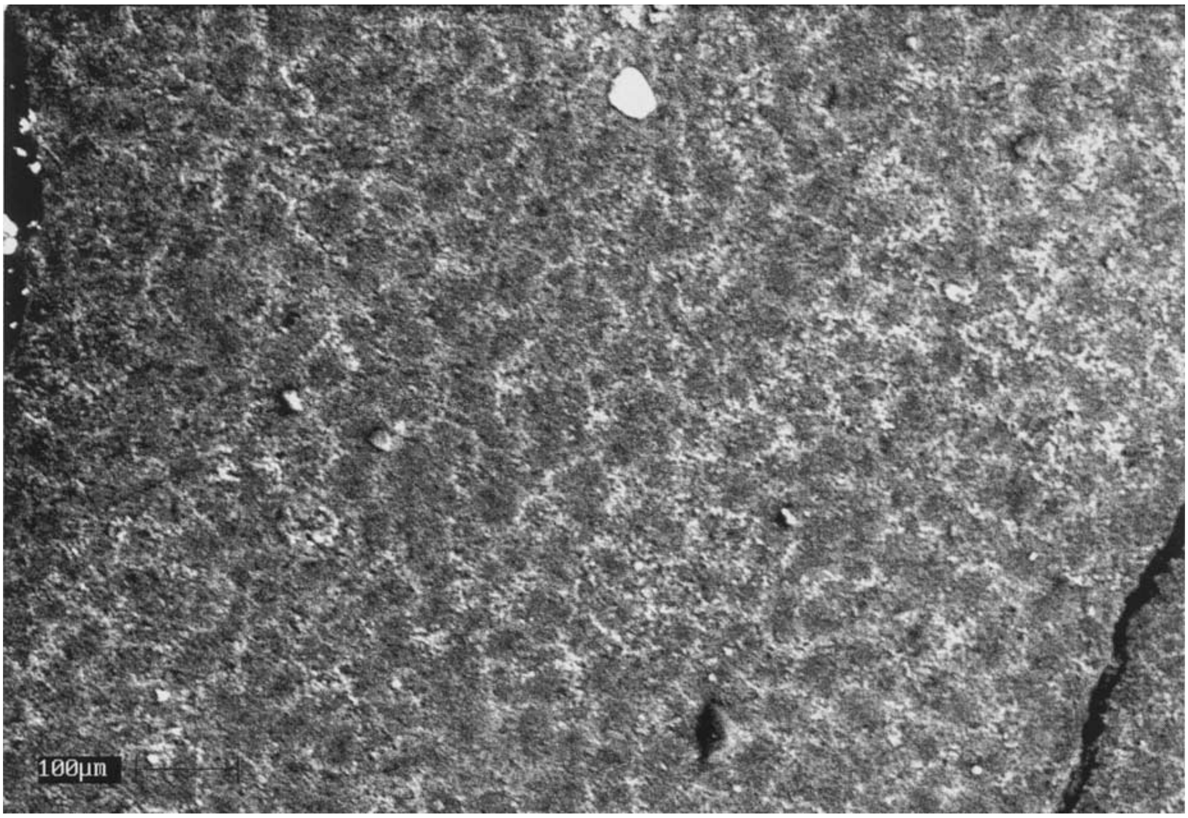


Fig. 6. SEM microphotograph of sample 8.

3.2. PVC/POM blends

PVC/POM modificated by PEG were first analysed by DSC. The melting transitions have been found to occur in the 150–180°C temperature range—Fig. 5. The surface microstructure, as revealed by the SEM technique, can be described in terms of a dense uniform network with no cracks—such a structure can be relatively highly resistant towards decomposition reactions, since (i) they are mainly localized on the surface, and (ii) the breaking of polymer bonds is usually initiated in irregular structural arrangements (internal defects), such as voids or impurities [25]—Fig. 6.

TGA results show that the initial decomposition temperatures for PEG-modificated blends are higher than for the pure PVC/POM blend (1:1 by weight) by approximately 70°C—Fig. 7. This effect was also confirmed by the TG/FTIR data—the Gram–Schmidt chromatograms show that the maximum of volatile products emission occured after 5.05 min (approximately 1 min later than for the pure PVC/POM blend)—Fig. 8.

Stacked plots in the region of 900–3500 cm^{-1}, depicted in Fig. 9, show the main absorption bands of HCl (2960 cm^{-1}) and C=O (1750 cm^{-1}).

The stabilizing action of PEG on the PVC/POM blend can be explained by analysis of the decomposition routes at an elevated temperature. It is well known that PEG decomposes mainly via a radical mechanism, because the high strains at the chain folds of the lamellar structure lower the activation energy of hydrogen abstraction [16]. Main products of the thermal degradation of PEG are low molecular weight esters, including formic esters. The mechanism of ester formation can be summarized as follows [26]:

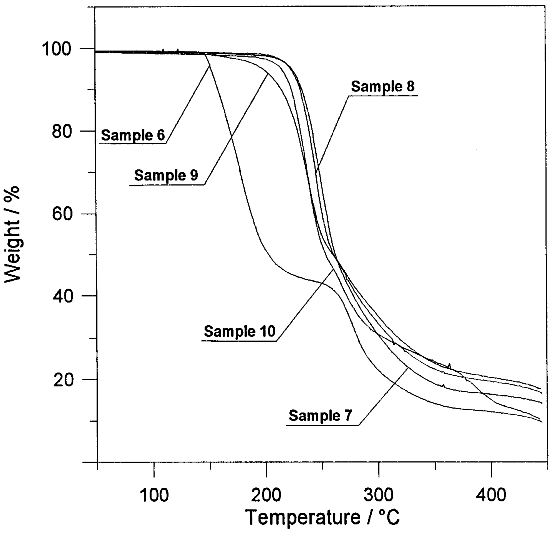


Fig. 7. TG curves of samples 6–10.

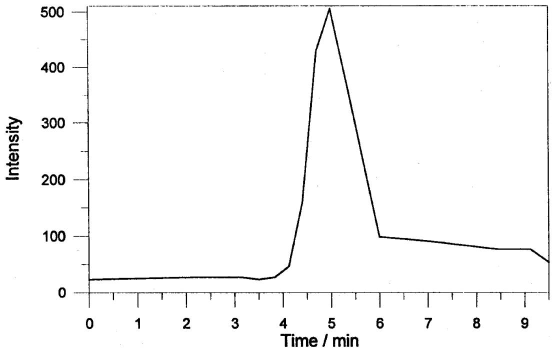


Fig. 8. A Gram–Schmidt chromatogram of sample 8.

1. PEG reacts with oxygen during polymerization, processing or storage to form α-hydroperoxide:

$$-O-CH_2-CH_2-O-CH_2- + O_2 \longrightarrow -O-CH_2-(COOH)H-O-CH_2-$$

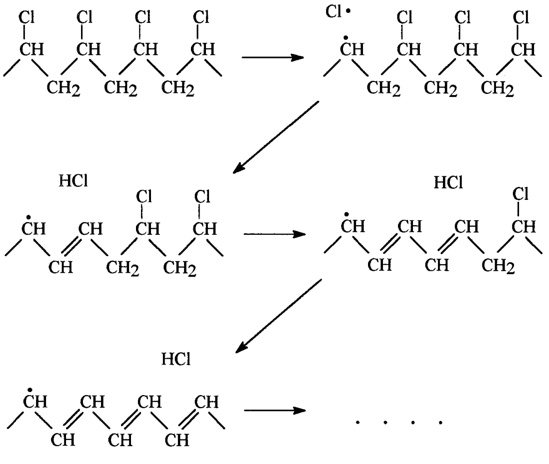
2. This peroxide is expected to be thermally labile; it decomposes according to a radical mechanism:

$$-O-CH_2-(COOH)H-O-CH_2 \longrightarrow -O-CH_2(CH)O^{\cdot}-O-CH_2- + OH$$

3. Esters are produced as the thermal degradation end-products

$$-O-CH_2-(CH)O^{\cdot}-O-CH_2- \longrightarrow -O-CH_2-CHO + O^{\cdot}-CH_2-$$

Peroxide radical or a PEG radical formed in the chain breaking cycle can anihilate PVC macroradicals formed, initially through C–Cl bond scission and then via a propagation stage with hydrogen abstraction from an adjacent C-atom [27, 28]—Scheme 1



Scheme 1. Radical decomposition scheme of PVC.

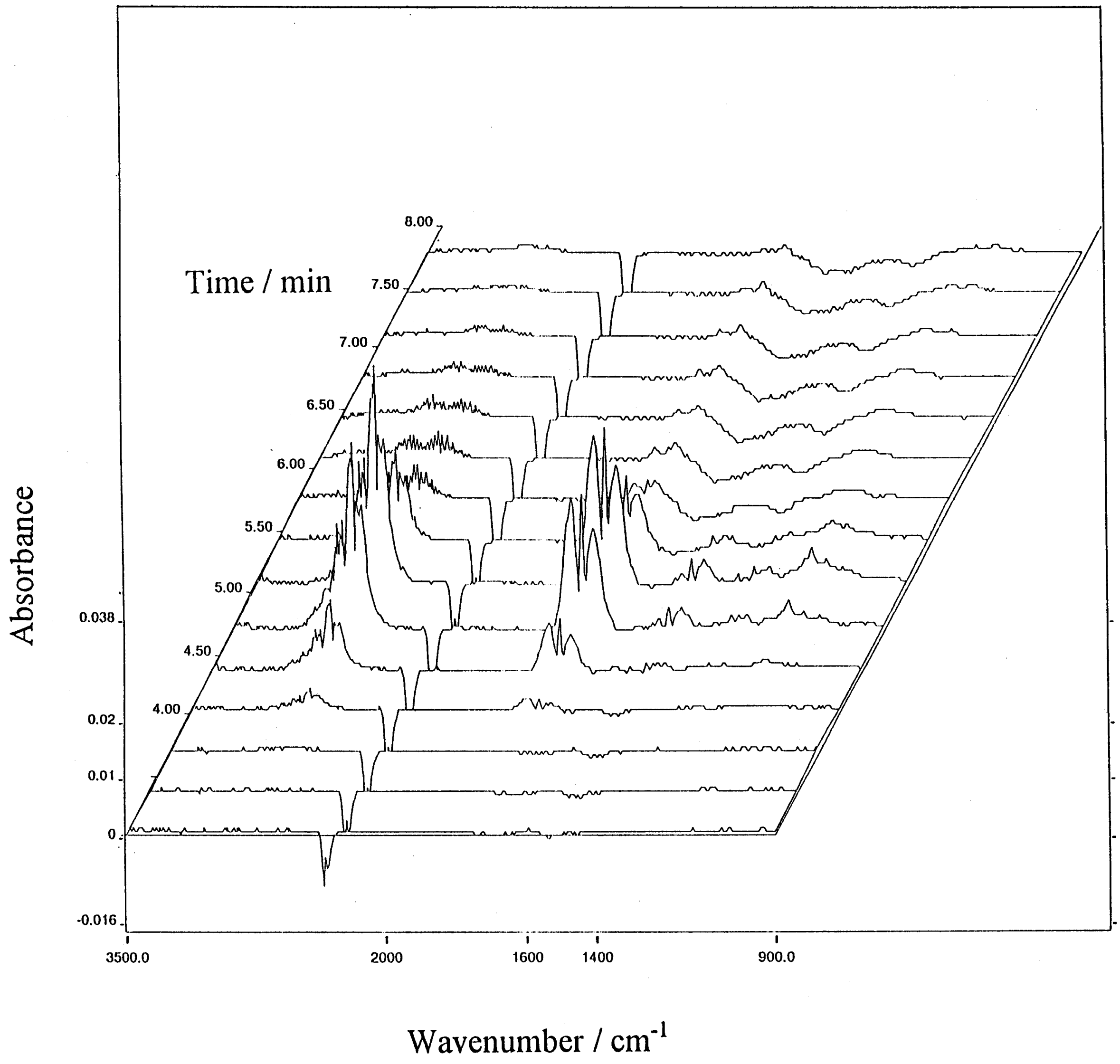


Fig. 9. Stacked plots of FTIR spectra of sample 8 from 3.00 to 8.00 min.

This intramolecular process is stopped when recombination with an other radical takes place. The other reason for greater thermal stability is connected with structural arrangements of the blend, as it was also observed in the case of other PVC blends [29]. When semicrystalline polymer is mixed with amorphous, or with an other semicrystalline polymer, the misfit of packing because of different chemical structures causes an increase in free volume, and thus favours the formation of crystalline regions, which in turn are thermally more stable due to the dense microstructural orientation.

4. Conclusions

Poly(ethylene glycol) was added to PVC/PMMA and PVC/POM blends to improve the thermal properties of these systems containing polymers of commercially primary importance. As was assumed through the analysis of possible interactions between PEG and PVC structures on different microstructural levels, a stabilization effect leading to an improvement of surface morphology, increase of initial decomposition temperature, and suppression of low molecular volatile products emission for PVC blends, is observed. These observations may further be utilized for multicomponent PVC systems to enhance their heat performance.

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