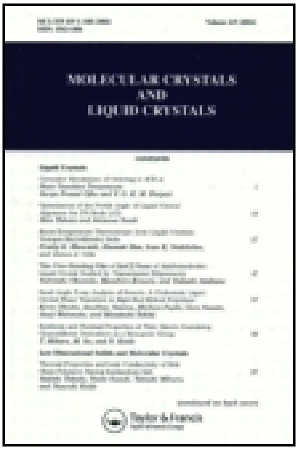

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Photostability of Poly(Vinyl Chloride)/Poly(Vinyl Alcohol) Blends

Halina Kaczmarek [a] & And Podgórski [a]

[a] Faculty of Chemistry, Nicolaus Copernicus University, Toruń, 87-100, Poland

To cite this article: Halina Kaczmarek & And Podgórski (2004): Photostability of Poly(Vinyl Chloride)/Poly(Vinyl Alcohol) Blends, Molecular Crystals and Liquid Crystals, 416:1, 223-228

To link to this article: http://dx.doi.org/10.1080/15421400490482916

Mol. Cryst. Liq. Cryst., Vol. 416, pp. 223/[479]–228/[484], 2004

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490482916

PHOTOSTABILITY OF POLY(VINYL CHLORIDE)/POLY(VINYL ALCOHOL) BLENDS

Halina Kaczmarek and Andrzej Podgórski*
Faculty of Chemistry, Nicolaus Copernicus University, Gagarin 7,
87-100-Toruń, Poland

Photooxidative degradation and photocrosslinking of poly(vinyl chloride), poly(vinyl alcohol) and their blends with different components ratio has been investigated in accelerated laboratory conditions. It was found that PVC is less photostable than PVAL, in which the photocrosslinking is more efficient. The PVC/PVAL blends have higher photostability comparing to pure PVC but they were less photostable than PVAL alone.

Keywords: photocrosslinking; photooxidative degradation; photostability; polymer blends; poly(vinyl alcohol); poly(vinyl chloride); PVAL; PVC

INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the most extensively investigated polymers since many years. Recently its new applications, possibilities of using of PVC as a component in the blend or modification by other substances for the purpose of obtaining new materials with desired physical properties appeared [1–4].

Most of polymer blends are immiscible on molecular level. Such components form heterogeneous, domain structure dependent on fraction of one component in the matrix of second one. Some specific interactions between different macromolecules can cause partial diffusion of chains on phase boundary. These interactions are dipole–dipole, hydrogen-bonding, van der Waals, charge transfer and hydrophobic interactions. Strong forces (Coulombic or hydrogen bonds) usually enhance miscibility or leads to

Financial support from the Polish State Committee for Scientific Research (KBN; grant No 3 T09B 088 18) is gratefully acknowledged.

Address correspondence to Halina Kaczmarek, Faculty of Chemistry, Nicolaus Copernicus University, Gagarin 7, 87-100-Toruń, Poland. E-mail: halina@chem.uni.torun.pl

polymer complexation [5]. However, even the weak interactions (hydrophobic or dipole–dipole) influence the properties of composition.

The photochemical stability of polymer blends is difficult to predict on the base of photoresistance of pure components. In some compositions, the acceleration of photodegradation has been observed, while in some others – common stabilization effect has been found. It has been also shown that additivity rule is not applied in case of photostability of some blends [6–8].

The aim of our work was the investigation of photooxidative degradation of poly(vinyl chloride)/poly(vinyl alcohol) (PVC/PVAL) blends in accelerated conditions.

EXPERIMENTAL

PVC/PVAL blends with whole range of composition (from 100/0 to 0/100 weight ratio) were prepared by solution casting. N,N-dimethyloformamide (pure for analysis) was a common solvent. Thickness of polymer films obtained after solvent evaporation was 10–25 μm. The samples were irradiated by a low-pressure mercury vapor lamp TUV30W (Philips) emitting radiation of $\lambda = 254$ nm.

The course of photooxidative degradation was monitored by UV-Vis and FTIR absorption spectroscopy using UV-1601PC Spectrophotometer (Shimadzu, Japan) and FTIR Genesis II (Mattson, USA), respectively. On the base of absorption spectra, the changes in the amount of functional groups during UV-irradiation were estimated.

Insoluble gel containing crosslinked polymer was separated from soluble part, dried and weighted.

RESULTS AND DISCUSSION

FTIR spectra analysis showed that formation of carbonyl groups during UV-irradiation is very efficient in pure PVC (Fig. 1). In PVAL, the changes in carbonyl range are negligible and rather the decrease of C=O amount is observed. It indicates that residual carbonyl groups always present in PVAL (which is obtained by hydrolysis of polyvinyl acetate) are destroyed upon UV. In PVC/PVAL blends the amount of C=O groups is lower than it can be predicted on the base of additivity rule. It indicates that photooxidation leading to C=O generation is somewhat hampered in the blends.

Fast photooxidation of PVC leads also to formation of hydroxyl and hydroperoxide groups (Fig. 2). However, UV-irradiation causes the efficient destruction of PVAL connected with OH abstraction, thus it is

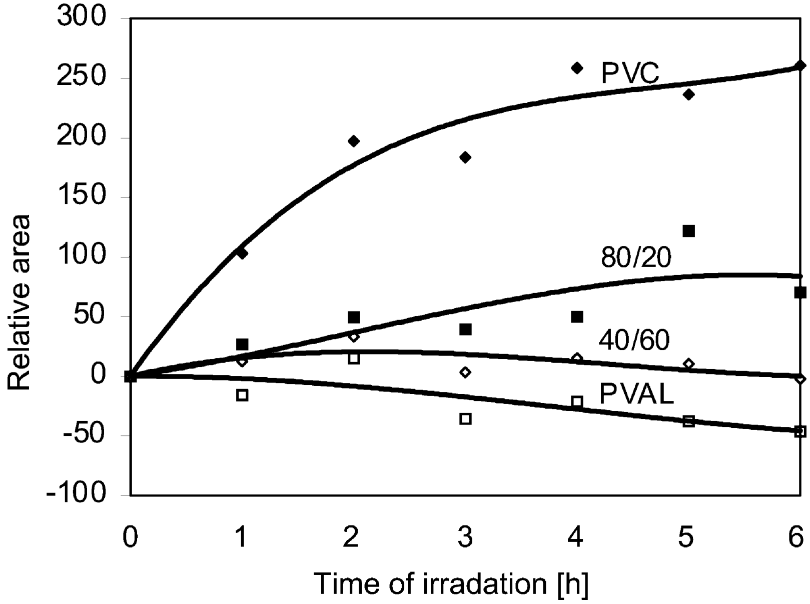

FIGURE 1 The changes in carbonyl groups amount in PVC, PVAL and PVC/PVAL blend (40/60 and 80/20) during UV-irradiation estimated from FTIR spectra (relative area = changes of integral intensity calculated as area of carbonyl peak at 1650–1800 cm^{-1} range).

difficult to draw conclusion for PVC/PVAL blends on the base of changes in OH amount. It can be seen that addition of PVAL to PVC impedes hydroxyl groups formation, however, the abstraction of these groups in PVAL is more efficient in the presence of PVC.

UV-Vis spectra supply the data about PVC photodehydrochlorination which is accompanying by the double bonds and/or polyenes formation. This process is efficiently accelerated in PVC containing PVAL (Fig. 3). These observations are supported by the decrease of absorbance due to C–Cl bonds in FTIR spectra (bands at 690, 635 and 610 cm^{-1}) in exposed PVC samples. The reason of higher efficiency of polyenes formation in PVC in the blends can be explained by mutual interaction between active species formed during UV-irradiation in both polymers. For example, small mobile $HO^{\bullet}$ radicals formed in PVAL can easy penetrate to PVC matrix and initiate its dehydrochlorination, which is a zip reaction.

Simultaneously photocrosslinking occurs in both polymers resulting of macroradical recombination (Fig. 4). PVAL is more susceptible for this process (leading to insoluble gel formation) than PVC. PVAL sample is almost completely crosslinked just after 1 h of exposure, while the amount

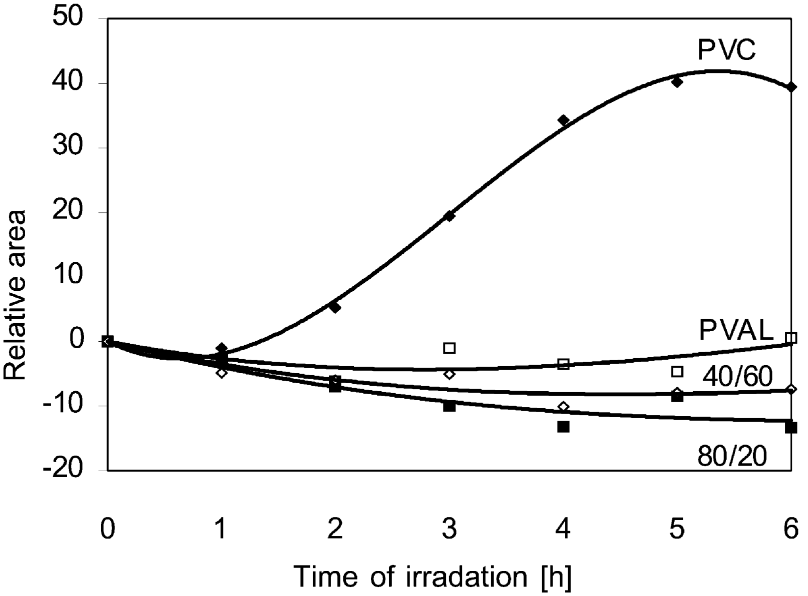

FIGURE 2 The changes in hydroxyl/hydroperoxide groups amount in PVC, PVAL and blend PVC/PVAL blend (40/60 and 80/20) versus irradiation time estimated from FTIR spectra (relative area = changes of integral intensity calculated as area of hydroxyl peak at 3085–3600 cm^{-1} range).

of gel in pure PVC does not exceed 50% after 6 h UV-action. Small decrease of gel amount after different exposure periods in some samples (e.g. in PVAL or in 50/50, 40/60 PVC/PVAL blends) reveals that degradation with chain scission occurs simultaneously.

CONCLUSIONS

It was found that both polymers differ their photochemical properties. PVAL is more resistant to UV-irradiation than PVC, which undergoes fast photo-oxidative degradation even after short irradiation time. However, the efficiency of photocrosslinking is significantly higher in pure PVAL than that in PVC alone.

The PVC/PVAL blends were characterized by higher photostability comparing to pure PVC but they were less photostable than PVAL.

The course of photodecomposition of PVC/PVAL blends depends on their composition as well as on interactions between components and products of their degradation.

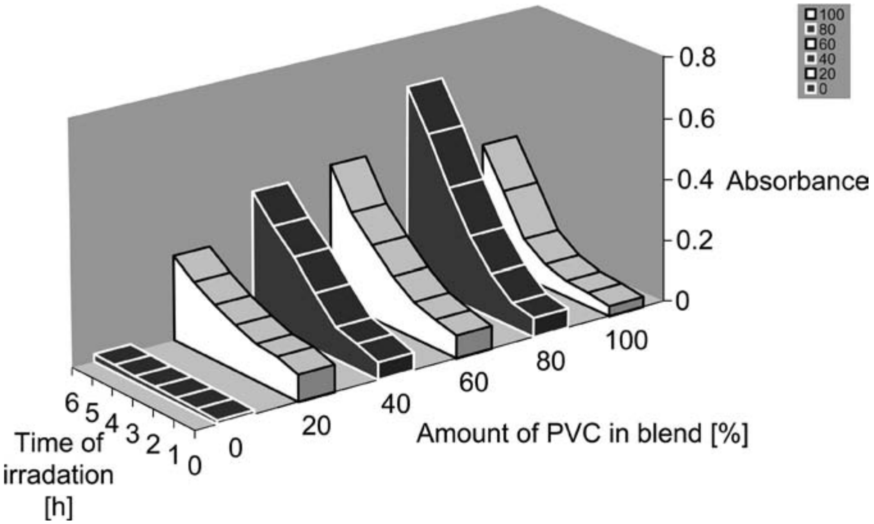

FIGURE 3 The formation of unsaturated groups in PVC and its blends with PVAL during UV-irradiation estimated from UV-Vis absorption spectra (values of absorbance at 425 nm corresponding to 9 conjugated double bonds are on ordinate axis).

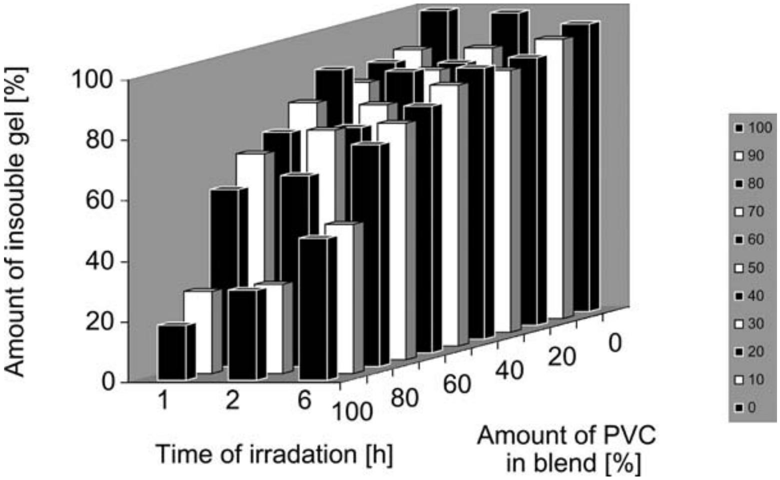

FIGURE 4 The amount of insoluble gel formed as a result of photocrosslinking in PVC, PVAL and PVC/PVAL blends versus irradiation time and sample composition.

REFERENCES

[1] Birer, Ö. & Süzer, S. (2001). UV-induced acid-base chemistry within the PVC matrix. *Polymer*, *42*, 1833–1835.

[2] Marentette, J. M. & Brown, G. R. (1998). The crystallization of poly(ethylene oxide) in blends with neat plasticized poly(vinyl chloride). *Polymer*, *39*, 1415–1427.

[3] Pielichowski, K. (1999). Thermal energy storage systems based on poly(vinyl chloride) blends. *Eur Polym J.*, *35*, 27–34.

[4] Torikai, A. & Hasegawa, H. (1999). Accelerated photodegradation of poly(vinyl chloride). *Polym Deg Stab.*, *63*, 441–445.

[5] Jiang, M., Li, M., Xiang, M., & Zhou, H. (1999). Interpolymer complexation and miscibility enhancement by hydrogen bonding. *Adv Poly Sci.*, *146*, 121–196.

[6] Kaczmarek, H. & Decker, C. (1995). Photodegradation of polystyrene and polymethylmethacrylate blends. *Polym. Networks Blends*, *5*, 1–10.

[7] Kaczmarek, H., Szalla, A., & Kamińska, A. (2001). Study of poly(acrylic acid)-poly(vinylpyrrolidone) complexes and their photostability. *Polymer*, *42*, 6057–6069.

[8] Kaczmarek, H., Drag, R., Świątek, M., & Ołdak, D. (2002). The influence of UV-irradiation on poly(vinyl chloride) modified by poly(vinyl acetate). *Surf Sci.*, 507–510, 877–882.