Macromol. Symp. ***176,*** *39–48 (2001)*

Stabilizing Action of Polymeric Plasticisers in PVC

*G. Maura - G. Rinaldi**

Dipartimento di Ingegneria Chimica, dei Materiali, delle Materie Prime, Metallurgia - Universita` di Roma La Sapienza, Via Eudossiana 18 - 00184 Roma, Italy
rinaldi@ingchim.ing.uniroma1.it

Summary: Polymeric plasticisers gained considerable success in PVC formulations in the early eighties and there are now several manufacturers of plasticising additives based on polymeric compositions in the USA. The good performance of these additives has been considered in the technical literature. For epoxy polymeric plasticisers, an improvement of heat and U.V. stability was also observed as a function of the oxirane oxygen content in formulations. In this paper we refer to some experimental tests on thermal and U.V. light stabilising action of linear low molecular polyesters, based on glycols and dibasic aliphatic acids, which possess a good plasticising effect and low toxicity. Creep tests and calculations of isochronous creep modulii were used to evaluate the stability of PVC formulations.

Introduction

The compounding of PVC essentially involves adding to the base PVC-resin some additives (plasticisers, stabilisers, lubricants, fillers, colorants, etc.) that will allow it to be processed into a finished product with the desired properties. Adding the correct type and amount of plasticiser, stabiliser, etc., results in a compounded mixture that can be processed, subsequently, on properly designed equipment into a satisfactory finished product with good performance.

The theory of PVC degradation and stabilisation mechanisms has been developed[1-6] over the years. PVC resin is inherently the most heat-sensitive of the major commercial thermoplastic resins, yet virtually all vinyl compounding and fabrication techniques require the application of high temperature and shear; the fabricated articles are subjected further to varying degrees of heat and aging during service. Consequently, all PVC compounders must use heat stabilisers.

When a stabiliser is incorporated in a PVC formulation, it can affect many of its properties, e.g. physical properties, chemical and radiation resistance, electrical, optical, rheological and toxicological properties, processability and mechanical behaviours; The search for the "perfect" stabiliser continues to be conducted mostly along a variation theme of the primary generic stabiliser types.

CCC 1022-1360/00/$ 17.50+.50/0

Some studies and applications concern the use of polymeric plasticisers as stabilising additives. Their advantages over the "oligomeric" products are their lower degree of volatilization and extraction: the polymeric materials are essential to avoid the loss of the plasticizer from finished articles; it also lowers the melt viscosity of the polymer (and increasing its workability), permitting the use of lower processing temperature (due to plasticising action) and with reduced rates of thermoxidative degradation, hence contributes indirectly to overall stabilisation.

The most useful polymeric plasticising agents[1-4-6] are the linear low molecular polyesters (above all for their low toxicity) and the epoxidized low molecular products (more advantageous for their action against thermal and U.V. attack from the environment). The epoxies could be considered as plasticizers, as well as stabilizers, with considerable savings in cost.

In this paper we refer of some experimental tests on thermal and ultra - violet light stabilising action of polymeric plasticisers like unsaturated linear polyesters and epoxies (cured and uncured).

Experimental

Materials - Polyvinylchloride B.D.H. (K = 70; Mn = 65000; porosity 25%) was used. Plasticising polymers: 1) the epoxy resin, a commercial product (Shell EC57), specific gravity (20°C) 1160 kg/cum, mean molar mass 380, epoxide equivalent 190, viscosity (20°C) 0.13 Pa·s ; tetraethylene pentamine (TEPA, B.D.H.) was added in some specimens as curing agent; 2) two types of linear unsaturated polyesters were prepared and used; the first (A) was based on hexanediol and maleic anhydride, the second (B) was a condensation product of ethylene glycol with maleic and phtalic anhydrides (1:1). An "artificial" PVC - reference compound was also employed for the tests: it was obtained from the same PVC B.D.H. (100), compounded with the whole set of additives for the "commercial" formulations: di-octyl-phtalate (30), butyl-benzyl-phtalate (10), di-iso-decyl-phtalate (20), tribasic-sulphate-Pb-phosphite (1,5) and a metal-based (Ba - Cd) stabilising agent (1,0).

Short-term mechanical tests - Specimens for tests were obtained by compression moulding (T = 180°C) without addition of any stabiliser. The formulations were initially prepared by mixing the liquid polymeric plasticiser in a mortar with the PVC powder (Table 1).

Table 1. PVC formulations.

	PVC without stabiliser or plasticiser
A	PVC (60g) + epoxy resin (30g)
B	PVC (60g) + epoxy resin (30g) + TEPA (2.5g)
C	PVC (75g) + polyester A (25g)
D	PVC (80g) + polyester B (20g)
E	Commercial PVC compound

The yield and breaking strength (DIN 53455) and the elastic modulus (DIN 53437) were measured (Table 2).

Table 2. Short-term tensile tests of formulations (Strain rate: 5 mm / min).

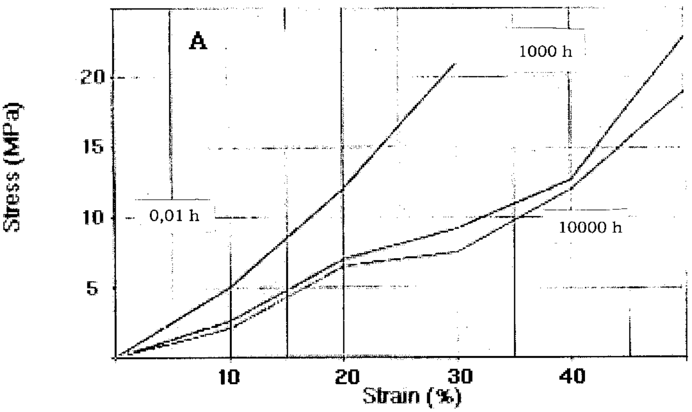
Formulation	Yield strength MPa	Breaking strength MPa	Yielding strain %	Breaking strain %	E (tangential) MPa	E (secant) 5% MPa
PVC + Epoxy	21.4	22.2	17.0	35.0	41.8	37.1
PVC + Epoxy + TEPA	20.0	26.4	2.0	5.0	68.5	57.5
PVC + polyester A	28.0	30.0	7.0	10.0	17.1	12.1
PVC + polyester B	25.0	26.0	5.0	6.0	42.8	36.7
Commercial PVC	6.6	20.8	64.0	312.0	22.4	16.4

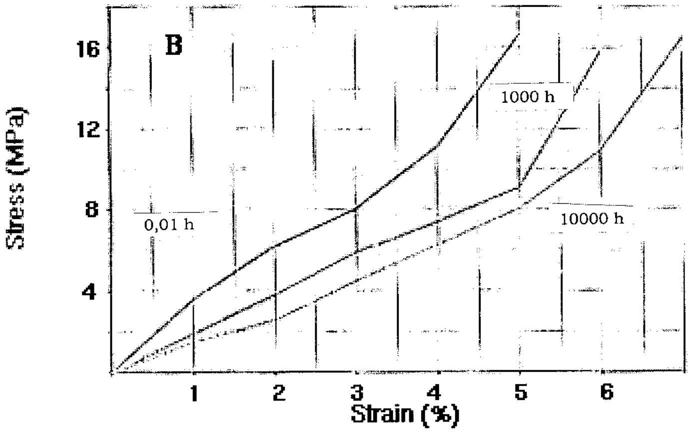
Long-term creep tests - Creep tension tests (DIN 53444) were carried out at 20°C, with different applied stresses (Table 3), up to 1000 hours.

Table 3. Long-term tensile creep tests at 20°C.

Formulation	Constant tensile stress, Mpa			
	σ_1	σ_2	σ_3	σ_4
PVC + Epoxy	3.0	7.1	10.2	14.3
PVC + Epoxy + TEPA	2.9	6.7	9.5	13.3
PVC + polyester A	5.0	9.4	13.5	18.7
PVC + polyester B	4.2	8.3	12.1	16.7
Commercial PVC	2.1	3.1	5.9	-

By assuming a logarithmic creep-strain behaviour of the type[7-8] Strain (t) = B + C·ln t; the creep - strain at 10000 hours was then extrapolated (least squares method). From the creep - strain curves and the extrapolated values, the isochronous curves were finally obtained (Figure 1) and the secant (2%) modulus evaluated (Table 4).





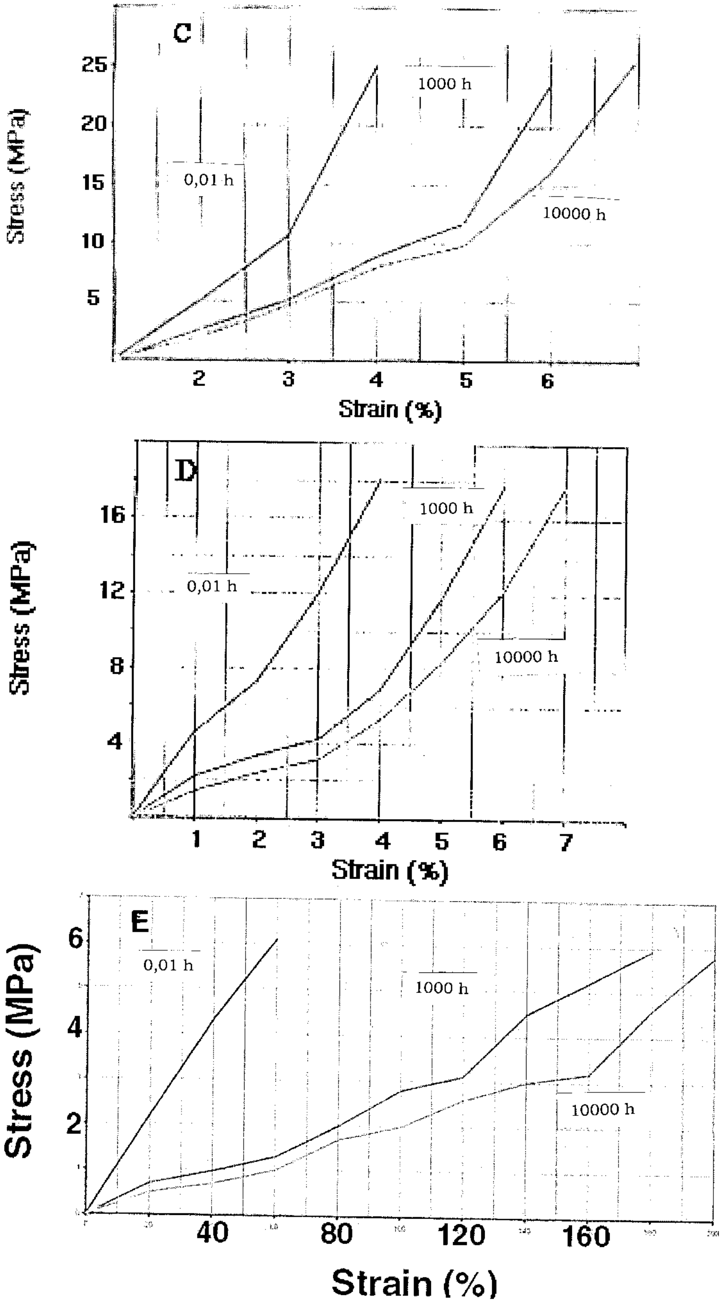


Figure 1. Isochronous curves (20°C) determined from creep tests.
A. PVC + Epoxy resin, B. PVC + Epoxy resin + TEPA, C. PVC + polyester A
D. PVC + polyester B, E. PVC commercial formulation

Table 4. Secant creep modulus (2%) after 1000 and 10000 hours (from the isochronous curves).

Formulation	Applied tensile stress, Mpa (*)	Secant creep modulus, 20°C, Mpa	
		1000 hrs	10000 hrs
PVC + Epoxy	7.1	8.81	6.71
PVC + Epoxy + TEPA	6.7	3.04	2.45
PVC + polyester A	9.4	3.56	2.71
PVC + polyester B	8.3	8.47	6.74
Commercial PVC	3.1	2.50	2.05

(*) Approximately 1/3 of the yield strength

Stabilising Action

The thermo-oxidative "stabilising" action of the polymeric plasticisers was evaluated by means of thermogravimetry. The powdered homogenised formulations(2g), were placed into the porcelain crucible of a thermobalance, then held in air at 250°C. The weight loss (+/- 0,1 mg) was registered up to 20 minutes (Figure 2).

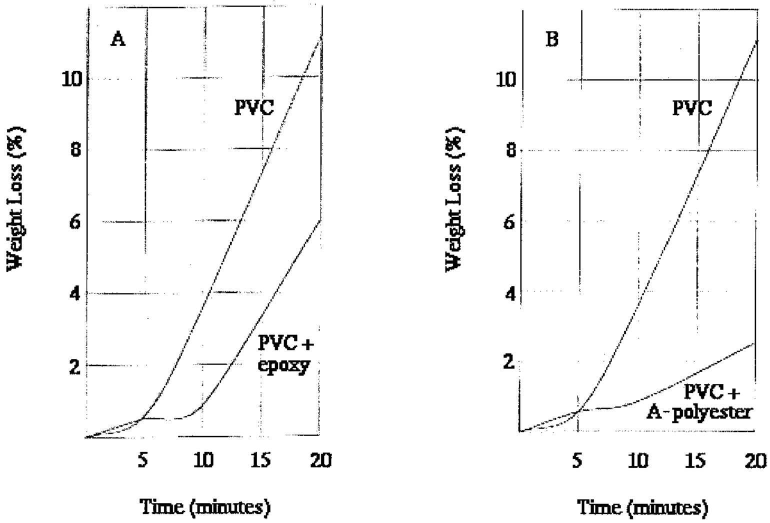


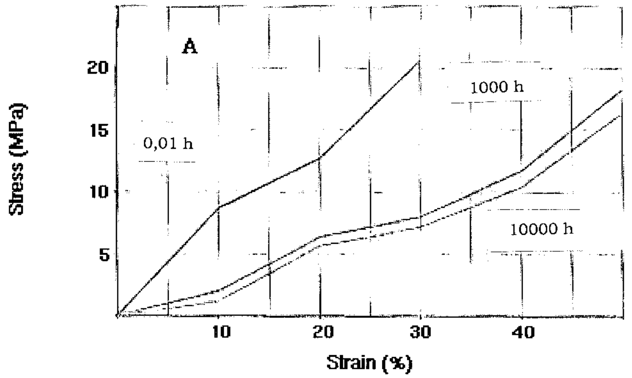
Figure 2. Thermogravimetric curves of pure PVC and of formulations (T = 250°C, in air).

The U.V. stability of the formulations was tested by means of short - and long - term mechanical tests. Specimens for mechanical and creep tests were exposed to U.V. radiations (254 nm) for two hours, by means of a transilluminator (Spectronics) with 8x8" filter area and six 15 W short-wave tubes (power of $8 \cdot 10^{-13}$ W/sqcm), the irradiated area reached a temperature of 25°C (circulating air fan). Short term mechanical properties of the irradiated samples were then measured (Table 5), in comparison with specimens of the commercial PVC formulations.

Table 5. Short-term tensile properties of formulations before and after U.V. irradiation; N.I. not irradiated, I. irradiated (strain rate: 5 mm/min).

Formulation		E (secant) 5%, MPa	σ_r, MPa	ε_r %
PVC + Epoxy	N.I.	41.8	22.2	35.0
	I.	47.9	18.9	27.2
PVC + polyester A	N.I.	17.1	30.0	10.0
	I.	18.1	27.8	6.8
PVC + polyester B	N.I.	42.8	26.0	6.0
	I.	45.4	19.5	4.2
Commercial PVC	N.I.	16.4	20.8	312
	I.	17.1	17.3	265

Long-term tensile creep tests (same conditions as the preceding tests) were also carried out to obtain the isochronous curves of the formulations containing the polymeric plasticisers alone, in comparison with the product containing the normal set of plasticisers and stabilisers (Figure 3).



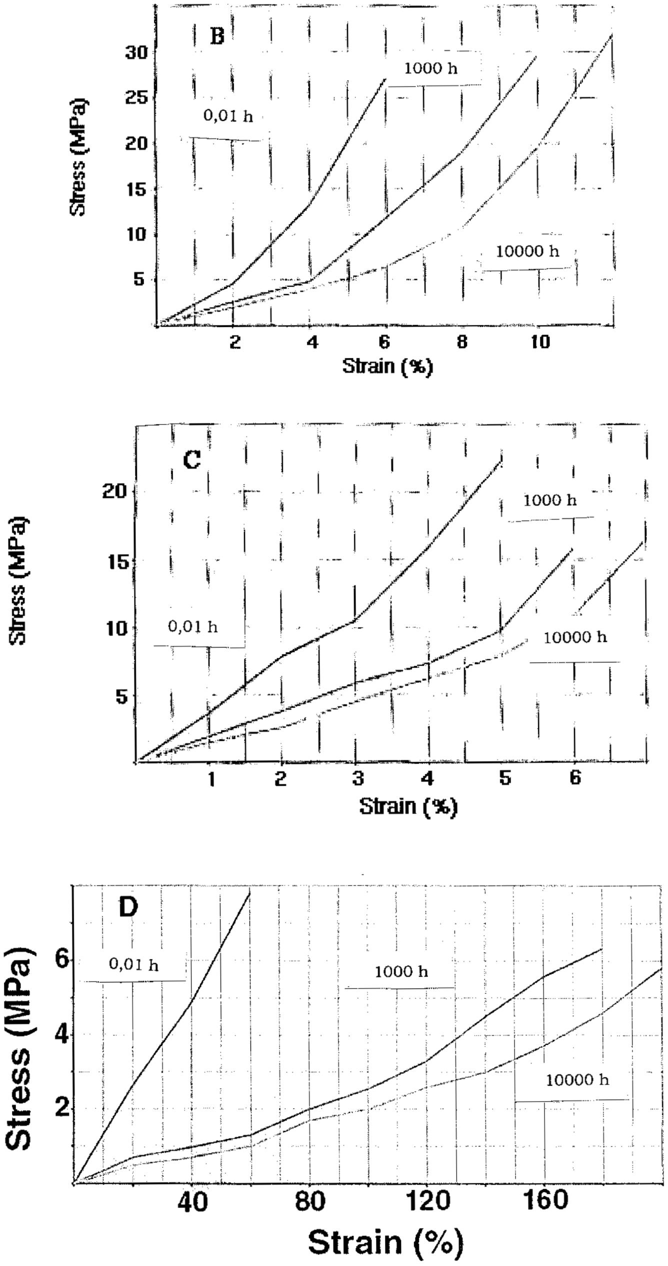


Figure 3. Isochronous curves (20°C) of irradiated specimens, from the creep tests. A. PVC + Epoxy resin, B. PVC + polyester A, C. PVC + polyester B, D. PVC commercial formulation.

Results and Discussion

It should be pointed out that both the epoxy resins and the linear polyesters could be considered as "primary" plasticisers, owing to their solubility parameters and the electric constants. Primary plasticisers can be added in high concentrations to the PVC - formulations without tackiness and can be employed without the aid of other "cooperative" plasticisers. Both epoxies and linear polyesters can be considered to be chemically and physically compatible with PVC.

For the short term behaviours of the formulations, the good performance of the polymeric plasticisers (Table 1) can be seen from examination of data in Table 2, bearing in mind that the commercial PVC used is a "complete" product. The experimental formulations (containing only one plasticiser) show high values of elastic modulus and of strength (see Table 2) together with acceptable values of strain at yield and break. The effect of the epoxy resin alone is remarkable on the strain at break(35%), with high strength and modulus. In contrast, the presence of the curing agent (TEPA) is less satisfactory, showing lowest values of strain and excessively high value of stiffness. Nevertheless the highest stiffness is obtained in presence of polyester B, whereas polyester A gives higher values of strain at yield and break.

The long term behaviour of the formulations are a little more complex, but it can be concluded that the epoxy resin alone and, polyester B, behave better: the creep-strain tests carried out at room temperature and under various constant tensile stresses indicate the best performance of the epoxy resin alone and polyester B as plasticisers. The evaluated secant creep modulus of these formulations under a tensile stress of about one third of the yield strength (Table 4) show only a comparatively small decrease both at 1000 and 10000 hours, in front of a drastic drop for the formulations containing the epoxy+TEPA, for those containing polyester A and for the commercial PVC.

As far as their stabilising action is concerned, the polymeric plasticisers behave very well for the thermo - oxidative stabilising action: both polyesters behave somewhat better than the epoxy resin (Figure 2) at 250°C in air, but all the formulations can be easily processed by injection moulding without addition of other stabilisers, i.e. the resin does not degrade, discolour, or give off hydrogen chloride.

The U.V. irradiation shows similar good results. From the morphological point of view the commercial PVC turns yellow - brown, whilst both epoxy - or polyester - containing formulations turn a little yellowish; the former (originally transparent) becomes dull.

The short-term mechanical behaviour after U.V. irradiation (see Table 5) indicates a small decrease in the breaking strength and strain similar to those of the commercial complete formulation.

Long-term tensile creep-strain tests show a regular slow increase of the creep modulus for the irradiated formulations (see Figure 3); the commercial PVC containing both plasticisers and stabilisers shows a similar effect, but it can be pointed out that the increase is less dramatic at longer periods: the slope of the isochronous curves at 1000 and 10000 hours is in fact definitely smaller (see Figure 4).

Conclusion

Epoxies and the linear polyesters, well known polymeric plasticising agents for PVC, are suitable above all for their cooperative effects: they can be regarded as stabilisers as well as good plasticisers. Their presence in the formulations (20 - 30% w/w) greatly enhances the thermal and oxidative endurance as well as the U.V. stability, with good short- and long- term mechanical characteristics. The low toxicity of polyesters, and savings on expensive metal-based stabilising agents, as well as low volatilization and extraction and lower processing temperature requirement will promote a wider use of epoxies and polyesters as multi-purpose additives in PVC formulations.

[1] "*Encyclopedia of PVC*", L. I. Nass and C. A. Heiberger, Eds., vols 1 & 2, Marcel Dekker, New York 1986.
[2]"*Polymer Science and technology of plastics and rubbers*", P.Ghosh, Tata Mc Graw-Hill, New Delhi, 1990.
[3] "*Handbook of PVC Formulating*", E. J. Wickson, Ed., Wiley & Sons, New York 1993.
[4] *"Area of action and criteria for a preventive sustainable control policy using PVC"*, U.B.A. Report, Doc. 140200, German Federal Environment Agency study, Frankfurt (Germany), 1999
[5] "*The Effect of U.V. Light and Weather on Plastics and Elastomers*", Plastics Design Library Ed., William Andrew Inc., New York, 1994.
[6] "*The use of plasticisers in PVC*", E.C.P.I. European Seminar, Brussells (Belgium), Nov. 1999.
[7] T. Sterrett, E. Miller, *J. of Elastomers and Plastics* **1988**, 20, p.346.
[8] *"Plastics Engineering"*, R.J. Crawford, Butterworth Ed., Oxford (U.K.), 1998