

Study of Poly(vinyl chloride) Blends with Solid-State Chlorinated Polyethylene

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ABSTRACT: The influence of solid-state chlorinated polyethylene of various chlorine content and residual crystallinity on the mechanical properties of rigid poly(vinyl chloride) has been studied. The impact strength of poly(vinyl chloride) was found to increase significantly as 10–20 mass% chlorinated polyethylene, containing from 10.2 to 27.3% chlorine content (preferably 21.8% Cl) were added. This dependence corresponded to the higher elasticity and impact strength of the solid-state chlorinated polyethylene with chlorine content below 30% as well as the microstructure of its chlorinated block fragments. Multicomponent system of high impact strength and good flowability, consisting of poly(vinyl chloride), chlorinated polyethylene, hydroxyl-terminated polybutadiene, and ethylene-propylene-

ethylidenenorbornene terpolymer was also obtained. Regardless of the incompatibility between the polymer components of this blend, the similarity in the chemical nature of poly(vinyl chloride) and chlorinated polyethylene blocks on one hand, and the methylene sequences in the chlorinated polyethylene and elastomers on the other, resulted in the formation of an efficient interfacial layer. The changes in the structure of the blends were established by both calorimetric and microscopic studies. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2602–2613, 2006

Key words: blends; poly(vinyl chloride); solid-state chlorinated polyethylene; mechanical properties; structure

INTRODUCTION

Chlorinated polyethylene (CPE) is introduced into various polymers and copolymers to improve a number of valuable properties such as oil resistance, flame-retardancy, impact strength, etc. One of the most prospective applications of CPE is associated with the improvement of the impact strength and processability of poly(vinyl chloride) (PVC) used as a major component in different compositions.^{1–5} The efficiency of CPE as impact-resistant modifier depends on its average molecular mass, the chlorine content and its distribution along the polymer chains, and the amount of CPE with respect to PVC.^{1,4,6} A number of reports have been published concerning the preparation of blends consisting of PVC and polyethylene (PE) chlorinated in solution or suspension.^{7–17} The most widely used CPE for these research purposes contained 30–45% chlorine, particularly, 35–38%. Depending on the utilization of the blends, the amount of CPE changed within wide intervals, e.g., 0.5–50 mass% with respect to PVC.^{1,8,9,11,13,14} To prepare compositions of high impact strength based on PVC, however, 5–20 mass% CPE have commonly been introduced.^{1–3,7,18,19}

Only very few publications associated with the use of solid phase-chlorinated PE as a modifier causing high impact strength of PVC have appeared in the literature so far.^{20–23} The blend prepared by Bonotto and Wagner²⁰ consisted of PVC and CPE obtained through chlorination of PE under static conditions by agitation in laboratory reactor. The chlorinated PE contained preferably 30–38% Cl and random distribution of the latter along the macromolecular chains was observed. The effect of CPE on the impact strength of PVC was found to be, approximately, the same as that of the nonrandomly chlorinated PE. Unlike the uniformly chlorinated PE, however, the polymer mentioned earlier had the advantage that it did not significantly deteriorate the mechanical properties of PVC. According to the authors,²⁰ CPE containing 20% Cl and combined with poly(methyl methacrylate) did not improve the impact strength of PVC, due to incompatibility between the two polymers. Frey et al.²¹ prepared a thermoplastic composition of high impact strength by blending PVC and PE chlorinated in a fluidized-bed reactor to give a product of 36.5% chlorine content. In this case, the chlorination was conducted at temperatures close to the melting temperature of PE and the distribution of chlorine atoms along the polymer chains was nearly regular.

In some reports published in the recent years, the chlorinated PE obtained in solid phase or in aqueous suspension was added to blends of PVC with polyole-

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fins such as high and low density polyethylene (HDPE and LDPE respectively)²²⁻²⁵ as well as polyolefin elastomers such as ethylene-butene and ethylene-octene copolymers or ethylene-propylene-diene terpolymers.²⁶⁻³⁰ PVC was incompatible with these polymers; however, its use in the corresponding compositions was desirable because of lowering of the glass-transition temperature. CPE itself promoted the increase of the adhesion forces between the components of the interfacial layer and the mechanical properties of the resulting blends were improved.²² Huang et al.²³ found that the solid-state chlorinated PE prepared at relatively low temperature was quite efficient as an additive, improving the compatibility of PVC and LDPE, due to its block-like structure consisting of chlorinated and nonchlorinated regions along the polymer chains. CPE containing 32.8–36.5% Cl^{22,24,29} was commonly used in these multicomponent blends. According to Berard and coworkers^{18,19} as well as Eastwood et al.,^{26,27} PE chlorinated in aqueous suspension to a polymer of 20–25% chlorine content could also be successfully employed in compositions based on PVC. Such compositions had a good impact resistance, low temperature of processability, and increased adhesion forces between PVC and the polyolefin elastomer. The efficiency of CPE as an additive, improving the polymers compatibility, was found to depend on the chlorine content in the blocky chlorinated regions as well as the residual PE crystallinity, and the average length of the methylene-containing segments in the macromolecules of the elastomeric additive.¹⁶

A series of samples were prepared as a result from the solid-state chlorination of HDPE at temperatures below its melting temperature. The microstructure of these samples was studied by employing the ¹³C NMR method.³¹ Depending on the chlorine content in CPE, formation of single chloromethylene (CHCl) structural units (up to 10% Cl) or both the single and vicinal CHCl groups (up to 30% Cl) was detected. Samples with chlorine content of ~36% or more indicated also the presence of dichloromethylene (CCl₂) functional groups. In our opinion, studies concerning the effect of the degree of PE chlorination on the mechanical properties of suspension PVC and its blends with both the hydroxyl-terminated polybutadiene oligomer and ethylene-propylene-diene terpolymer (EPDM) deserve research attention. Moreover, the results from additional studies on the possible changes in the structure of some of the polymer blends by employing both the differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) methods can be discussed and, indeed, the present work is focused on the implementation of these tasks.

EXPERIMENTAL

Materials

A suspension PVC with Fikentcher constant of 68.1, $[\text{Mac}]M_n = 86,000 \text{ g mol}^{-1}$, bulk mass of 540 kg m^{-3} ,

and moisture content of 0.03% was used in all experiments. The experimentally determined chlorine content in PVC was 56.48%.

The chlorinated polyethylene (CPE) was prepared by chlorination of high-density polyethylene (HDPE) with $\bar{M}_n = 96,500 \text{ g mol}^{-1}$ and particle size of 0.125–0.250 mm. The chlorination of HDPE was conducted in a fluidized-bed reactor in the presence of a gaseous mixture, consisting of chlorine and nitrogen in the volume ratio of 3:7, respectively. The experiments were carried out within the temperature interval from 20 to 80°C. The combined chlorine content was determined by burning out a 15–25 mg sample, according to the Schöniger method, followed by potentiometric titration with 0.1N AgNO₃ solution.

The hydroxyl-terminated polybutadiene (HTPB) was prepared by radical polymerization in 2-propanol in the presence of 60% aqueous solution of H₂O₂. The characteristics of HTPB were as follows: $[\text{Mac}]M_n$ was 3150 g mol⁻¹; viscosity at 25°C was 41.5 Pas; the glass temperature (T_g) was -91°C, and functionality was 2.2.³²

The ethylene-propylene-diene terpolymer (EPDM) was Vistalon 2504 (Exxon) and contained 56.6% ethylene, 39.0% propylene, and 4.4% 2-ethylidene-5-norbornene. The corresponding viscoelastic characteristics were as follows: viscosity (Moony) was 40; tensile strength was 1.3 MPa and elongation at break was 1455%. The DSC method showed that the polymer product was amorphous and its glass transition temperature was -46°C.

Preparation of blends

A series of PVC-CPE blends were prepared. CPE used contained 10.2% Cl, 21.8% Cl, 27.3% Cl, 37.0% Cl, 45.2% Cl, and 54.8% Cl. The amount of CPE was calculated with respect to PVC and was changed from 0.25 to 75.00 mass%. Combination of stabilizers such as calcium stearate (1.0 mass%), modified dibutyltin maleate BT-22 (4.0 mass%), pentaerythritol-tetrakis[3-(3,5-ditert-butyl-4-hydroxyphenyl)]propionate, i.e., Irganox 1010 (0.25 mass%) was added to PVC, CPE, and each polymer blend. The ingredients were first dry-mixed and then homogenized on rolls at 172–178°C for 8–10 min. Sheets were subsequently pressed on a laboratory press type PHI (England) at 180°C under the pressure of 3.0 MPa and the average cooling rate of 25°C min⁻¹. They were conditioned at room temperature for 24 h.

Measurements

The strength-deformation indices (i.e., yield strength, σ_Y ; stress at break, σ_B ; elongation at break, ϵ) of CPE and PVC/CPE blends were measured on an Instron 4203 testing machine (England) at 25°C, according to

the Bulgarian State Standard BSS EN ISO 527.³³ The drawing rate was 50 mm min^{-1} . The sizes of the specimens were as follows: length of the operating section, $22 \pm 1 \text{ mm}$; width, $4 \pm 0.2 \text{ mm}$; and thickness, $0.4 \pm 0.01 \text{ mm}$. The value of each parameter (σ_Y , σ_B , ϵ) was calculated as the average one from 8 to 10 specimens of each composition examined.

The notched Charpy impact strength (σ_{IM}) was measured on an Universal Pendulums (Zürich, Switzerland) at 25 ± 2 and $-(20 \pm 2)^\circ\text{C}$, according to BSS EN ISO 179.³⁴ The specimens were conditioned at the testing temperatures for 24 h. The sizes of the parallelepipedal specimens were as follows: length, $50 \pm 1 \text{ mm}$; width, $6.0 \pm 0.2 \text{ mm}$; and thickness, $4.0 \pm 0.2 \text{ mm}$. A $2.7 \pm 0.2 \text{ mm}$ deep notch was made on the specimens by a sliding machine. The width of the notch was $0.3 \pm 0.1 \text{ mm}$. The value of σ_{IM} was determined as an average one from 6 to 8 specimens.

The melt index (MI) was determined on an MFI-MVI 3350 apparatus (Prodemat, France) at 200°C and a load of 21.2 kg, according to the BSS ISO 1133.³⁵

The Vicat softening temperature was determined on an apparatus of Frits Heckert company (Germany), according to the BSS EN ISO 306³⁶ at a force of 50 N and a rate of temperature rising $(50 \pm 5)^\circ\text{C h}^{-1}$. The single value of softening temperature was determined as an average one from six specimens with the thickness of $3 \pm 0.1 \text{ mm}$.

METHODS

Differential scanning calorimetry

Thermal analyses were carried out, using a PerkinElmer DSC-7 differential calorimeter. The instrument was calibrated by using indium and lead as standards, and the measurements were conducted under argon atmosphere. The heating rate in the range of -50 to 150°C for the samples studied was $10^\circ\text{C min}^{-1}$. The values of the glass-transition (T_g) and melting (T_m) temperatures were obtained on the first and second heating runs of PVC, CPE (21.8% Cl), and some of their blends.

Scanning electron microscopy

The specimens were fractured under cryogenic conditions using liquid nitrogen. The fracture surfaces obtained were coated with thin layers of gold of 200Å . Their morphology was monitored by means of JEOL JSM-5300 scanning electron microscope (Japan), without prior treatment such as staining or etching. The SEM machine used was in conjunction with a secondary electron mode using a voltage of 25 kV.

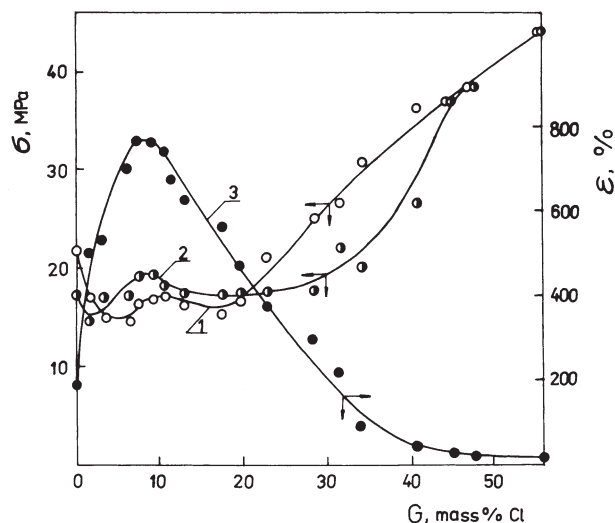


Figure 1 Plot of (1) yield strength, σ_Y , (2) stress at break, σ_B , and (3) elongation at break, ϵ as a function of the chlorine concentration in solid-state chlorinated polyethylene.

RESULTS AND DISCUSSION

Mechanical properties of solid-state chlorinated high density polyethylene

Before discussing the properties of PVC-CPE blends, the changes in the mechanical characteristics of CPE, depending on the degree of chlorination, should be considered. These changes depend on the heterogeneous structure of the solid-state chlorinated PE, whose macromolecules contain nonchlorinated structural fragments as well as ones of low and high chlorine content.

The strength-deformation indices of the CPE samples, containing from 1.3–56.1% Cl are shown in Figure 1. As seen from the figure, the stress at break (σ_B) and the yield strength (σ_Y) were almost equally affected by the chlorine content (curves 1 and 2). Up to chlorine content of nearly 20%, the values of these parameters were found to be almost the same or slightly lower than those of the HDPE starting material. With the higher chlorine content, however, a continuous increase of the parameters mentioned earlier was observed. Apparently, for the process of solid-state chlorination, the change in the degree of crystallinity (ca. 18.7% until the introduction of 20% chlorine, Table I), did not significantly affect the polymer strength characteristics. The relative elongation at break, however, was markedly influenced by the degree of chlorination and the crystallinity of samples. A well-pronounced maximum of this parameter within 5–15% chlorine content was observed. In this region the corresponding ϵ -values reached 600–800%, i.e., approximately, four times as high as those of HDPE.

The principal part of the mechanical load causing the deformation of semicrystalline polymers is consid-

TABLE I
Characteristics of the Solid-State Chlorinated HDPE

Chlorine content (mass% Cl)	T_m^a (°C)	T_g^b (°C)	T Vicat (°C)	$W_{c,x}^c$ (%)	σ_{IM} at 25°C (kJ m ⁻²)
0 (HDPE)	130.2	-70	76.6	64.8	5.6 ± 0.4
10.2	123.3	-10	49.9	58.5	26.0 ± 1.2
21.8	114.1	15	42.2	46.1	37.8 ± 1.1
27.3	111.6	22	49.0	39.5	27.4 ± 0.5
37.0	111.7	28	54.6	29.2	5.6 ± 0.8
45.2	108.9	47	59.5	19.6	4.4 ± 0.2
54.8	108.9	55	71.7	13.0	2.7 ± 0.3

^a T_m of CPE foils determined by means of differential scanning calorimetry.

^b T_g determined by dynamic mechanical analysis at a frequency of 1 Hz.

^c $W_{c,x}$ is the degree of crystallinity of CPE foils, determined by wide angle X-ray diffraction.

ered to be attributed to the so-called passing macromolecules.³⁷ Polymers with lower degree of crystallinity possess longer macromolecules of this type, which leads to an enhancement of the rubber-like elasticity.³⁸ The high ε -values of CPE samples containing up to ca. 10–15% chlorine are probably associated with the increase in the sequence length of the passing polymer chains, located between the crystals. Nonchlorinated methylene sequences within the passing chains of CPE should mainly contribute to the increased elasticity. At low chlorine content, a favorable combination between nonchlorinated methylene sequences of appropriate length with chlorinated ones of weakly pronounced polar interactions is likely to take place. As the degree of chlorination increased, the elongation at break decreased nonlinearly and, over 40% chlorine content, a fragile break of the CPE samples was observed (σ_Y was equal to σ_B). The CPE prepared in a fluidized-bed reactor and containing 56% Cl had a high tensile strength (σ was 44.7 MPa). It represented a rigid polymer, due to the increased intermolecular forces, which apparently compensated for the reduced crystallinity (Table I). The course of the curves for parameters σ and ε of solid-state chlorinated PE was different from that of PE chlorinated in solution or suspension.^{39–41} This is very likely to be determined by the difference in the chlorine atoms distribution along the macromolecular chains, resulting in different crystalline structures of CPE prepared by various methods.

Properties of the blends consisting of suspension PVC and PE chlorinated in a fluidized-bed reactor

The dependencies of the yield strength (σ_Y) and stress at break (σ_B) for PVC-CPE blends of various degree of chlorination are shown in Figures 2 and 3 respectively. The CPE content was changed from 0.25% to 75% with respect to the PVC amount. Blends of PVC with the starting polymer HDPE of melt index of 4.28 g/10 min and particle size within 0.125–0.250 mm were also

prepared. Almost all blends, including those containing HDPE, indicated some increase of the parameters σ_Y and σ_B up to, approximately, 1% additive introduced. This trend was more pronounced with σ_B of blends containing up to 1% CPE (Fig. 3) and was different from the corresponding behavior of σ_B for blends of PVC and PE chlorinated in suspension. The stress at break σ_B for the latter was found to decrease continuously.⁴² Although with blends of CPE content within 1–3%, the parameters σ_Y and σ_B decreased, some values were still higher or equal when compared with those of PVC.

According to Yamada et al.,⁴³ PE chlorinated in aqueous suspension to a product with chlorine con-

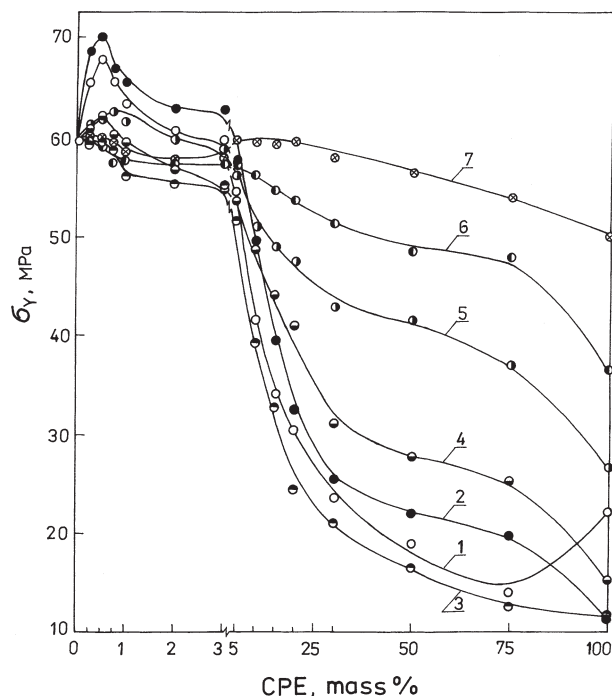


Figure 2 Plot of yield strength, σ_Y for PVC blends as a function of the amount of (1) HDPE and CPE containing (2) 10.2% Cl, (3) 21.8% Cl, (4) 27.3% Cl, (5) 37.0% Cl, (6) 45.2% Cl, (7) 54.8% Cl.

tent up to 48% was incompatible with PVC. Therefore, the blends of PVC with solid-state chlorinated PE should also represent two-phase systems, consisting of mutually incompatible polymer components. Usually, the mechanical properties of the two-phase polymer systems are mainly determined by the corresponding content of the disperse phase as well as its mechanical properties and the strength of the bonds in the interfacial layer.^{44,45} For the blends of PVC with a low amount of additive, CPE is likely to be located within the interfacial boundary, behaving as an internal lubricant, similarly to the PE chlorinated in an aqueous suspension to product with a block-like structure.³⁰ The parameters σ_Y and σ_B were found to decrease with the higher CPE concentration and this was more pronounced for the systems with chlorine content ranging from 0 to 27.3% (Figs. 2 and 3, curves 1–4). The higher the degree of chlorination was, the better mechanical properties were ensured (Figs. 2 and 3, curves 5–7). The reason for this could be both the higher strength of CPE (Fig. 1) and increased technological compatibility of CPE and PVC. Even blends of PVC (56.5% Cl) with CPE of 54.8% chlorine content had values of the parameters σ_Y and σ_B , which were equal or higher with respect to those of initial PVC, provided the relative amount of the additive did not exceed 75%.

The effect of CPE on the strength-deformation indices of PVC was also confirmed by the experimental

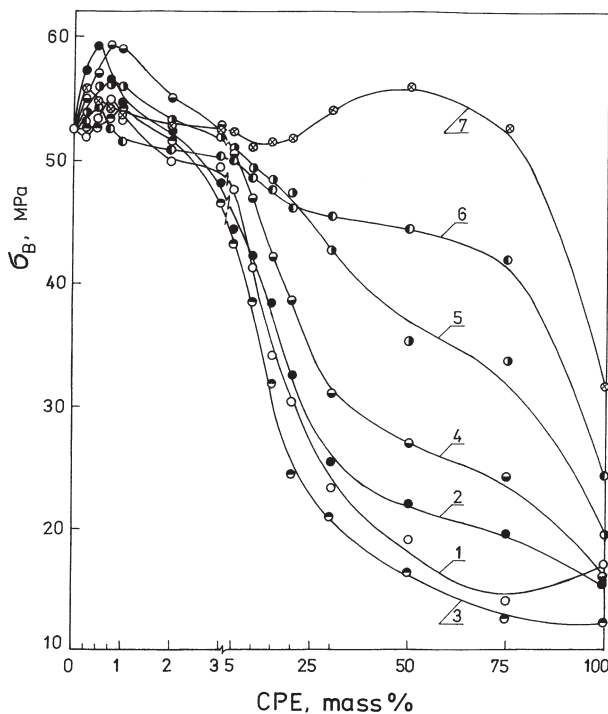


Figure 3 Plot of stress at break, σ_B for PVC blends as a function of the amount of (1) HDPE and CPE containing (2) 10.2% Cl, (3) 21.8% Cl, (4) 27.3% Cl, (5) 37.0% Cl, (6) 45.2% Cl, (7) 54.8% Cl.

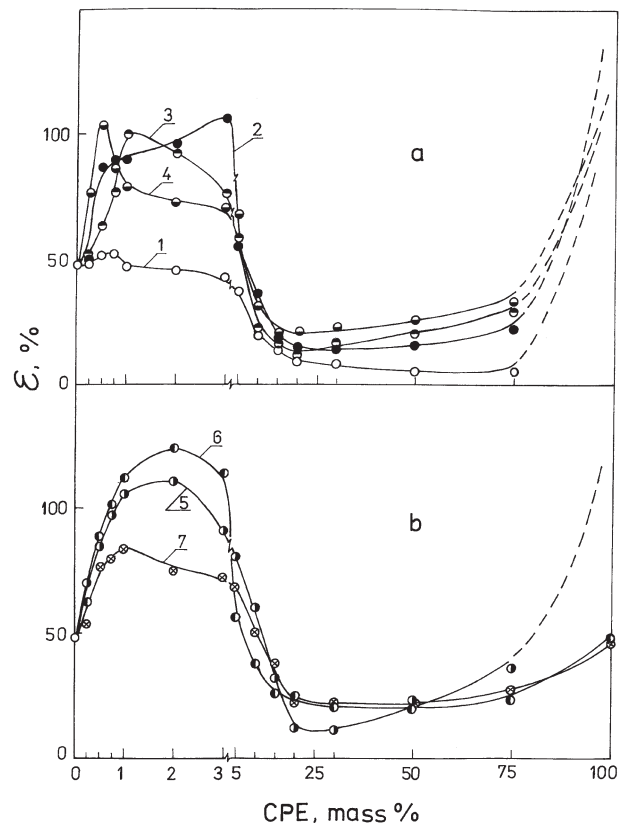


Figure 4 Plot of elongation at break, ϵ for PVC blends as a function of the amount of (1) HDPE and CPE containing (2) 10.2% Cl, (3) 21.8% Cl, (4) 27.3% Cl, (5) 37.0% Cl, (6) 45.2% Cl, (7) 54.8% Cl.

results for the change of the elongation at break ϵ as a function of the blends composition. Introducing small amounts (0.25 to 3–5%) of CPE into PVC resulted in the increase of ϵ for all blends studied (Fig. 4, curves 4–7). The concentration region for the higher values of the elongation at break with respect to those of PVC (48%) was wider and more pronounced than that concerning the parameters σ_Y and σ_B , particularly, for chlorine content within 37.0–45.2%. The range of CPE content from 5–10 to 25–30 mass% was associated with a significant decrease of the parameter ϵ . The nearly constant values of ϵ observed with the CPE content in the blends within 30 to 50–75 mass% corresponds to the fact that, in this concentration range, phase reversal occurs.^{44,46} With CPE content in the polymer blends, exceeding 75%, the higher elasticity of the latter takes precedence and the relative elongation increases.

The introduction of additives, which are structurally distributed within the PVC polymer system, is known to lead to an increased elongation at break, and this trend is more pronounced with the additive content of up to 3%.⁴⁷ The higher values of ϵ for the PVC–CPE blends within the range of 0.5–3% CPE are, obviously, determined by the CPE behavior as a struc-

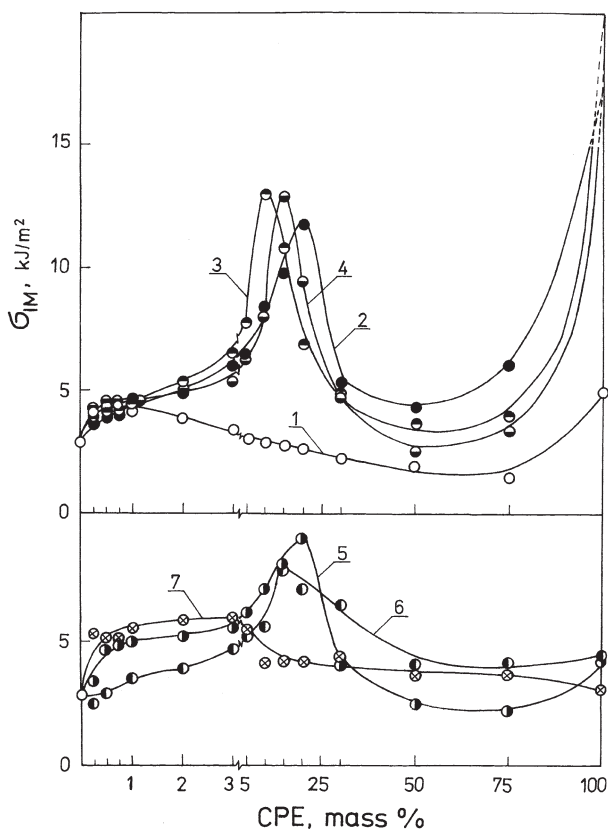


Figure 5 Plot of notched impact strength, σ_{IM} for PVC blends as a function of the amount of (1) HDPE and CPE containing (2) 10.2% Cl, (3) 21.8% Cl, (4) 27.3% Cl, (5) 37.0% Cl, (6) 45.2% Cl, (7) 54.8% Cl.

tural plasticizer. For blends of PVC with CPE containing 45.2% Cl, the elongation at break reached 125%. This confirmed the findings of Bonotto and Wagner,²⁰ which have claimed, that the solid-state chlorinated PE prepared under static conditions and containing 45% Cl acted as a plasticizer for the rigid PVC. CPE added in small amounts is likely to break the contact sites, involving the aggregates of primary PVC particles and thus facilitates their mutual mobility. One of the results from this was the increase in the elasticity of the blends. Moreover, the higher mobility of the structural formations in PVC favored their mutual orientation and caused an increase of the strength-deformation indices of the polymer. The increase of the CPE amount in the polymer blends led to stronger physical interactions between two polar polymers and the corresponding decrease of the elongation at break. Therefore, the chlorinated PE in the fluidized-bed reactor could act as a structural plasticizer with respect to PVC if introduced in small amounts. Higher amounts of the additive, however, resulted in the predominance of the so-called solvating effect, typical for polar additives⁴⁷ such as CPE.

The change of the notched impact strength σ_{IM} for some samples is shown on Figure 5. The values of this

parameter increased, approximately, twice as 0.5–5 mass% CPE were added but the corresponding maximum was found within the 10–20% region of additive content. CPE containing 54.8% Cl (Fig. 5, curve 7) was the exception from this trend. CPE of 21.8% chlorine content was found to increase the impact strength of PVC to the highest degree. Introduced in relative content of 10%, the latter caused the increase of the impact strength to 13.0 kJ m^{-2} , i.e., four times higher than that of the nonmodified PVC (2.9 kJ m^{-2}). Unlike the corresponding literature data for solid-state CPEs,^{20,21} the present study showed that PE chlorinated in a fluidized-bed reactor and containing 10.2–27.3% Cl had more favorable effect on the PVC impact strength (Fig. 5, curves 2–4), than the polymer of 37.0 and 45.2% Cl (Fig. 5, curves 5,6). This is probably associated with changes in the structure and mechanical properties of solid-state CPE, depending on the degree of chlorination.

According to Gull and Kuleznev,⁴⁵ the properties of polymer blends, particularly, their impact strength, depend on the presence (or the absence) of transitional interfacial layer. Such a layer usually emerges at the expense of the segmental solubility of the contact surface between two incompatible polymers under the appropriate conditions of blending. Bearing in mind the established dependence of the parameter σ_{IM} on both the composition of the PVC/CPE blends and CPE chlorine content, the most efficient interfacial layer in this case is assumed to be built up at CPE concentration in the blends from 10 to 20 mass% and CPE chlorine content from 10.2 to 27.3%. The following assumptions can be made in this respect: (i) The presence of certain structural similarities between the PVC segments and the chlorinated PE block fragments facilitate their mutual penetration and promote the corresponding polar interactions. This similarity is due to the fact that in the solid-state chlorinated PE, containing from 10 to 30% Cl, single CHCl groups as well as ones of 1,2-, 1,3- and 1,4-mutual location are formed.³¹ The latter correspond to a certain mode of binding in PVC, particularly, head-to-head, head-to-tail, and tail-to-tail. (ii) The combination of high impact strength and good elasticity, particularly, for CPE, containing 21.8% Cl (Fig. 1, Table I) leads to an effective dissipation of the impact energy among the polymer chains of its blends with PVC.

The effect of the CPE amount and its chlorine content on the flowability of PVC is shown in Figure 6. Chlorinated PE, containing 21.8 to 54.8% Cl and introduced up to 3 mass%, did not appreciably influence the melt index (MI) of PVC (curves 3–7), whereas HDPE and CPE of 10.2% Cl caused an increase of this parameter within the lower concentration regions (curves 1 and 2). Significant changes in the flowability of the blends were found over 5–10% additive introduced. These changes were even more pronounced

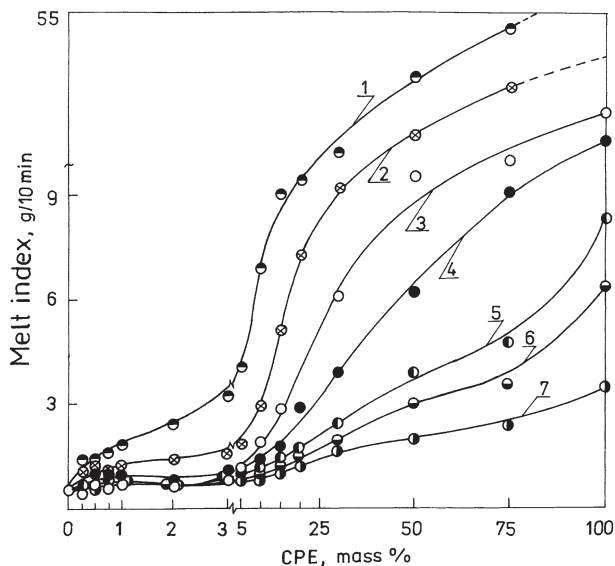


Figure 6 The melt index of PVC blends plotted as a function of the amount of (1) HDPE and CPE containing (2) 10.2% Cl, (3) 21.8% Cl, (4) 27.3% Cl, (5) 37.0% Cl, (6) 45.2% Cl, (7) 54.8% Cl.

with the lower chlorine content in CPE. The higher flowability of PVC is associated with the enhanced mobility of its primary particles, which is a consequence from the decreased dipole-dipole interactions between the latter.^{47,48} Apparently, the decrease of the polar interactions between the structural units of PVC and the facilitation of the geometric changes within these units⁴⁸ takes place at the expense of the sequences of the nonchlorinated methylene (CH_2) groups in CPE, located among them. This assumption was confirmed by the high values of the melt flow index for the PVC-HDPE blends (Fig. 6, curve 1).

The softening temperature of the PVC-CPE blends, determined by the Vicat's method,³⁶ was affected by both the concentration of CPE in them and the chlorine content in CPE (Fig. 7). The values of this parameter, which is the quantitative characteristic of the heat resistance of the blends, were found to be approximately the same as those of PVC up to a certain content of additive. Following that, the softening temperature decreased stepwise, depending on the degree of chlorination of HDPE. For blends of PVC with CPE of 10.2 and 21.8% Cl the decrease was detected over 15% additive; for blends with CPE of 27.3 and 37.0% Cl the corresponding effect took place over 20% additive introduced; and for blends with CPE of 45.2 and 54.8% Cl, the limit was 30% (Fig. 7, curves 2-7). Moreover, at the same composition of the blends, the values of reduction of their softening temperatures when compared with that of PVC decreased as the chlorine content in CPE became higher. For example, the corresponding ΔT value for blends of PVC with 75 mass% CPE was 13.8°C if CPE of 10.2% Cl was used; and

value of $\Delta T = 2.2^\circ\text{C}$ was obtained as CPE containing 54.8% Cl was added. For blends of PVC and HDPE (Fig. 7, curve 1), a slight linear decrease of the softening temperatures was detected, with $\Delta T = 6.2^\circ\text{C}$ for the blend of PVC with 75% HDPE.

The heat resistance of polymers is known to depend on the interactions between the corresponding polar groups as well as the degree of crystallinity, degree of crosslinking, introduction of active fillers, etc.⁴⁴ Therefore, the higher degree of chlorination of PE is associated with stronger interactions between the polar groups of CPE and PVC and lower values of the softening temperatures decrease for their blends. On the other hand, the influence of the methylene structural sequences in HDPE on the diminished polar interactions in PVC should be compensated by the high degree of crystallinity of HDPE. As a result, insignificant decrease in the heat resistance of their blends is believed to be observed.

The mode of the change in the softening temperatures of CPE itself, depending on its chlorine content is more specific. The corresponding temperature decrease observed up to 22% Cl content (Fig. 7) was probably related to both the lowering degree of crystallinity of CPE and increase of its elasticity. Following that, the observed increase in the CPE softening temperatures, associated with chlorine content from 27 to 55% was determined exclusively by the increased intra- and intermolecular polar interactions in the chlorinated PE block segments. However, due to the difference in the microstructures of PVC and the solid-state chlorinated PE, at approximately the same chlorine content (56.5% for PVC and 54.8% for CPE), the corresponding softening temperatures differed by ca. 13°C (Fig. 7, curve 7).

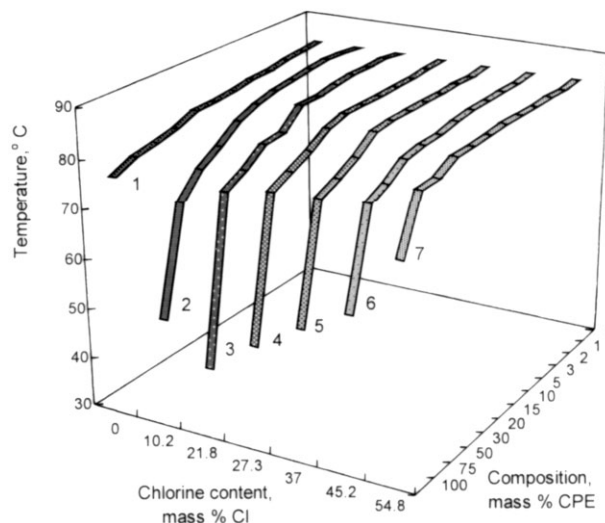


Figure 7 The Vicat's softening temperature versus the amount of (1) HDPE and CPE containing (2) 10.2% Cl, (3) 21.8% Cl, (4) 27.3% Cl, (5) 37.0% Cl, (6) 45.2% Cl, (7) 54.8% Cl.

TABLE II
Strength-Deformation Properties of PVC Blends with Chlorinated Polyethylene (CPE), Hydroxyl-Terminated Polybutadiene (HTPB), and Ethylene-Propylene-Ethylidenenorbornene Terpolymer (EPDM)

No	COMPOSITION	σ_Y (MPa)	σ_B (MPa)	ϵ (%)	σ_{IM} (kJ m ⁻²)		MI (g/10 min)	T Vicat (°C)
					25°C	-20°C		
1	PVC + stabilizers	59.7	52.5	48	2.9	2.8	0.66	84.8
2	PVC + 10% CPE (21.8% Cl)	55.0	47.2	20	13.0	3.2	1.61	84.4
3	PVC + 3% HTPB	51.8	46.9	59	8.4	5.1	0.98	84.2
4	PVC + 5% EPDM	51.4	42.4	29	5.9	3.7	2.54	83.7
5	PVC + 3% HTPB + 5% EPDM	35.5	35.5	19	13.1	4.3	1.18	82.5
6	PVC + 10% CPE (21.8% Cl) + 3% HTPB	42.9	42.3	20	22.6	5.2	2.63	83.3
7	PVC + 10% CPE (21.8% Cl) + 5% EPDM	34.3	34.0	27	21.3	4.2	2.17	80.6
8	PVC + 10% CPE (21.8% Cl) + 3% HTPB + 3% EPDM	35.5	34.1	30	36.8	7.8	2.48	82.1
9	PVC + 10% CPE (21.8% Cl) + 3% HTPB + 5% EPDM	31.9	30.2	40	47.3	14.8	2.55	81.9
10	PVC + 10% CPE (21.8% Cl) + 3% HTPB + 10% EPDM	22.7	22.3	28	25.0	14.5	2.87	77.7
11	PVC + 10% CPE (10.2% Cl) + 3% HTPB + 5% EPDM	33.8	31.9	47	32.1	12.8	2.92	79.2
12	PVC + 10% CPE (27.3% Cl) + 3% HTPB + 5% EPDM	31.2	30.6	31	29.5	7.3	2.43	81.4
13	PVC + 10% CPE (37.0% Cl) + 3% HTPB + 5% EPDM	30.1	30.1	20	27.7	5.4	2.06	81.0
14	PVC + 10% CPE (45.2% Cl) + 3% HTPB + 5% EPDM	27.1	27.1	21	21.2	5.8	2.36	81.0

In our previous studies,^{49,50} we have found that PE of 21.8% Cl, chlorinated in a fluidized-bed reactor, was an efficient compatibilizer for blends of PVC with ethylene-propylene-ethylidenenorbornene terpolymer (EPDM) as well as hydroxyl-terminated polybutadiene (HTPB). The composition and the mechanical properties of various blends of PVC, CPE, EPDM, and HTPB are shown in Table II. The binary blend of PVC with 10 mass% CPE (21.8% Cl) was regarded as a basic polymer system for the multicomponent blends, since it had the highest impact strength observed. The combination of different amounts of the elastomers led to the observation that the composition, consisting of PVC, 10% CPE (21.8% Cl), 3% HTPB, and 5% EPDM had the highest impact strength (Table II, No. 9). As seen from Table II, each of the components used singly improved the impact strength of PVC; however, their joint introduction into a blend led to the multiple increase of this parameter. In this case, the impact strength was, approximately, sixteen times higher than that of PVC containing only stabilizers. Moreover, the blend of such composition had good processability because of its high flowability (MI was 2.55 g/10 min).

The use of block-copolymer with structural units, similar to the polymer components in a blend is known to regulate the size of the interfacial layer.^{16,26,45,51} The presence of both the chlorinated and nonchlorinated blocks in the solid-state chlorinated PE is one of the factors, improving the interfacial adhesion in the blends of PVC with HTPB and EPDM, since each of its blocks penetrates into the corresponding polymer phase. The extension of the interfacial area improves their impact resistance.⁴⁵ The experimental results indicated, however, that the use of CPE containing 10.2, 27.3, 37.0, and 45.2% Cl led to an impact strength of the multicomponent blend,

which was 1.5 to 2 times lower than that of the blend containing CPE with 21.8% Cl (Table II). In this connection, it should be noted that the difference in the behavior of the block-chlorinated PE as compatibilizer in the blends studied was determined by both the structure of the solid-state chlorinated PE (CPE) and its own impact strength at the corresponding chlorine content. Apparently, with CPE of ca. 22% chlorine content, the structural similarities of the chlorinated PE blocks with the PVC chains as well as those of the nonchlorinated methylene sequences with the macromolecular elastomer chains were best pronounced. As mentioned earlier, this CPE sample had the highest inherent impact strength observed (Table I).

Structure and compatibility for blends containing PVC, CPE, and elastomeric additives

The thermal transitions of PVC, CPE (21.8% Cl), and some of the polymer blends studied were determined by DSC (Fig. 8). The single polymers and their blends containing the corresponding stabilizers were indicated in the experimental section. The course of the DSC curves for the first heating runs was found to be different from that for the second ones. This is probably determined not only by the thermal history of the samples, but also by additional homogenization of the polymer blend components in the calorimeter at heating to temperatures higher than the glass-transition ones (T_g).⁵² The observed basic differences in the DSC curves are expressed as follows: (i) abnormalities in the change of heat capacity (ΔC_p) for the first heating scans of PVC and its blends; (ii) decrease in C_m of CPE in the blends when compared with T_m of the single polymer component not only for the first heating scan, but also for the second one.

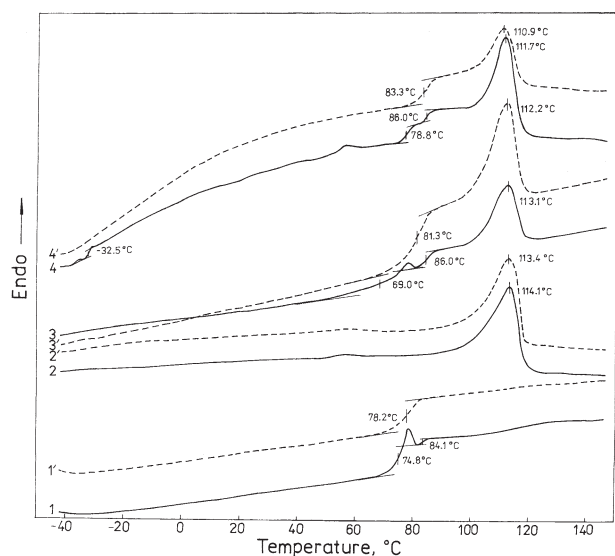


Figure 8 DSC thermograms for the first and second heating scans of (1, 1') PVC, (2, 2') CPE with 21.8% Cl, (3, 3') PVC + 10% CPE (21.8% Cl) and (4, 4') PVC + 10% CPE (21.8% Cl) + 3% HTPB + 5% EPDM.

The presence of two-step transitions in the region of vitrification of PVC and its blends suggests the formation of two glass-like phases in the polymer matrix (Fig. 8, curves 1, 3, and 4). According to Bartenev and Barteneva,⁴⁸ the multiplicity of the α -relaxation in PVC is due to various factors such as structural heterogeneity of the macromolecules involved, the existence of microregions of different conformational modes, the presence of supersegmental structures (clusters) in the amorphous polymers, the existence of interfacial layer together with the polymer matrix, etc. The stepwise course of the DSC curve of PVC, containing only stabilizers is likely to be due to the various degrees of penetration of the latter into the polymer matrix. This is particularly true for the modified dibutyltin maleate BT-22 as an additive of 4 mass % with respect to PVC. Similar course of DSC curves was observed for the studies of some PVC/plasticizer systems.^{53,54} The formation of the first glass-like phase ($T_g = 74.8^\circ\text{C}$) in this case is probably associated with the participation of more easily solvated atactic chain segments of PVC. The weakly pronounced leap in the ΔC_p values at, approximately, 84.1°C indicates that some microregions of hampered penetration of the stabilizers exist in the PVC starting material. According to Bair and Warren,⁵³ such microregions are mainly non-crystalline syndiotactic PVC sequences. If the particular course of the DSC curve of PVC for the first heating scan is neglected and the corresponding transition is regarded as a single one, a value of T_g about 76°C is obtained, which is different from T_g of PVC for the second heating scan (Fig. 8, curves 1, 1').

The registration of two-step transitions with the binary and the multicomponent blends (Fig. 8, curves

3 and 4) suggests the existence of interfacial layer together with the polymer matrix, regardless of the fact that PVC, CPE, and other additives are incompatible.^{43,50,55,56} It should be assumed, that the low-temperature values at 69.0 and 78.8°C take into account the presence of such a layer. The latter is formed because of the implementation of the corresponding segmental solubility of the contact interface of the polymers. For the PVC-CPE blend, its T_g value (69.0°C) is between the lower T_g value of PVC (74.8°C) and the T_g value of CPE (21.8% Cl), which is 15°C (Table I). The higher value of T_g for the multicomponent blend when compared with the analogous one of the binary blend suggests stronger physical interactions between the polar and polarizing groups in PVC and the additives. On the other hand, the formation of interfacial layer is likely to impose some limitations on the mobility of the PVC syndiotactic sequences, since their T_g value is higher (86.0°C), compared with the upper T_g value of only PVC (84.1°C). The values of T_g of PVC in the blends, recorded with the second heating scans, are also higher than the T_g value of PVC (Fig. 8, curves 1', 3' and 4').

One more transition from the glass-like to the highly elastic state in the low-temperatures region (-32.5°C) was registered with the multicomponent polymer blend. This transition temperature region was located between the glass-transition temperatures of EPDM (-46°C) and CPE, containing 21.8% Cl (15°C). The presence of this transition suggested the build-up of an interfacial layer with the participation of PE component of CPE and similar structural units (CH_2 -sequences) derived from the elastomer additives.

The single melting peak on the DSC curves of the samples showed that only one crystalline phase formed by the nonchlorinated CH_2 groups in the block-chlorinated PE existed there (Fig. 8, curves 2–4). By using the DSC method, it was found that the elastomer additives studied were amorphous substances. Shift of the peak maximum toward the lower temperatures was observed with the binary as well as the multicomponent blend. The change in the T_m for the crystalline phase of the PVC-CPE blend was small ($\Delta T = 1^\circ\text{C}$) and was probably associated with the corresponding influence of the interfacial layer. The non-crystallizing structural units of the latter, consisting of PVC segments and chlorinated CH_2 sequences, located in the vicinity of PE crystallites, appear to slightly affect the structural arrangement of the latter. With the PVC-CPE blend and the elastomers, the decrease in T_m was more pronounced ($\Delta T = 2.4^\circ\text{C}$). The increase in the degree of deficiency of the PE crystallites was probably related to both the influence of the interfacial layer and possibilities of inclusion of segments from the elastomers in their surface layers predominantly. This assumption corresponds to the structural model proposed by Lee and Chen,²⁹ accord-

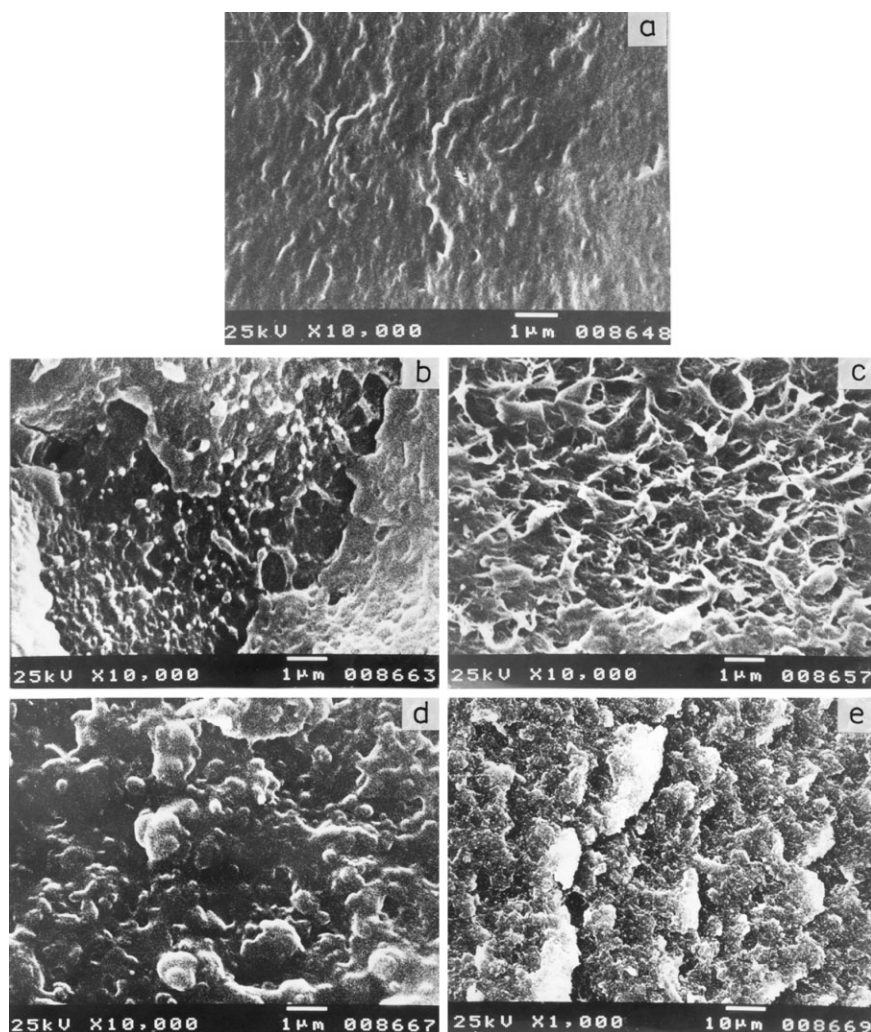


Figure 9 Scanning electron micrographs of fracture surfaces of (a) PVC and its blends with (b) 5% CPE (21.8% Cl), (c) 10% CPE (21.8% Cl), (d) and (e) 10% CPE (21.8% Cl) + 3% HTPB = 5% EPDM.

ing to which the elastomer is preferably located within the boundary layers of the CPE phase and, more rarely, in its internal part. The repeated scan of the samples registered an additional decrease of T_m for CPE studied as a single polymer or as component in the blends (Fig. 8, curves 2'–4'). Apparently, this suggests some disturbance in the perfection of its crystalline phase and should be regarded as consequence from the efficient blending of the sample components.

The slightly pronounced transition at ca. 52°C observed on the DSC curve of CPE at the first heating scan can be related to certain type of segmental mobility in specific regions of the nonchlorinated PE blocks, located between the lamellas (Fig. 8, curve 2). According to Berstein et al.^{52,57} the relaxation transition in the temperature region of 27–97°C is associated with different types of motions; however, the predominant part of the latter occurs within the weakly bent passing chains and the short folds, located within the

amorphous layers of PE. This type of motions is usually limited by the presence of PE crystallites. Regardless of this, similar higher-intensity transition at ca. 54°C was observed with the multicomponent blend (Fig. 8, curve 4). In this respect, it can be assumed that some relaxation segments of identical character are present in the nonchlorinated PE block fragments and the amorphous EPDM, located between the lamellas.

The microphotographs of fracture surfaces of PVC and some of the blends studied are shown in Figure 9a–e. The break at impact of the PVC starting material was, typically, brittle but one can see the obvious particulate morphology of the nonfused PVC (Fig. 9a). The primary PVC particles and their aggregates were well distinguishable, since the blending of PVC with the stabilizers took place within the temperature range of 172–178°C, i.e., below their melting point. It is usually presumed that at temperatures above 190–195°C the structure of the primary particles is destroyed.^{58,59}

The structure of the blend, consisting of PVC and 5 mass% CPE (21.8% Cl) was rather heterogeneous (Fig. 9b). Some regions can be noticed on the microphotograph, in which separate PVC particles and their aggregates are covered by CPE phase. Other regions are characterized by initial formation of network structure. The discontinued network structure, on the other hand, is less efficient on impact influence than the continuous one^{6,60} and the latter was observed for the PVC blend with 10% CPE (Fig. 9c). This structure is similar to that detected for the first time by means of SEM analysis by Fleischer et al.,⁶¹ who have studied blends of PVC with PE, chlorinated in an aqueous suspension and containing 36–40% Cl. The critical concentration of CPE in its blends with PVC is usually ca. 10 mass%, as confirmed also by the present study. According to Siegmann and Hiltner,⁶ the formation of a two-phase network structure was due to the inherent incompatibility between PVC and CPE as well as the particulate nature of PVC.

The morphology of the multicomponent system, consisting of PVC, 10% CPE, 3% HTPB, and 5% EPDM is shown in Figures 9(d) and 9(e) at different magnification values, which are $\times 10,000$ and $\times 1000$ respectively. With the higher magnification, various sizes of PVC particles as well as their aggregates were observed, which were relatively uniformly covered by the phase of impact-resisting modifiers. Even with the lower magnification, the formed domain structure of CPE and the elastomers was well pronounced. These structural formations obviously acted like a binding substance between the globular surfaces of the PVC particles and effectively took the load caused by the impact,⁵⁹ since the impact strength of the multicomponent blend had the highest value observed (47.3 kJ m^{-2}). Therefore, the change in the morphology of the blends, particularly, the transition from brittle to ductile breakage corresponded to the increase of their impact resistance.

CONCLUSIONS

CPE of different chlorine content has been prepared by the solid-state chlorination of HDPE at temperatures below its melting temperature. The strength-deformation indices of CPE as a function of its degree of chlorination are described. The chlorine content of 5–15% in the CPE prepared by solid-state chlorination is associated with a rather high elasticity and good mechanical properties.

The influence of the chlorinated PE of a mixed amorphous-crystalline structure with 10.2–54.8% chlorine content on both the mechanical properties and structure of PVC is studied. Added in small amounts to PVC (1–3 mass%), PE chlorinated in a fluidized-bed reactor acts as a structural lubricant. CPE, containing chlorine below 30% and, more particularly, 22% ap-

pears to be a convenient impact-resisting modifier for the PVC material, because of its high impact strength and good elasticity. On the other hand, the chlorinated sequences of CPE, containing around 22% Cl indicates the best pronounced structural similarity with the PVC polymer chains and such similarity also exists between the nonchlorinated methylene sequences and the macromolecular chains of the elastomer additives. As a result, the formation of an efficient interfacial layer is facilitated, which leads to an increased impact resistance of the polymer blends. The calorimetric and microscopic studies prove the heterogeneous nature of the blends. The formation of continuous network structure represents characteristic feature of the two-component systems based on PVC and CPE with 21.8% Cl.

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