

Investigating poly-(vinyl-chloride)-polyethylene blends by thermal methods

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Abstract Poly-vinyl-chloride (PVC)-polyethylene (PE) alloys were prepared by melt blending using both low- and high-density polyethylene without applying a compatibilizer. The PVC and the PE are incompatible polymers; in spite of this fact stable microheterogeneous materials were obtained. Mechanical methods e.g. tensile tests generally (measured in the usual concentration range) do not support any compatibility. At higher concentrations, the incompatible parts mask the effect of molecular mixing, easily detected at low PE contents. Dynamic mechanical (DMA), differential scanning calorimetric tests were carried out. Glass transition temperatures were determined by both methods. DMA tests were made at four frequencies, and the energy of activation of PVC main transition was also calculated. The decrease of glass-transition temperatures and energy of activation show that there is a slight mixing of the polymers. Specimens were also investigated by infrared method. From the results of IR spectra, grafting reaction of PE can be assumed onto the PVC because of its dehydrochlorination.

Keywords PVC · PE · Polymer blend · Compatibility · DMA · DSC · FTIR · Glass transition

Introduction

The poly-vinyl-chloride (PVC) is a widely used commodity polymer because of its excellent properties; such as high stiffness, good transparency, low flammability and

favourable price. PVC is recyclable, but incompatible contaminations; in particular polyolefines diminish the mechanical properties. The polyethylene as a polymer of low glass-transition temperature should be a good impact modifier of PVC but the incompatibility makes its application seemingly impossible. In order to overcome this problem compatibilizer resins are used, e.g. chlorinated polyethylene (CPE) [1, 2], or ϵ -caprolactone grafted polymers [3]. The primary goal of this research was to investigate the compatibility limits, impact modifying effects, the changes in mechanical and chemical properties of adding different polyethylenes (PEs). The thermal stability of PVC is limited, it requires special care during processing because thermal degradation by dehydrochlorination [4]. The reaction is a rapid 'zip' type one, forming conjugated polyene sequences of a length of 6–14 double bonds. The yellowing, browning and the final black colour of degraded PVC are caused by these polyenes. The polyenes are very reactive substances; therefore, a chemical reaction between the partly degraded PVC and PE cannot be excluded.

Sombatsompop and co-workers [5] investigated PVC/LDPE blends and the effect of multiple extrusions, i.e. the effect of heat and shear. They found slight discoloration of the material, in addition the increase of gelation temperature, i.e. the increase of molecular weight as a result of crosslink formation.

Although thermodynamic compatibility is rather an exception, a number of polymer alloys are utilized industrially. The best examples are the impact modified plastics. Impact modifiers always form stable microheterogeneous systems with the matrix polymers. The partial compatibility, the phase boundary and the phase structure [6] are the keys for the preparation of polymer blends. In case of PVC, it is rather complicated because of the thermal degradation processes described above. There were many

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efforts using compatibilizers to form stable PVC/PE mixtures. The CPE is one of the best compatibilizers because it consists of a broad range of different structural units on the same molecule [7]. Marossy [8] and Merche [9] analyzed the effect of CPE in PVC/PE blends and stated that the polyethylene improves the stiffness if the concentration is not too high. In order to avoid the phase separation Fang [10] crosslinked the PE in melt state and investigated the rheological behaviour of the PVC/PE mixtures in an other article [11]. CPE, NBR and polyurethane was also used in PVC/PE blends as compatibilizer [12].

The thermal stability of PVC/PE blends was also investigated because of the need of PVC recycling. Arnold and Maud [13] found that even a 0.2% contamination range of PE considerably accelerates the degradation of PVC and explained it by the free radicals produced during the thermo-oxidative degradation of PE. These radicals 'consume' the stabilizers of PVC, but in our opinion these species are also making possible the grafting of PE on the double bonds of degraded PVC. The compatibility of non polar polymers with PVC can be improved by grafting. Hou and Zhao [14] successfully mixed PVC with PP using the grafting technique.

Experimental

Materials

Suspension type PVC of low molecular weight (K value = 58, ONGROVIL S-5258) was used. The PVC was pre-mixed with commercial grade additives according to Table 1. The base mixture was mixed to 110 °C with a fluid mixer of 20 L; type MT20 FU (Mischtechnik Germany).

High density polyethylene: Eltex 4009 MFN 1325.
Melt-flow index: 0.9 g/10 min (190 °C, 2.16 kg).
Density: 960 kg/m³.
Melting temperature: 136 °C.
Average molecular weight: 140,000 (M_w).

Low density polyethylene: Tipolen FA 2210.
Melt-flow index: 0.3 g/10 min (190 °C, 2.16 kg).
Density: 922 kg/m³.
Melting temperature: 113 °C.
Average molecular weight: 64,000 (M_w).

Table 1 PVC base mixture

	phr.
PVC S-5258	100
TM-181 methyl-tin stabilizer	1.5
PA-190 oxidized polyethylene wax, external lubricant	0.15

Test methods and instruments

Dynamic mechanical tests were carried out with a Rheometric Scientific DMTA MK-III instrument in dual cantilever mode. The free length of the samples was 5 mm, the applied amplitude 64 µm peak to peak. The maximum deformation is less than 0.15% in this mode. The scanned temperature range was -70 to 140 °C by using a 2 °C/min ramp, the frequency 0.3, 1, 3 and 10 Hz, respectively.

DSC tests were carried out with a Setaram EVO 131 instrument in the 30 and 220 °C range using a 10 °C/min heating rate. The 4 mm diameter round specimens to be tested were punched from the compression moulded plates of 1 mm.

Infrared spectra were acquired using a Bruker Tensor 27 FT-IR instrument in ATR mode in the range of 4,000–700 cm⁻¹. By this means the top 1–2 µm of the surface is tested.

Tensile tests were carried out at room temperature on an INSTRON 5566 type tensile tester using 50 mm/min crosshead speeds. Test specimens were cut from compression moulded plates of 1 mm thickness (Table 2).

Results and discussion

Both DSC and dynamic mechanical (DMA) tests allow the determination of glass transition temperature. These values are not equal, moreover, in case of DMA the determined T_g depends on the frequency used. The frequency dependence of T_g values allows the determination of activation energies of transitions [15].

The original software of the used DMA instrument gives the highest measured value as T_g . In order to improve the accuracy, a new evaluation software was developed for the determination of the temperature of $tg\delta_{max}$, and calculates the half width and the integral of the transition, as well. Glass transition temperatures are plotted in Fig. 1 for all frequencies.

The T_g of PVC decreases undoubtedly even at low PE content, but tend to increase over 8% PE in case of LDPE. That means a small amount of PE acts as weak plasticizer in PVC. Because the T_g of polyethylene is low, -114 °C, 1% of PE should cause about 1.5 °C decrease of T_g using the Gordon-Taylor equation with $k = 1$. Figure 2 shows the DMA thermogram of PVC (P0) and the 4% HDPE containing sample (P5) at 1 Hz frequency. The shift of main transition of PVC is undoubtedly greater than the measuring error. Measuring the same sample, the deviation of T_g is less than 0.3 °C. Although we did not analyse the β relaxation of PVC, a similar shift was observed as in case of main transition as demonstrated by the Fig 3.

Half width of $tg\delta$ peaks increase by frequency but there is no significant changes as a function of PE content.

Table 2 Composition of tested blends, numbers represent weight parts

Identifier→	P0	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10
PVC base mixture	100	99	98	99	98	96	92	84	96	92	84
HDPE	–	1	2	–	–	4	8	16	–	–	–
LDPE	–	–	–	1	2	–	–	–	4	8	16

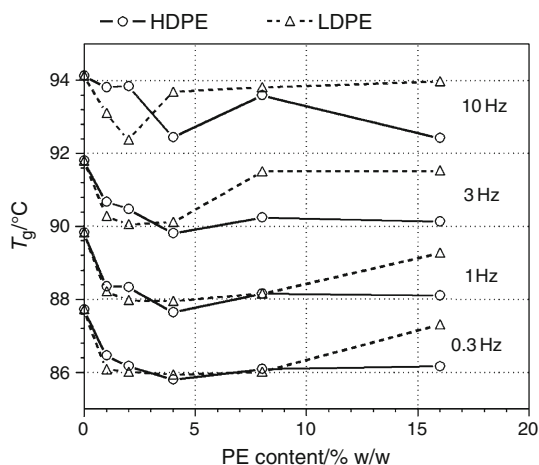


Fig. 1 Glass transition temperatures of PVC/PE blends determined by DMA method. *Solid line* HDPE, *dashed line* LDPE

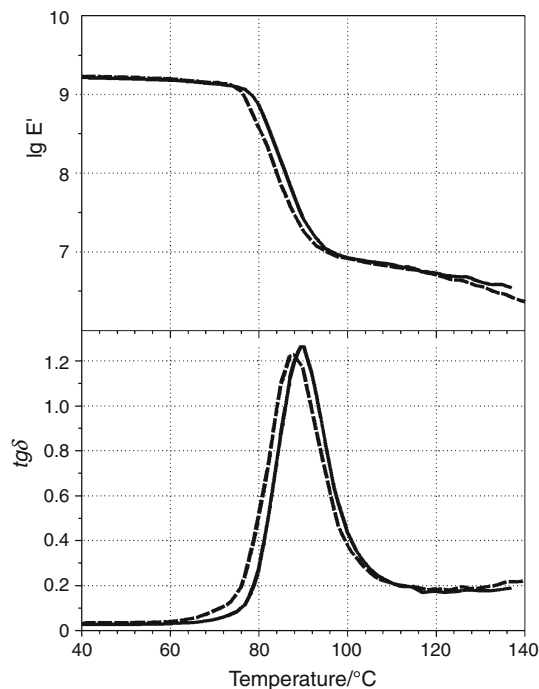


Fig. 2 DMA thermogram of PVC (P0 *solid line*) and 4% HDPE containing PVC/PE blend (P5 *dashed line*). Frequency: 1 Hz (Unit of E' modulus: Pa)

Integrating the $tg\delta$ versus temperature curves a value representing the peak intensity can be obtained. At low PE content it lies over the value of pure PVC. Figure 4 shows

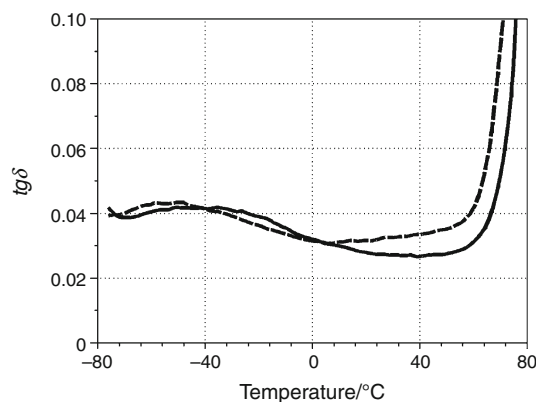


Fig. 3 Low temperature (β relaxation) part of DMA thermogram of PVC (P0 *solid line*) and 4% HDPE containing PVC/PE blend (P5 *dashed line*). Frequency: 1 Hz

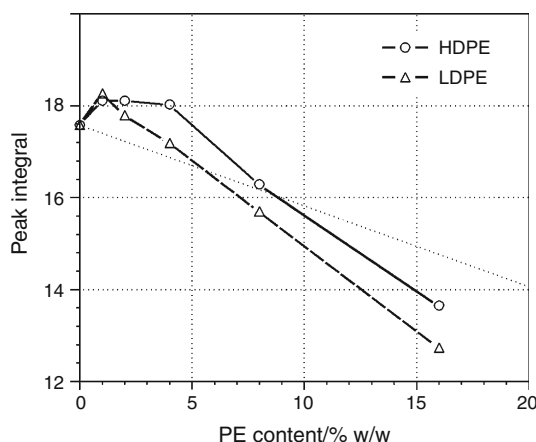


Fig. 4 PVC α transition peak integrals of PVC/PE blends at 1 Hz frequency. *Dotted line* represents additivity

the peak intensities as the function of PE content for 1 Hz frequency. (The shape of curves is similar for all frequencies tested.)

Peak intensity is over the additivity until 4–8% PE; the PE increases the mobility of PVC molecules. Over the 4–8% concentration the effect of PE is reversed.

Energy of activation decreases rapidly with the PE content until 4%, and then increases to the value of pure PVC (Fig 5). The energy of activation of PVC transitions depend on the processing history, too. It causes uncertainty in the values, but also shows a clear tendency.

Determination of T_g by DSC method seems to be simple, but the heat flow step in the a transition range of PVC shows

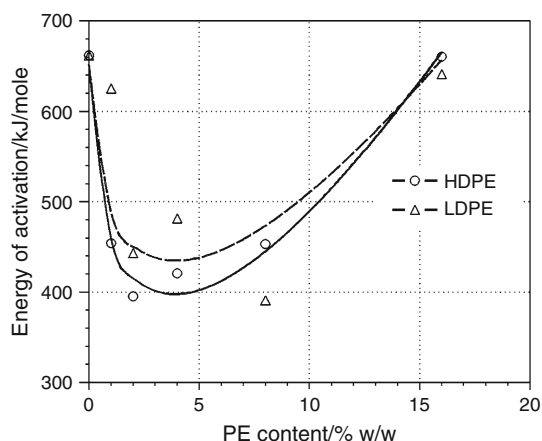


Fig. 5 Activation energy of PVC α (main) transition of PVC/PE blends

double step in presence of LDPE making the determination of T_g unsure. Such a thermogram is shown in Fig. 6. The measured T_g values are plotted in Fig. 7 but it needs further investigations. In case of HDPE, the change of T_g is similar to the results obtained by DMA. It must be noted that even in case of PVC/CPE blends, the accurate determination of T_g [1] are difficult, and the effect remains hidden.

By infrared spectroscopy we have found the band of around $1,730\text{ cm}^{-1}$ to be characteristic. This band originates from the carbonyl groups and are formed both because of oxidation of double bonds of degraded PVC and the oxidation of polyolefins. Because the highest absorbance was measured on the P0 sample without PE we suppose that this peak is resulted almost exclusively from the thermo-oxidative degradation of PVC.

Fig. 6 DSC thermogram of PVC/PE blend containing 2% LDPE (P4)

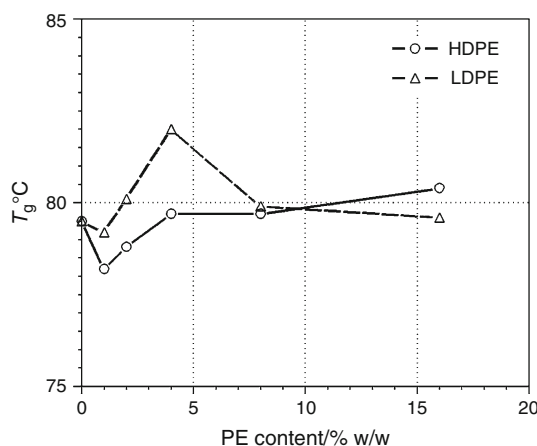
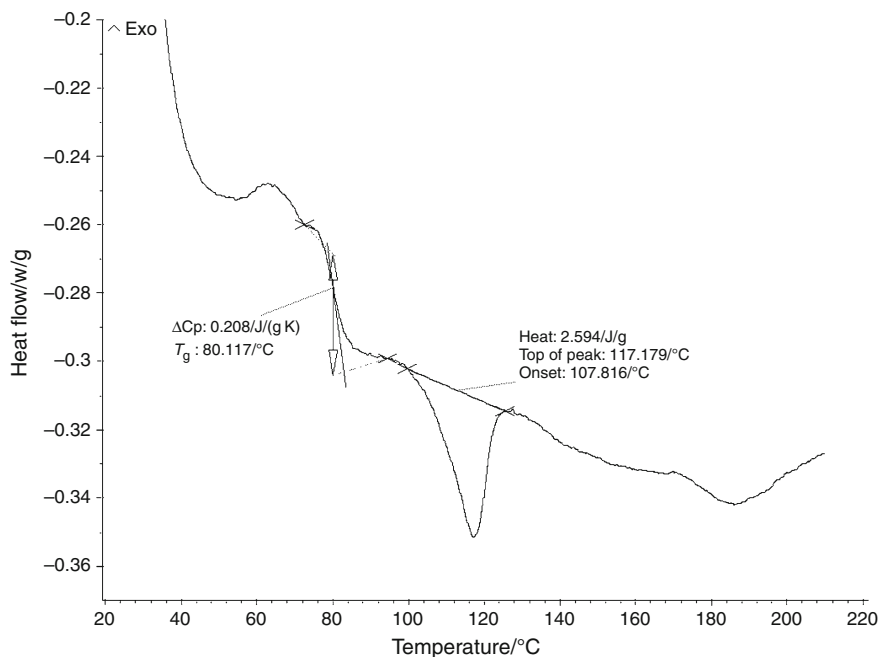


Fig. 7 Glass transition temperatures of PVC/PE blends determined by DSC method

Figure 8 demonstrates the relative peak intensity of this band as function of PE content. In case of HDPE, the peak intensity is proportional to the PVC content (thin solid line) but in case of LDPE the decrease is much more significant. Because the LDPE has a branched structure the probability of grafting is higher, this reaction consumes the carbonyls.

Unfortunately, the PVC and the polyethylene have no common solvent; therefore, the determination of gel content is not possible.

Tensile strength values are plotted against the polyethylene concentration in Figs. 9 (LDPE) and 10 (HDPE). The tensile strength has a maximum value in both cases at low, 0.5–1% polyethylene content. Considering the standard deviations this effect is higher than the measuring errors.

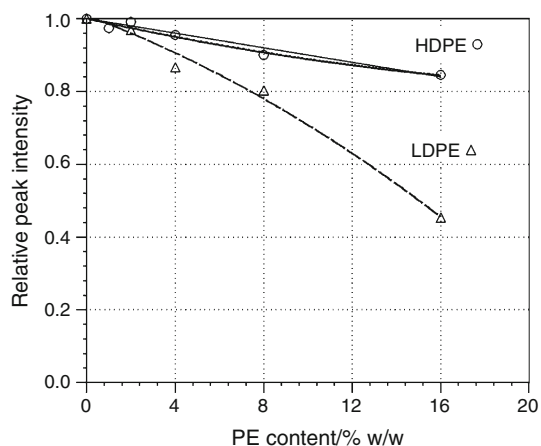


Fig. 8 Relative infrared peak intensity of $1,730\text{ cm}^{-1}$ band (carbonyl) of PVC/PE blends

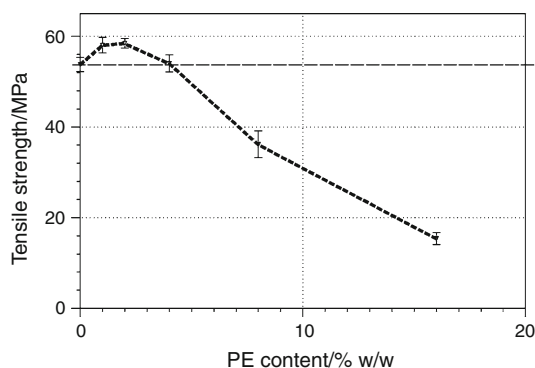


Fig. 9 Tensile strength versus LDPE concentration

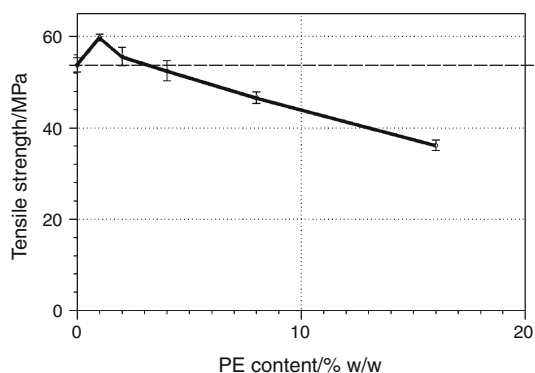


Fig. 10 Tensile strength versus HDPE concentration

At higher polyethylene content the tensile strength decreases, as expected in a multiphase system.

Conclusions

Although it is generally accepted that PVC and PE are thermodynamically incompatible polymers, during our

experiments we have managed to prepare single phase compositions of HDPE/LDPE with PVC, without using compatibilizer. Our intention was to evaluate the impact modifying properties of ethylene polymers on PVC, but the findings show much more significant effects on the structure and behaviour on the PVC caused by PE. These behaviour modifications indicate a partial compatibility at low PE concentrations. At less than 1% PE content the blend is a molecular solution according to DSC and DMA measurements. The change in T_g plotted versus the PE content indicates for both types of blending polymer (LDPE/HDPE) that a very small amount of PE is dissolved on a molecular level and acts as a plasticizer in PVC, significantly increasing the molecular mobility. At higher concentrations an agglomeration of PE occurs, and less to none gets dissolved.

Another interesting result is that using IR spectroscopy the peak related to carbonyl-groups—results of thermal degradation of PVC (dehydrochlorination and subsequent oxidation)—decreases in intensity more rapidly with increasing PE content than it can be explained with the decrease of the relative PVC content. This decrease is much more dominant in case of the LDPE than for the HDPE, and it is most probably is a result of a grafting reaction between the degraded PVC and the PE. The branched structure of LDPE makes the grafting reaction between the PVC and PE more probable. This was proven by infrared measurements only, because the determination of gel content was not possible.

The results of the tensile tests at appropriately low PE concentrations also support the molecular level solution at low concentration. This effect is very similar to the so called anti-plasticizing effect, when the PVC is plasticized with a few percent plasticizers.

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