Polymer Bulletin 13, 301-306 (1985)

Polymer Bulletin

Compatibility

Study of the Compatibility in the Poly (Vinyl-Chloride) -Poly (Vinyl-Alcohol) System

Silvia Paţachia[1], Cornelia Vasile[2] and E. Mavru[2]

[1] Chemical Enterprise, Rîşnov, 1, Cîmpului Str., R-2221 Risnov, Brasov County, Romania
[2] Institute of Macromolecular, Chemistry "P. Point", R-6600 Iasi, Iasi County, Romania

Summary

Although poly (vinyl-chloride) - PVC - and poly (vinyl-alcohol) - PVA - mixtures are used in practice for coatings, containers, fibers, few studies are encounterd concerning their compatibility (7, 8).
This paper establishes both the optimum compatibility ratio and the thermal behaviour of the mixtures.
The compatibility study in solid state was realised using the methodes: optical microscopy, thermogravimetry, DSC, inverse gaschromatography and IR spectroscopy.

EXPERIMENTAL

Materials. PVC was obtained by suspension polymerization. The molecular weight is $M_w = 57.ooo$.

PVC was purified by extraction with petroleum ether, for eight hours in a Soxhlet apparatus.

PVA was obtained by the basic hydrolysis of poly (vinyl acetat).
Two PVA samples were used. The PVA_1 - (the first sample) has a polymerization degree of 16oo, the PVA_2 - (the second sample) of 5oo. Both samples have the same hydrolysis degree 98%.
Mixture films, with mixture ratio of 1o/9o; 3o/7o; 5o/5o; 7o/3o; 8o/2o were obtained by polymer solubilisation in dimethyl sulfoxide (DMSO) - common solvent.
A 1o% polymer mixture solution was deposed in thin layers on glass lamella. The solvent was evaporated at $6o^o$-$7o^oC$. The so obtained films were extracted with methanol to eliminate last solvent traces.

Investigation methodes. The compatibility study in solid state was realised with the following methodes: optical microscopy, thermogravimetry, DSC, inverse gaschromatography and IR spectroscopy.
The microscopic examination of the films was executed using an IOR MC-1 microscop, in phase contrast, magnification 4oo.
Recording conditions for TG curves were: MOM Budapest derivatograph,

heating rate 1o°C/min., polymer sample weight for decomposition was of 2o mg.

The polymer mixtures were obtained by precipitation from common solution with a mixture of 4o% methanol, 4o% acethone and 2o% ethanol .

From TG curves the temperatures for different weight losses were determinated.

Activation energy of the first thermal decomposition (2oo-37o°C) step, was calculated using the Freeman - Carroll (3) method.

The experimental errors were appreciated with the least squares method.

DSC curves were recorded with a Perkin - Elmer DSC2 using a heating rate of 32°C / min and polymer weight of 2o mg. From these curves, were evaluated the glass transition temperatures (T_g) and those of the decomposition.

T_g values were compared with those obtained by inverse gaschromatography, according to Guillet's method. (5).

Chromatographic columns were prepared in the following way: pure polymers and polymer mixtures in DMSO solution were deposed on the W Chromosorb by continuously agitation.

After solvent evaporation and vacuum drying, a chromatographic column with 1,52 m in lenght and 4 mm in the interior diameter was filled.

The chromatographic columns were activated by heating in an inert gas (Argon) stream.

Toluen was used as "molecular probe".

The variation of the toluen retention time, log t_R , versus reciprocal temperature was recorded.

The glass transition temperature, T_g, was determined by the inflexion point of these curves.

For pure polymers T_g data were compared with literature values.

The concordance was satisfactory: $T_{g,PVC} = 78^{o}C$, $T_{g,PVA} = 6o,4^{o}C$ (1)

IR spectra were recorded with the Perkin-Elmer spectrometer 625 on films of aproximative constant thickness of o,o2 mm. For optical density comparison of the 332o cm^{-1} (O-H) and 61o cm^{-1} (C-Cl) bands, internal standards bands in polymer mixtures were used. These are 295o cm^{-1} and 2895 cm^{-1} bands and 63o cm^{-1} and 69o cm^{-1} bands respectively.

RESULTS AND DISCUSSIONS

Microscopic aspect of pure and mixture polymers films are presented in Fig.1.

It may easily be noted that for mean mixture ratios the phase separation is clear. The extreme mixtures look like an advanced dispersion.

The thermodynamic incompatibility is evident.

Consequently, the time coexistence in relatively homogenous mixtures should be conditioned only by the limit phase interactions.

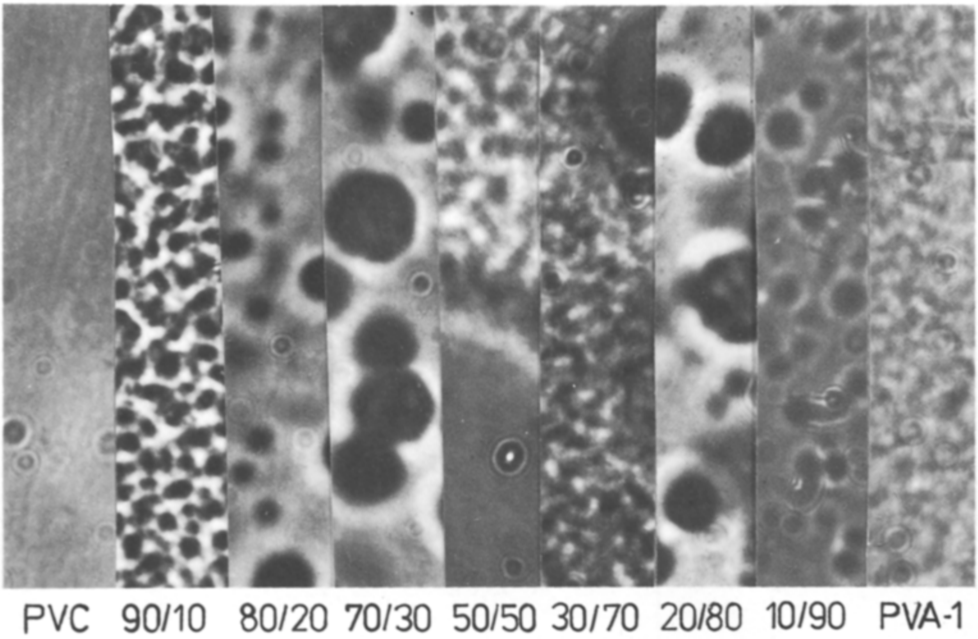

Fig.1. Microscopic aspects of PVC, PVA, and their mixtures in different ratios, Magnification 4oo.

The existence of these interactions is emphasized by the thermal characteristics modifications, as presented in Tab.1.

It may be remarked that mixtures with 7o% - 2o% PVA and 3o% - 8o% PVC show two thermal decomposition processes in the same temperature range. The temperatures corresponding to the maximum reaction rate are different from those of the pure components or from those calculated by additivity rule. The experimental weight losses are smaller in all cases. The diminution may be caused by some cross-linking reactions along with the dehydroclorination of PVC or the dehydration and degradation of PVA.

Generally, the mixtures show multiple glass transition temperatures smaller than T_g of pure components.

By inverse gaschromatography, which is more sensible than the other methods, a suplimentary glass transition temperature T_g, observed at smaller temperature.

This may be caused by the chain segment movements in the interphasic range where the mobility is higher. (4)

The compatibility diagram including the two coordinates: activation energy - for the first thermal decomposition step - and composition (Fig.2), evidences the fact that the components present a pseudocompatibility caused by the functional groups interactions for 9o% - 6o% PVA_1 and 1o% - 4o% PVC. The pseudocompatibility range for a PVA with a smaller molecular weight extends up to 4o% PVA_2 - 6o% PVC.

TABLE 1

Thermal characteristics of PVC/PVA mixtures.

SAMPLE	T_m, DTG (°C) exp.	T_m, DTG (°C) calc.	w(%) exp.	w(%) calc.	T_g, DSC (°C)	Tg, CI (°C)
1. PVA_2	253	-	59	-	59	59
2. 90% PVA_2/10% PVC	250	258	35,8	59,28	55;80	52;62;71
3. 80% PVA_2/20% PVC	252	263	44,34	59,52	59;82	41;55;64
4. 70% PVA_2/30% PVC	266;303	268	42,04	59,78	59;81	-
5. 50% PVA_2/50% PVC	249;318	278	49,79	60,29	58;79	40;68
6. 30% PVA_2/70% PVC	258;312	288	48,69	60,82	56;82	-
7. 20% PVA_2/80% PVC	262;318	293	55,0	61,08	57;82	27;47
8. 10% PVA_2/90% PVC	335	298	51,87	61,34	59;73	47;55;73
9. PVC	303	-	61,59	-	84	78

CI - inverse gaschromatography

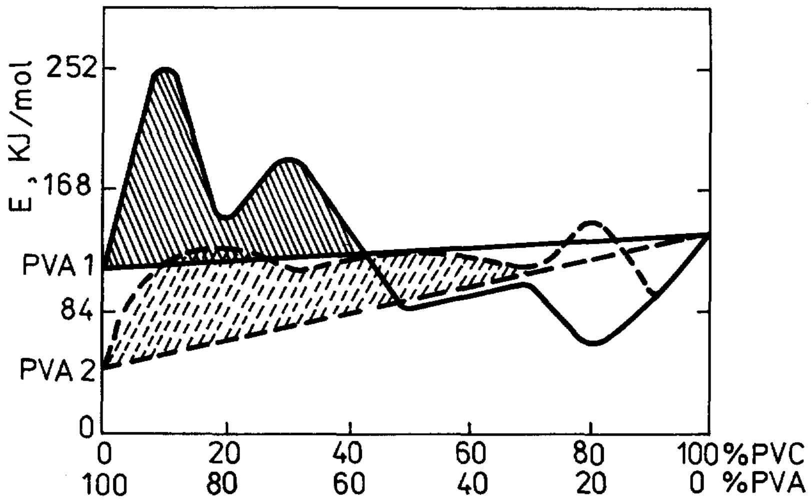

Fig. 2. Compatibility diagram for PVC/PVA system.

Functional groups interactions were evidence by IR spectroscopy for the mixture ratios mentioned above.
The optical densities have more different values than those evaluated if the independent behaviour hypothesis of the components would be observed.

CONCLUSIONS

1. From a thermodynamic point of view PVC/PVA mixtures are incompatible.

2. In 9o% - 5o% PVA - 1o% - 5o% PVC composition range a pseudo-compatibility caused by functional groups interactions appears, conferring the mixture some improved properties. Among these properties we mention: the increasing thermal stability along with the lowering of the glass transition temperatures.
This fact indicates a possibility for an easier processing.

3. At high temperatures, the components interact forming cross-linking structures.

REFERENCES

1. J.BRANDRUP, E.H.IMMERGUT, Polymer Handbook, Intersci. Publ., John Wiley and Sons, N.Y. London. Sydney, 1966.

2. J.B.CLARK, Polym. Eng. Sci. 7137 (1967); T.N.KALININA ; G.N.AFANAS EVA, L.A.VOLF, A.I.MEOS, E.B.KREMER, S.JA FRENKEL and S.S.MNATSAKANOV, Vîsokomol. Soedn. B-12, 661 (1970).

3. E.S.FREEMAN and B.CARROLL, J.Phys.Chem.62, 314 (1958); 73, 751 (1969).

4. YU K. GODOVSKII, N.P.BESSONOVA, Vîsokomol. Soedn. A-XXI (10) 2293 (1979).

5. J.E.GUILLET, J.Macromol. Sci. Chem. 4,1669, (1970) Macromolecules 3, 102, (1970).

6. S.A. JOBST and J.A.MANSON, ACS Preprints 11, 765 (1970); S.C.TEMIN, J.Appl. Polym.Sci. 9, 471 (1965).

7. J.C.Mc NEILL, N.GRASSIE, J.N.R. SAMSON, A.JAMIESON and T.STRAITON, J.Macromol.Sci.Chem. A-12 (4) 503 (1978).

8. SAKATO MAOGUKI and NAKAMURA HIDETOSHI, Japan Kokai 78-61705 (C1D21 H1/40) 1978; CA 89-131426.
ATO - Chemie S.A,Japan Kokai 78-73246 (C1 C08L27/07) (1978); CA 89-111648.
T.OSUGI - Polyvinylalcohol Fibers, Man Made Fibers Sci. Technol., Ed.H.F.Mark, S.M.Atlas and E.Cernia, Interscience Publ., New York, 1968, Vol.3.p.245.

Accepted March 14, 1985