Mixtures of Poly(vinyl chloride) and Copolyesters Based on ε-Caprolactone and L-Lactide: Miscibility, Thermal Stability, and Weathering Resistance

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ABSTRACT: Properties of the blends of Poly(vinyl chloride) (PVC) and poly(ε-caprolactone) (PCLO) and copolyesters based on ε-caprolactone and L-lactide (LLA) prepared by rolling were studied. Incorporating the LLA units into the structure of PCLO the content of the crystalline phase was controlled. Miscibility of the blends was assessed using DMA, and basic mechanical properties were correlated with the type and content of the polymer plasticizer. The PVC blends containing up to 20 wt parts polyesters were miscible. The presence of the LLA units in the copolyester influenced negatively the thermal stability. On the other hand even small content of copolyester in the blend enhanced the resistivity against aging. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 2395–2402, 2012

Key words: PVC blend; poly[(ε-caprolactone)-*co*-(L-lactide)]; miscibility; thermal stability; aging; poly(vinyl chloride); polyesters; polymer blends

INTRODUCTION

Using various additives, basic properties of poly (vinyl chloride) (PVC) can successfully be modified and application possibilities can be broadened. Besides necessary stabilizers, fillers, etc., they are plasticizers that affect markedly both processing and user properties of PVC.

Plasticizers interact with the polymer on the molecular level and enhance intrinsic mobility of the polymer chains. As a result, glass transition temperature (T_g) and polymer melt viscosity decrease, flexibility and workability increase, brittleness and hardness drop, frost resistance improves etc.[1]

Plasticizers are usually classified according to their chemical composition and ability to interact with the polymer (primary, secondary, polar, nonpolar), possibly also according to molar mass (low-molar-mass, polymeric). When compared with the low-molar-mass plasticizers, the polymeric ones, when processed, are stable, exhibit minimum extractability and neither migrate nor evaporate from the plasticized product.[1,2] On the other hand, they show lower plasticizing effect.

To plasticize PVC, aliphatic polyesters are predominantly used, based on adipic, sebacic, azelaic or a similar acid, and diols having $\sim$ 900–6000 g/mol molar mass.[2] Miscibility of the polyesters and PVC is ensured by specific interactions between the carbonyl groups of the polyester and the α-hydrogen on the PVC chain; however, when the concentration of the carbonyl groups in the polymer is too high, miscibility deteriorates. It is poly(ε-caprolactone) (PCLO) that possesses an ideal methylene to carbonyl groups ratio ($CH_2/CO = 5$), as well as a favorable interaction parameter.[3–5] The glass transition and melting temperatures of this biodegradable, nontoxic, semicrystalline polyester are -60 and $60°C$, respectively. It is well miscible with chlorinated polymers, decreases their glass transition temperatures and can be considered as an effective plasticizer.[3,6]

However, the application of PCLO as a plasticizer is substantially limited by its crystalline character and low melting temperature. Since, the blending of the polymers takes place in amorphous phases, the tendency to crystallize represents a considerable drawback of PCLO. If the PVC blend contains 35 wt % PCLO, the crystalline phase starts to separate and the fraction of the separated phase increases with increasing concentration of polyester in the blend.[7]

Obviously, the efficiency of PCLO can be increased by decreasing its crystallinity. One of the possibilities is to break the linearity of its chain by, e.g., branching.[8,9] Highly branched PCLO shows a higher plasticizing efficiency, as compared to linear polyester, and does not migrate to the surface of the PVC body. It

was demonstrated[9] that the plasticizing effect increases with increasing degree of branching of PCLO.

Another possibility is to incorporate in the PCLO chains different structural units, e.g., ε-caprolactam (CLA), possibly also aliphatic or aromatic ester units.[6,10–12] Aliphatic-aromatic copolyester based on ε-caprolactone (CLO) and ethylene terephthalate containing 60 mol % or more CLO structural units is fully miscible with PVC and exhibits plasticizing effect.[11] A product of the copolymerization of CLO and solvolyzed recyclate from disposed PET bottles represents also a promising plasticizer.[12]

Plasticizing efficiency of polyesteramides (PEA), prepared by an anionic polymerization of CLA and CLO, was studied in Ref. [10] PEAs containing 90 or 80 mol % CLO structural units are miscible with PVC. PVC and PEA containing 20–70 mol % CLO units are immiscible; the highest values of notch impact strength were achieved for an equimolar ratio of CLA/CLO structural units in PEA. To further increase the toughness of the PVC/PEA blends, it is possible to apply a higher content of PEA combined with a small amount of PCLO which improves the miscibility of both components leading to a microheterogeneous two-phase system.[10]

The degree of crystallinity can successfully be reduced by a copolymerization of CLO with L-lactide (LLA). It was found that poly[(ε-caprolactone)-*co*-(L-lactide)] [P(CLO-LLA)] thus prepared, with less than 30 wt % structural units derived from lactic acid which is already amorphous.[6] The content of the LLA component decreases the crystallinity of the copolyester and limits its miscibility with PVC. Copolyesters having 80 wt % CLO structural units are well miscible with PVC and the blends show a single glass transition temperature value. Although, this fact indicates miscibility of both polymers, it does not guarantee homogeneity of the blend on the molecular level.[6] P(CLO-LLA) with 34 wt % CLO is no more miscible with PVC and the blend exhibits two T_g values (PVC, copolyester).

In absolute majority of studies, the PVC/polyester blends were prepared from solutions. This way of preparation is simpler but, for processing conditions, uninteresting. In the present article, the blends of PVC and the P(CLO-LLA) were prepared by melt blending, i.e., under conditions imitating technological process. The blends prepared were assessed predominantly from the standpoint of thermal stability (TS) and resistance to aging.

EXPERIMENTAL

Materials

PVC Neralite 682—suspension type, Kh = 68, was kindly supplied by Spolana Neratovice. Weight-

TABLE I
Characterization of (Co)polyesters Used as Polymeric Plasticizers

	P(CLO-LLA)-0[a]	P(CLO-LLA)-15[a]	P(CLO-LLA)-30[a]
M_n (g/mol)	19,200	12,000	10,800
Đ[b]	2.1	2.4	2.2
T_g (DSC)[c] (°C)	−64	−49	−34
T_g (FOX)[d] (°C)	−64	−45	−30
y_w[e] (%)	99	95	83
$\Delta w_{180°C}$[f] (%)	0.5	0.9	1.4

[a] The number indicates content of LLA structural units in the copolymer (determined by ^{1}H NMR).

[b] Đ, the dispersity index (i.e., M_w/M_n).

[c] T_g, glass transition temperature determined from DSC.

[d] T_g, glass transition temperature calculated from Fox equation (Ref. 15).

[e] y_w, content of polymer determined by extraction with methanol.

[f] $\Delta w_{180°C}$, weight loss at 180°C (TGA).

average molar mass M_w = 101.8 kg/mol, number-average molar mass M_n = 51.4 kg/mol, dispersity 1.98 were determined by SEC in tetrahydrofurane (THF) (35°C, MALLS detector, the refractive index increment dn/dc of THF solutions of PVC was 0.101 cm^3/g). The heat stabilizer Tinstab MB360 (di-*n*-buthyltin maleate) was purchased from Akcros Chemicals, GB, and dosed in an amount of 1.0 wt part per 100 wt parts of PVC. Lubricant Bralen SA 200-22 (LDPE) (Slovnaft, the Slovak Republic) was dosed in an amount of 1.0 wt part per 100 wt parts of PVC.

PCLO was prepared by the polymerization of CLO initiated by tin(II) 2-ethylhexanoate (Sn(Oct)$_2$; 0.5 mol %) at 130°C (polymerization time 6 h).

Poly[(ε-caprolactone)-*co*-(L-lactide)] copolymers [P(CLO-LLA)] (used as the plasticizer) were prepared by copolymerizations of CLO and LLA. The initial monomer feed mole ratios, identical with the monomer unit mole ratios in the resulting copolymer, were 85/15 and 70/30 (determined by ^{1}H-NMR). The mole ratio of the CLO structural units and those derived from L-lactic acid in the copolyester was 74/26 and 54/46. Polymerization conditions: 0.5 mol % of the Sn(Oct)$_2$ catalyst, 150°C, 4 h.

Number-average molar mass (M_n) of PCLO and the P(CLO-LLA) copolymers was determined by SEC (MALLS detector, the refractive index increments dn/dc of chloroform solutions of PCLO and the copolymers were 0.060 and 0.055 cm^3/g, respectively). Characterization of copolyesters is shown in Table I.

Preparation of the blends

Blends of PVC and polyesters in the form of foils 0.4 mm thick were prepared on a Polymix 80T two-roll mill, roller size 80/300 mm, slip 1.2 (rotation velocity
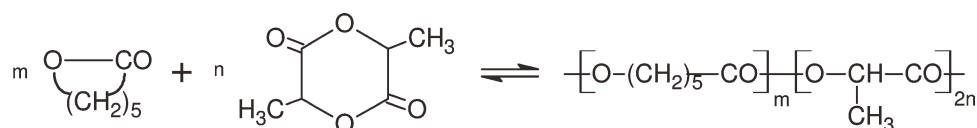
Scheme 1

ratio 22:19). Rolling temperature 180°C ± 0.1°C, blend preparation time 8 min (optimum period of time with respect to the TS and the notch impact strength of blends[10]). The specimens (thickness 0.4 or 4 mm) were obtained by 5 min compression at 195°C and 30 MPa.

Procedures

PVC is inherently unstable because HCl is eliminated from the polymer backbone and conjugate double bonds are formed during thermal treatment.[13] That is why the processing of PVC requires the presence of a thermal stabilizer which, in addition to the inhibition of dehydrochloration, reacts with eliminated HCl and chlorides are formed. HCl that does not react with the heat stabilizer any more and is released from the sample (referred to as "liberated HCl") was quantified by continuous potentiometer.[14] The thermal stability (TS) values were read from the kinetic curves obtained for the individual blends. The TS value represents the time interval (in minutes) from the start of the heat treatment to the moment of a rapid increase of the amount of liberated HCl.

The color stability of the blends in the foils treated at 180°C in air using TESTER TOM Model 204 was evaluated visually.

Two methods were used to determine glass transition temperatures blends. The DSC measurements were performed using DSC-Q100 (TA Instruments) in the temperature range −80 to 120°C with constant heating rate of 10°C/min and nitrogen purge (50 cm³/min). The DMA measurements were performed using DMA DX04T tester (RMI, Czech Republic), in a temperature range between −50 and 120°C at a heating rate of 3°C/min; bending mode Single Cantilever with constant deformation of ±0.2 mm and sinusoidal force at a frequency of 1 Hz was used.

TGA of samples was carried out employing TGA Q 500 (TA Instruments) in the temperature range of 20–600°C at a heating rate of 10°C/min and nitrogen purge flow rate of 50 cm³/min.

Notched impact strength (a_k) was measured with the Charpy pendulum on specimens (60 × 6 × 4 mm) with an average notch depth of 1 mm at 23°C.

Tensile test was carried out with standard specimens, conditioned at 52% humidity for 14 days at 23°C, on an Instron instruments (Model 3365) at a clamp distance 50 mm and a displacement rate of 10 mm/min.

Specimens in the form of plates (50 × 20 × 0.4 mm) were exposed to the conditions of accelerated aging in the xenon testing chamber Q-sun X-3 according to the ISO 11341 standard (a filter simulating the effects of daylight, UV sensor with 340 nm, irradiation intensity of 0.51 W/m² and 70% humidity were applied; during the 2-h cycle, the specimens were sprayed for 18 min).

Optical parameters were measured using the ColorQUEST Xe instrument. The CIE 1976 *L* a* b** scale was used to assess the color changes.

RESULTS AND DISCUSSION

Poly(ε-caprolactone) (PCLO) and poly[(ε-caprolactone)-*co*-(ʟ-lactide)] copolymers [P(CLO-LLA)] containing 0, 15, and 30 mol % of LLA units (i.e., 0, 26, and 46 mol % of structural units derived from L-lactic acid) were used to prepare the blends as obtained by polymerization, Scheme 1:

Polymer additives used in this study are denoted as P(CLO-LLA)-0 (i.e., PCLO), P(CLO-LLA)-15, P(CLO-LLA)-30, where the number indicates content of LLA units in the copolymer. Blends thus prepared contained 0, 0.75, 2, 5, 10, and 20 wt parts of the additive per 100 wt parts of PVC.

Characterization of polymeric PVC additives

Polymeric plasticizers were prepared by (co)polymerization of CLO and LLA initiated by tin(II) 2-ethylhexanoate. The values of number–average molar masses ranged between 10,000 and 20,000 g/mol and the molar–mass distribution was relatively broad (Table I).

Glass transition temperature of the materials to be mixed with PVC was determined by DSC (Fig. 1). After the first heating above the melting temperature, the samples were cooled in liquid nitrogen and had therefore equal thermal history which is necessary for reliable reading the value of T_g. The materials show a single T_g which increases from −64°C (PCLO) with increasing content of the LLA units incorporated in the copolyester and is in good agreement with the values calculated using the Fox equation[15] (Table I). The copolymers are therefore statistical. For 15 mol % LLA [P(CLO-LLA)-15] in the copolymer, melting temperature and melting enthalpy are lower than for PCLO which indicates a lower content of the crystalline phase. The melting temperatures
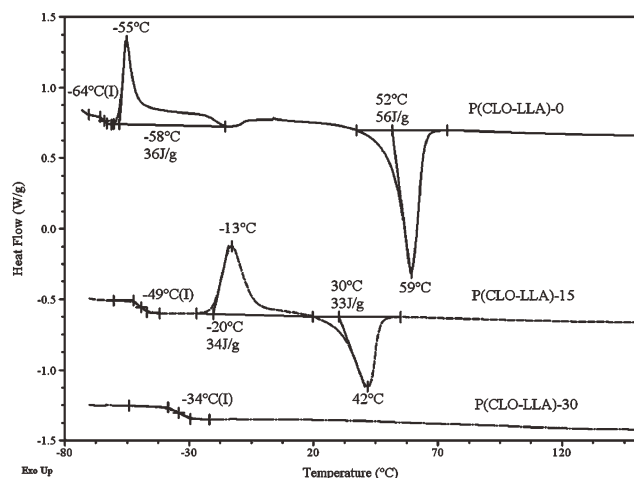
Figure 1 DSC of copolyesters quenched in liquid nitrogen.

are more than 100°C below the processing temperature of PVC. The sample P(CLO-LLA)-30 was amorphous. By incorporating the LLA units into the structure of PCLO, the flexibility of chains is reduced which manifests itself as a shift of the peak of cold crystallization from T_g by 10°C for PCLO and by 36°C for P(CLO-LLA)-15.

The content of fractions extractable by methanol increases with increasing fraction of the LLA units in the copolymer (Table I). One percent of unreacted monomer and oligomers was extracted from PCLO, and this fraction markedly grows in copolymers because methanol dissolves also statis-

tical copolymers with a higher content of the LLA units.[16]

Polymeric plasticizers (as obtained by polymerization, nonextracted) were measured also by TGA (Fig. 2). The drop of the mass of samples occurs already at temperatures above 180°C. By incorporating the LLA units into PCLO, the temperature, at which a maximum decomposition rate is achieved, is decreased by ~ 100°C.

Miscibility of PVC and P(CLO-LLA)

Miscibility of mixtures of PVC and (co)polyesters was assessed according to the T_g values read from maxima of loss component of dynamic modulus determined by DMA. For all mixtures prepared, only a single value of T_g was found which decreases with increasing fraction of copolyesters (Fig. 3). PCLO, as well as both copolyesters, shows plasticizing effect; T_g of the mixtures decreases more slowly when copolyester containing LLA units is present which is undoubtedly related to higher T_g values of copolyesters in comparison with PCLO (Fig. 1). All PVC blends containing 20 wt parts of P(CLO-LLA) show T_g values about 50°C, irrespective of the content of LLA in the copolymer. Consequently, our original assumption that introducing LLA units and thus lowering the fraction of the crystalline phase in the copolymer would increase the efficiency of plasticizing has not been confirmed for the case of melt blending.

Incorporation of LLA into PCLO influences the methylene/carbonyl group ratio (CH_2/CO) which is
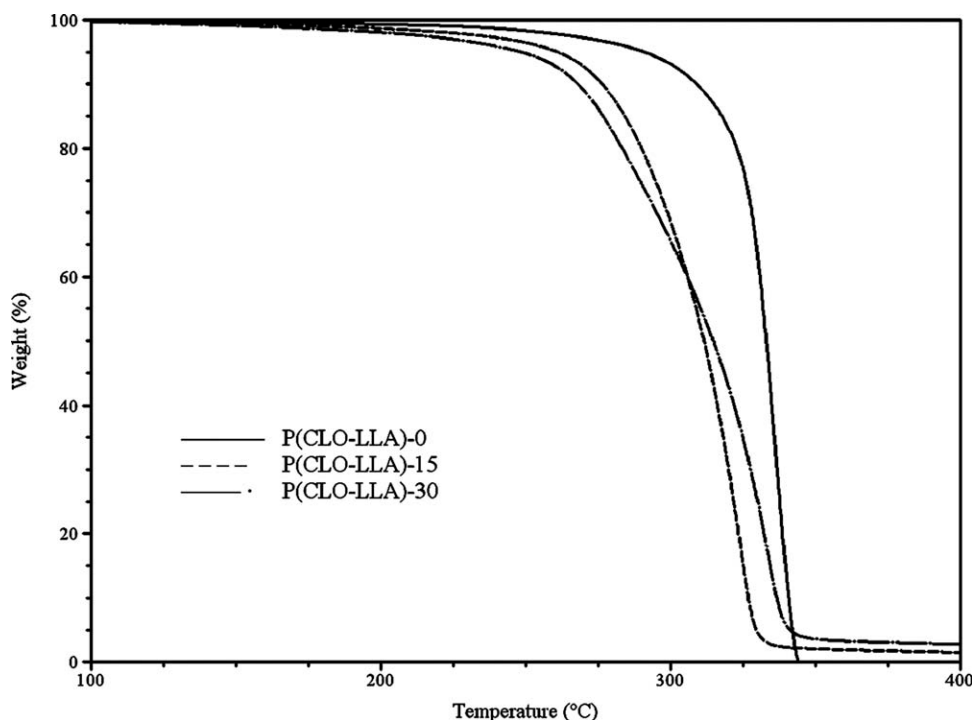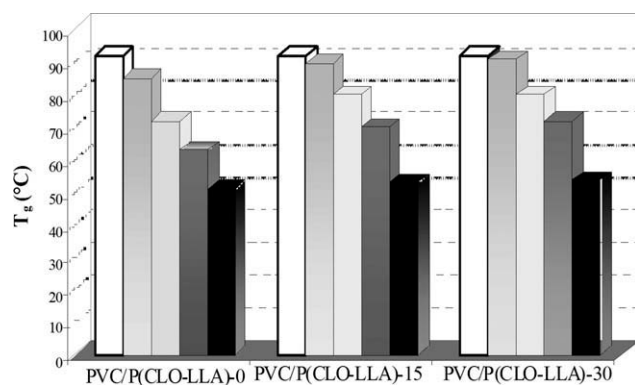

Figure 2 TGA of polymeric plasticizers.

Figure 3 Dependence of T_g on type of used polymeric plasticizers and their content (from left 0; 2; 5; 10; 20 wt part/100 wt part of PVC).

essential for the miscibility of PVC with polyesters, see earlier. With increasing content of LLA in the copolyester, the fraction of methylene groups in the chain rapidly decreases. This decrease was expressed as a ratio of peak heights pertaining to carbonyl groups (1713–1730 cm^{-1}) and those relating to methylene groups (at 2920 cm^{-1}) (Table II). With increasing content of the LLA units in the chain, the absorption band maximum of the carbonyl groups is shifted toward shorter wavelengths. A higher content of the carbonyl groups in the plasticizer may deteriorate homogeneity of the PVC blends. Finding a single T_g value need not necessarily imply good miscibility on a molecular level.[6]

Mechanical properties of blends

Tensile strength, elongation at break, and notched impact strength were determined for the blends prepared (Table III). Tensile strength values were read at the yielding point; it is apparent from their dependence on the content of P(CLO-LLA) in the blend that strength passes through a minimum at the concentration of 10 wt parts. Highest strength was found for blends of PVC and amorphous P(CLO-LLA)-30. Elongation at break increases for all blends with increasing content of copolyester in the blend with PVC.

Notched impact strength declines slightly with increasing content of copolyester in the blends.

TABLE II
Ratio of Peak Heights of the Carbonyl and Methylene Groups (CO/CH$_2$) from IR Spectroscopy in Used Polymeric Plasticizers

Copolymer	CO/CH$_2$	v(C=O) (cm^{-1})
PVC/P(CLO-LLA)-0	0.061	1713
PVC/P(CLO-LLA)-15	0.177	1721
PVC/P(CLO-LLA)-30	0.184	1730

Those containing 16.4% additive show ~ 2/3 of original values of notched impact strength. The slowest decrease occurs with the PVC/(CLO-LLA)-30, that is, with the blend modified by the copolyester having the highest content of the LLA units. The drop of a_k for samples having a higher content of the modifier was probably caused by deteriorating the homogeneity of the blends, in which P(CLO-LLA) forms domains without any reinforcing effects.

Although, the PVC/P(CLO-LLA) blends show a single T_g value indicating miscibility of PVC and copolyesters, the dependences of mechanical properties on the content of plasticizer do not confirm. It can be assumed that a part of the additive is not sufficiently dispersed in the matrix. Hence, we prepared also blends by mixing in a blender and their mechanical properties were similar to those obtained by rolling.

An attempt was made to improve dispersing the polymeric plasticizer in PVC matrix by solution mixing. Both components of the blend, i.e., PVC and P(CLO-LLA) (10 wt parts) were dissolved separately in THF, the solutions combined and, after 5 h of stirring at room temperature, the blend was precipitated into methanol or hexane. A part of the dissolved mixture was separated and the solvent was evaporated. The T_g values of foils prepared by evaporation are substantially lower than those prepared by rolling. This is especially marked for the blends of PVC and copolyesters containing a small fraction of the crystalline phase (Table IV). It is evident that the solution mixing is more efficient than melt mixing. Foils prepared from the PVC/P(CLO-LLA) blends "precipitated" by methanol (or hexane) have much higher T_g. In this case, precipitation removed both low-molar-mass portions of copolyesters (which

TABLE III
Mechanical Properties of PVC/P(CLO-LLA) Blends

Polymeric plasticizer and its content (wt part/100 wt part PVC)	P(CLO-LLA)-0					P(CLO-LLA)-15			P(CLO-LLA)-30		
	0	0.75	5	10	20	5	10	20	5	10	20
σ^a (MPa)	60.5	59.3	60	62	46	62.4	64.2	60.5	65.7	68.7	55.7
ε^b (%)	137	144	156	187	211	167	186	223	165	185	243
a_k^c (kJ/m^2)	4.9	5.0	4.7	3.2	2.7	3.9	3.4	3.1	4.5	4.0	3.1

[a] σ, tensile strength at yield.
[b] ε, deformation at break.
[c] a_k, notched impact strength at 23°C.

TABLE IV
Glass Transition Temperature (T_g) and Thermal Stability (TS) of the Blends PVC/P(CLO-LLA)
(10 wt part Copolyester/100 wt part PVC)

	T_g (°C)		TS (°C)	
Blend/method	Precipitation	Casting	Rolling	Precipitation
PVC/P(CLO-LLA-0)	68	48	72	70
PVC/P(CLO-LLA-15)	66[a]	35	36	32[a]
PVC/P(CLO-LLA-30)	74	36	32	40

Samples were obtained both by rolling and from THF solution by casting. Stabilized foils were prepared by rolling (max 2 min) from the powders obtained by precipitation from methanol.

[a] Precipitation from hexane.

had contributed to a reduction of T_g values by increasing the plasticizing effect of copolyesters) and those statistical copolymers in which the structural units CLO/LLA are present in a ratio of $\sim 50/50$ and which are methanol-soluble,[16] see Table I.

Thermal stability

By addition of more than 5 wt parts of PCLO, thermal color stability of PVC was slightly deteriorated. Darkening of the blend is faster by ~ 10–20 min, irrespective of the content of the additive in the blend [Fig. 4(a)]. The presence of thermally instable LLA structural units in the copolyester (15 or 30 mol %) (cf. TGA, Fig. 2) causes more intensive color changes and faster darkening of the PVC/P(CLO-LLA) blends. With increasing fraction of copolyester in the blend, color TS drops (Fig. 4b).

The problem of coloring PVC blends relates to releasing hydrochloride from the polymer chain during the degradation and to the formation of polyene sequences of various lengths, absorbing in the visible light region. In addition to neutralizing HCl released, the thermal stabilizer present in the matrix slows down elimination of HCl, and thus also deepening the color of the thermally stressed blend.

In accordance with the results of measurements of the color stability, the TS (expressed as a time period, after which only a minimum amount of HCl is released during the thermal stress of the blend) of the PVC blends was decreased by adding PCLO (Fig. 5). This phenomenon is not surprising because applying polyester in the PVC blend reduces the efficiency of the organotin stabilizer.[17] Sn-based stabilizer forms a stabilizing complex with the chlorine atom; also α-hydrogen on the PVC chain, which is necessary to trap the plasticizer within the PVC matrix, takes part in such nonbond interactions.
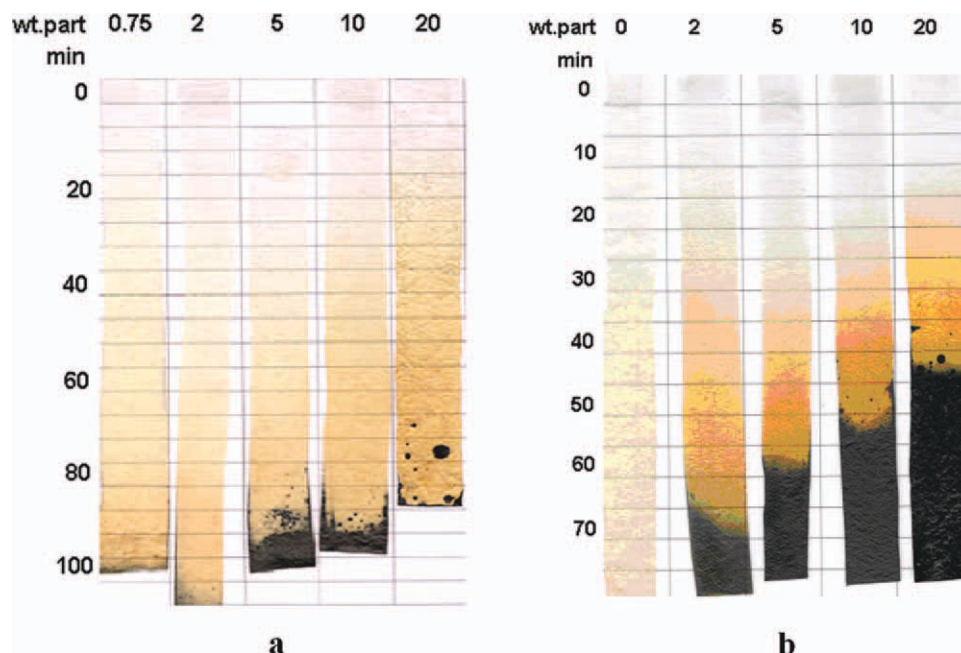

Figure 4 The color thermal stability of blends PVC/P(CLO-LLA)-0 (a), PVC/P(CLO-LLA)-15 (b) at 180°C and in air atmosphere. Graphs are parameterized by the content of plasticizers (in wt parts/100 wt parts of PVC). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]
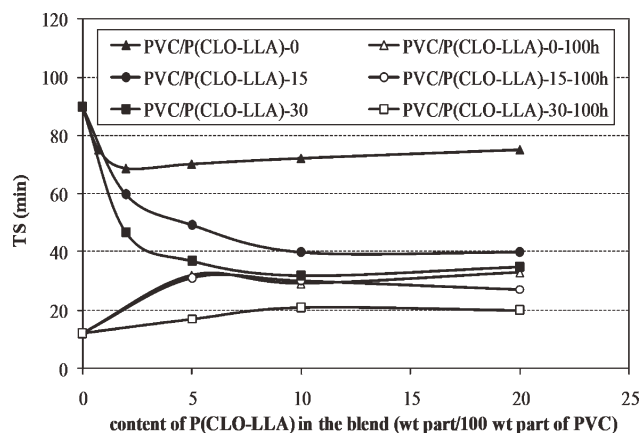
Figure 5 Dependence of thermal stability (TS) of PVC/P(CLO-LLA) blends on the type and content of polymeric plasticizers. PVC/P(CLO-LLA) blends were exposed 0 and 100 h in Q-Sun xenon test chamber.

The presence of the LLA units in the copolyester reduces substantially the TS of the PVC/P(CLO-LLA) blends (ca. to half the original value, Fig. 5). In these blends, due to more intensive degradation of the blend, the stabilizer is more quickly consumed by the reaction with hydrochloride released.

P(CLO-LLA) during degradation (180°C, "air" atmosphere, humidity 60%) is hydrolyzed and formed acid groups can deteriorate TS of PVC in the blend. TS of P(CLO-LLA) is lower than PCLO, see Table I and Figure 2. The negative influence of the presence of the LLA units (or LLA as a substance) is indicated by kinetic dehydrochloration curves of model PVC blends (Fig. 6). While the dehydrochloration rate of unstabilized PVC is 33 mmol HCl/g·s, by adding the copolyester or LLA this value increases to 60 or 80 mmol HCl/g·s, respectively. Reduction of the rate of release of HCl from PVC in the presence of PCLO can be explained by a stabilizing effect of $Sn(Oct)_2$, an initiator used to polymerize CLO and present in the plasticizer.

The way of preparation of blends (by rolling or by precipitation from a solution) has no substantial effect on the TS of the PVC/P(CLO-LLA) blends (Fig. 4).

Accelerated weathering

The blends were subject to accelerated aging in the xenon test chamber Q-Sun which simulates the conditions of natural weathering and accelerates the processes. Deepening the color of the PVC/P(CLO-LLA) blends during the process of accelerated aging was followed by optical parameters of yellow index (YI) and lightness (L*). TS were determined for the blends exposed for 100 h in Q-Sun (Fig. 5).

Comparing the resistance to aging for PVC and PVC/P(CLO-LLA) blends we arrived at a conclusion that introducing all the three additives increases the
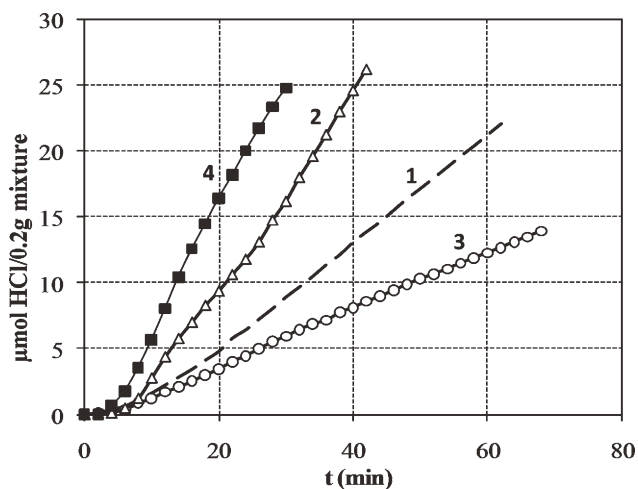

Figure 6 Dependence of the amount of liberated HCl from PVC and PVC mixtures on degradation time at 180°C in air. Composition of tested samples: nonstabilized powdered PVC (1), powdered mixture of PVC and P(CLO-LLA) (2), PVC and PCLO (3), PVC and L-lactide (4) at ratio of components 2:1.

resistance. It is evident from the dependence of the optical parameters of lightness on the time of exposition that the best stability is achieved for the blends of PVC and copolyesters. It is the presence of the LLA units in the copolyester which affects positively the resistance to aging, as illustrated by Figure 7. A slight darkening of these blends occurs after ~ 550 h, whereas the PVC foils darken after 250 h already.

The course of the dependence of the lightness parameter on the time of exposition for varying concentrations of, e.g., P(CLO-LLA)-15 in the blend with PVC suggests that the slowest aging takes place for blends containing the smallest amount of the additive (2 wt parts) (Fig. 8). By adding PCLO, and especially P(CLO-LLA), carbonyl groups absorbing in the UV region of sunlight are introduced to the blend (Table II). It can be
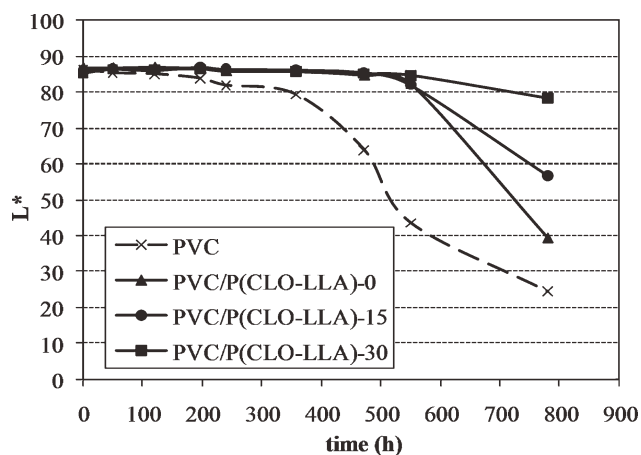

Figure 7 Dependence of optical parameter (lightness L*) of PVC and PVC/P(CLO-LLA) blends with 10 wt part P(CLO-LLA) on weathering time in Q-Sun.
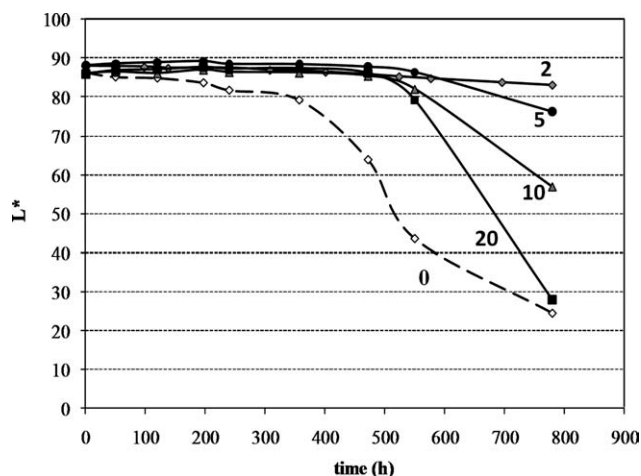
Figure 8 Dependence of optical parameter (lightness L*) of PVC and PVC/P(CLO-LLA)-15 blends on weathering time in Q-Sun. The curves are parameterized by the content of P(CLO-LLA)-15 (wt part/100 wt part of PVC) in blends.

deduced from the results that small amount of the additive acts as a light stabilizer.[18] With increasing concentration of the polymeric additive, however, the fraction of carbonyl groups increases and the stabilizing effect of copolyesters decreases.

Stabilizing effect of copolyesters is confirmed also by the change of yellow index (YI) which, for pure PVC, relatively markedly increases during the first 500 h of aging. After 780 h is almost zero which relates to the fact that the PVC is already totally black. For the PVC/P(CLO-LLA) blends YI passes through a minimum at ~ 200 h of exposition and marked increase occurs as late as after 550 h, as mentioned earlier (Fig. 9).

No mass losses take place during the exposition. The results of the determination of the TS support the conclusions given above, namely that during aging,
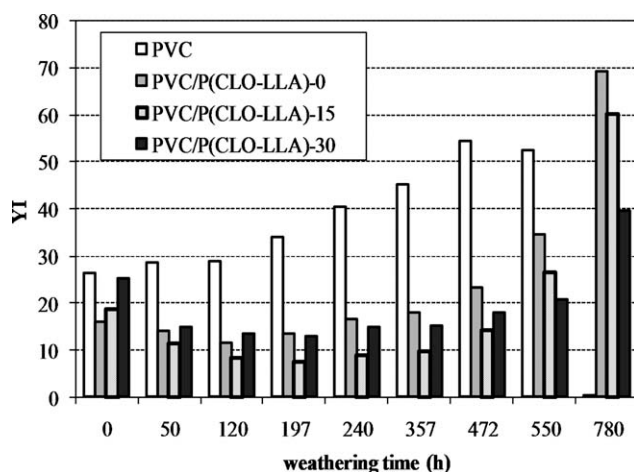

Figure 9 Dependence of optical parameter (yellowness index, YI) of PVC and PVC/P(CLO-LLA) blends with 10 wt part additive on weathering time in Q-Sun xenon test chamber.

the stabilizer is consumed more quickly in the blend not containing polyester. After 100 h of exposition, TS of pure PVC, the PVC/P(CLO-LLA) blends decreases by 80, 40, and 15 min, respectively, (Fig. 5).

CONCLUSIONS

Properties of the PVC/polyester blends, i.e., miscibility, mechanical properties and, in the first place, TS and resistance to aging were studied. PCLO and copolyesters containing, in addition to the CLO structural units, also 15 or 30 mol % of the LLA structural units were prepared. By incorporating the LLA units into the PCLO structure, the crystallinity of the copolyester was effectively affected: with 30 mol % LLA, the copolyester was completely amorphous.

The PVC blends containing 0.75–20 wt parts polyesters showed a single T_g value indicating miscibility. Mechanical properties depended on the content and type of the polymeric additive in the blend.

TS of PVC in the blend was affected by the type of the stabilizer used (based on Sn) and especially by the presence of the LLA units in the copolyester. By adding as little copolyester as 2 wt parts, TS dropped almost to half the original value. In contrast, the presence of this copolyester in the blend increased the resistance of PVC to accelerated aging. We have shown that the presence of copolyesters used at low concentration effectively influences weathering resistance without substantial restriction of TS.

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