

Plastification of Poly(vinyl chloride) by Polymer Blending

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ABSTRACT: Blends of poly(vinyl chloride) (PVC) with different copolymers have been studied to obtain a plasticized PVC with improved properties and the absence of plasticizer migration. The copolymers used as plasticizers in the blends were acrylonitrile butadiene rubber, ethylene vinyl acetate (EVA), and ethylene-acrylic copolymer (E-Acry). Blends were studied with regard to their processing, miscibility, and mechanical properties, as a function of blend and copolymer composition. The results obtained were compared with those of equivalent compositions in the PVC/dioctyl phthalate (DOP) system. Better results than PVC/DOP were obtained for PVC/acrylonitrile butadiene rubber blends. The plasticizing effect on PVC of EVA and E-Acry copolymers was similar to that of DOP. It is shown that crosslinking PVC/E-Acry blends or increasing the vinyl acetate content in PVC/EVA blends, are alternatives that can increase the compatibility and mechanical properties of these blends. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1303–1312, 2000

Key words: poly(vinyl chloride) blends; PVC plasticizers; polymeric plasticizers; blends interaction; PVC compounding

INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the commodity polymers with the highest consumption of merchandise. Applications of this polymer are derived from a wide range of mechanical requirements, ranging from a rigid material with a high modulus to plastisols of great flexibility, passing through a suite of intermediate states whose mechanical behavior depends on the amount of plasticizer added.^{1–3}

PVCs plasticized with low molecular weight compounds (conventional plasticizers) have an application limit in time and temperature, because of the migration phenomena of these plas-

ticizers, leading to a rigidification of the material thus becoming unable to serve. On the other hand, the migration of plasticizers is a subject of much discussion in the use of plasticized PVC in medical and food packaging applications.^{4–11}

The utilization of high molecular weight plasticizers could be a possible solution to this type of problem. In this respect, polymer blends have an important role, such as PVC/polymer blends in which the second component is a highly flexible polymer, since they have a mechanical behavior similar to that of common plasticized PVC, but without plasticizer migration. However, in this case it is primordial to consider the study of miscibility and compatibility of these blends, given that the final mechanical properties depend on these factors.

During recent years a great number of studies on blends of PVC with other polymers have been performed in different media, and recently these studies have been extended to blends with copol-

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Table I Characteristics of the Materials Used in the Blends

Compound	Specifications/Composition	Company
Poly(vinyl chloride) (PVC)	RB 8010 bulk polymerized	Elf Atochem (Burgos, Spain)
Poly(vinyl chloride) (PVC1)	Etinox-400 5% (molar) in vinyl acetate	Aiscondel (Huesco, Spain)
Butadiene-Nitrilic rubber (NBR1)	Krynac 50.75 50.75% (molar) in acrylonitrile	Polysar Ltd.
Butadiene-Nitrilic rubber (NBR2)	Krynac 29.60 29.60% (molar) in acrylonitrile	Polysar Ltd.
Poly(ethylene-co-vinyl acetate) (EVA)	27% (molar) in vinyl acetate	Repsol (Madrid, Spain)
Poly(ethylene-co-vinyl acetate) (EVA1)	33% (molar) in vinyl acetate	Repsol (Madrid, Spain)
Poly(ethylene-co-vinyl acrylate-acrylate) (E-Acry)	Vamac-G	DuPont
Dioctyl phthalate (DOP)	Plasticizer	Jaber (Spain)
Calcium stearate	Thermal stabilizer	Panreac (Spain)
Zinc stearate	Thermal stabilizer	Panreac (Spain)
Diak no. 1	Crosslinking agent	DuPont

ymers such as acrylonitrile butadiene rubber (NBR), styrene-acrylonitrile rubber (SAN), ethylene vinyl acetate (EVA), acrylic copolymers, and others.¹²⁻²⁹ In this research, the use of calorimetric and thermogravimetric measurements, infrared spectroscopy, X-ray diffraction, microscopy, and viscosimetry, has shown that in all the systems studied the miscibility of the blend depends on its composition and on the composition of the copolymer used.

The method and conditions of preparation of the blends has an enormous influence on the final properties of the materials. Mixing in a Rheocord system is the most suitable process from a technological viewpoint. In this respect, in our laboratory we have performed a extensive study on continuous and discontinuous reactive processing of PVC to correlate processing parameters, polymer structure, and polymer properties.³⁰⁻³⁵ The same methodology can be applied for studies of PVC blending with different compounds.

In the present work, results obtained on the preparation in the melt of blends of PVC with NBR, EVA, and an ethylene-vinyl acetate (VA)-acrylic copolymer, and the study of their miscibility and mechanical properties, are presented. Blends with modified PVC are also studied. All results are compared with that of a PVC plasticized with a low molecular weight compound, dioctyl phthalate (DOP).

EXPERIMENTAL

Materials

Information on the polymers and additives used is given in Table I. The composition of ethylene-VA-acrylic copolymers (denominated E-Acry to differentiate from EVA), determined by ¹H-nuclear magnetic resonance, was found to be 75.5 % ethylene and 23.5 % VA (mol %). The remaining 1% corresponds to a third unit derived from acrylic acid. This third monomer unit allows the crosslinking of the copolymer.

Preparation of Blends

Components of the blend were premixed in a glass beaker and the powdered dispersion obtained was processed in a Haake Rheocord 9000, using a Rheomix 600 mixer and roller blade rotors, at 150°C and 40 rpm for 5 min. The composition of the different blends processed is shown in Table II. Blends thus prepared were molded into sheets of 2-mm thickness by pressing in a Collin laboratory press, at 150°C and 50 bar for 2 min, followed by cooling at 15°C and 50 bar for 1 min.

Preparation of Crosslinked Blends

The crosslinked blends of PVC/E-Acry were obtained in a similar manner. To avoid the thermal degradation of PVC during the curing process at

Table II Weight Composition of Blends

Blend Components	Composition (wt %)
PVC/NBR1	85 : 15 80 : 20 75 : 25 70 : 30 65 : 35 60 : 40 55 : 45 50 : 50 40 : 60
PVC/NBR2	85 : 15 80 : 20 75 : 25 70 : 30 65 : 35 60 : 40 55 : 45 50 : 50
PVC/EVA	85 : 15 80 : 20 70 : 30 60 : 40 50 : 50 20 : 80
PVC/EVA1	70 : 30
PVC1/EVA1	70 : 30
PVC/E-Acry	85 : 15 70 : 30 65 : 35 60 : 40 55 : 45 50 : 50
PVC/E-Acry (crosslinked)	70 : 30
PVC/DOP	85 : 15 80 : 20 70 : 30 60 : 40 50 : 50

high temperature, 1 phr of a mixture 50:50 of Zn and Ca stearates was added to the initial premixture of components. Processing was performed at 120°C and 40 rpm. After 6 min of blending, 0.3 phr of the crosslinking agent Diak no. 1 was added directly into the mixer, and 4 min later the mixing was terminated. The hot blend is then molded into sheets by pressing at 177°C and 50 bar for 20 min to complete the crosslinking, and cooled at 15°C and 50 bar for 1 min.

Differential Scanning Calorimetry (DSC)

Thermal analysis of the blends was performed in a Perkin-Elmer DSC4 differential scanning calorimeter in the range of -70 to 120°C at a heating rate of 10°C/min. After two scans, glass transition temperatures (T_g s) were measured as the transition midpoint, and melting temperature as the peak maximum.

Mechanical Properties

The Young modulus, ultimate tensile strength, and elongation at break were determined from a

traction test in a universal dynamometer Instron 4301. Tests were performed on dumbbell probes with a width of 4 mm in the elongation zone and a thickness of 1.8–2.2 mm. Samples were tested at room temperature, using a 0.1 KN load cell, with a testing speed of 50 mm/min. Measurements for crosslinked samples were taken at 140°C.

RESULTS AND DISCUSSION

Processing

To compare the processing characteristics of different blends, final torque and final melt temperature values (after 5 min) of PVC/NBR and PVC/DOP are plotted in Figure 1 as a function of the blend composition. Whereas in the later case the magnitude of both decrease with the concentration of plasticizer, for PVC/NBR blends it can be observed that the closest values in torque and temperature are obtained independently of blend composition, thus indicating

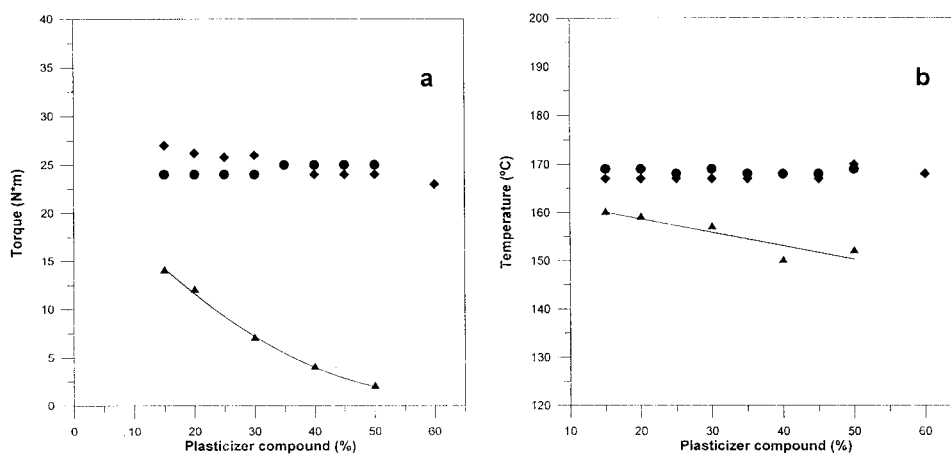


Figure 1 Processing parameters of blends processed at 150°C and 40 rpm for 5 min, as a function of blend composition. (a) Final torque; (b) final melt temperature. ◆ PVC/NBR1; ● PVC/NBR2; ▲ PVC/DOP.

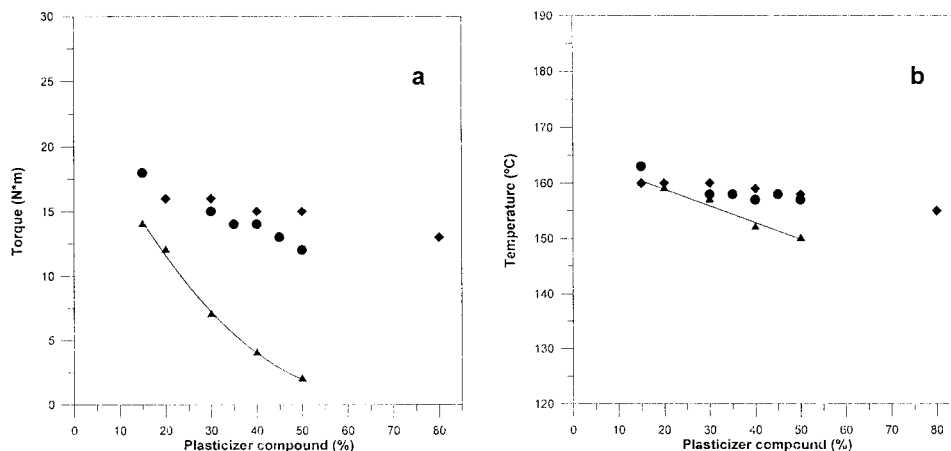


Figure 2 Processing parameters of blends processed at 150°C and 40 rpm for 5 min, as a function of blend composition. (a) Final torque; (b) final melt temperature. ◆ PVC/EVA; ● PVC/E-Acry; ▲ PVC/DOP.

that the shear stress during processing remains practically constant with composition, because of the similar viscosity of the molten components of the blends. On the other hand, in Figure 2 it can be observed that for PVC/ethylene copolymer blends, the torque and temperature decrease as the concentration of the plasticizer increases, as consequence of the diminishing shear stress in their processing.

The measurement of total torque allows us to evaluate the energy consumption during the overall process. A comparison of the torque for all blends studied, as a function of their composition, is shown in Figure 3. The different behaviors between PVC/polymer blends and the PVC/DOP system can be clearly observed—the first with a slow decrease in total torque as the amount of plasticizer increases, and the second with a sharp decrease that quickly leads to a minimum value of total torque. Differences in the magnitude of this parameter between the blends with NBR and with ethylene copolymers are due to the different melt viscosities.

In the particular case of PVC/EVA blends, the study has been broadened to the preparation of blends with a vinyl chloride-*co*-vinyl acetate copolymer and EVA copolymers with different contents in VA. The processing data from these blends is given in Figure 4. The most significant differences appear in torque and total torque data, such that their magnitudes decrease as the VA content increases in both polymers, thus favoring the processing of the blend.

Miscibility of Blends

The miscibility of the blends was evaluated as a function of their thermal behavior, observed by DSC, as described in Experimental.

PVC/NBR Blends

The results obtained for PVC/NBR blends are shown in Figure 5. For both types of PVC/NBR

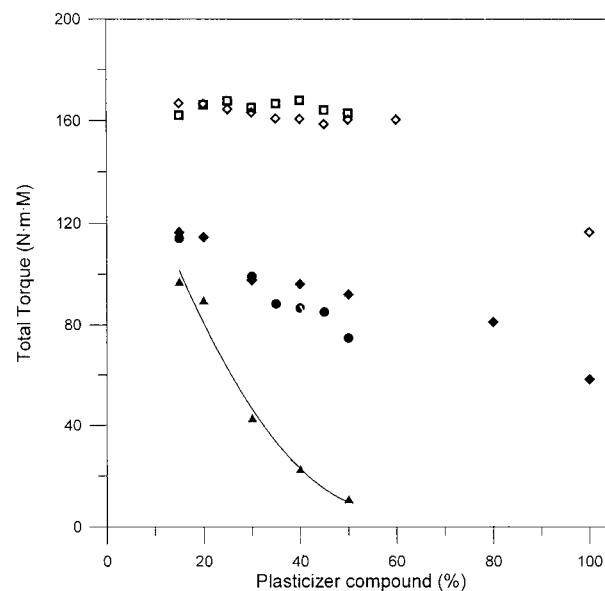


Figure 3 Total torque of blends processed at 150°C and 40 rpm for 5 min, as a function of blend composition. ◇ PVC/NBR1; □ PVC/NBR2; ◆ PVC/EVA; ● PVC/E-Acry; ▲ PVC/DOP.

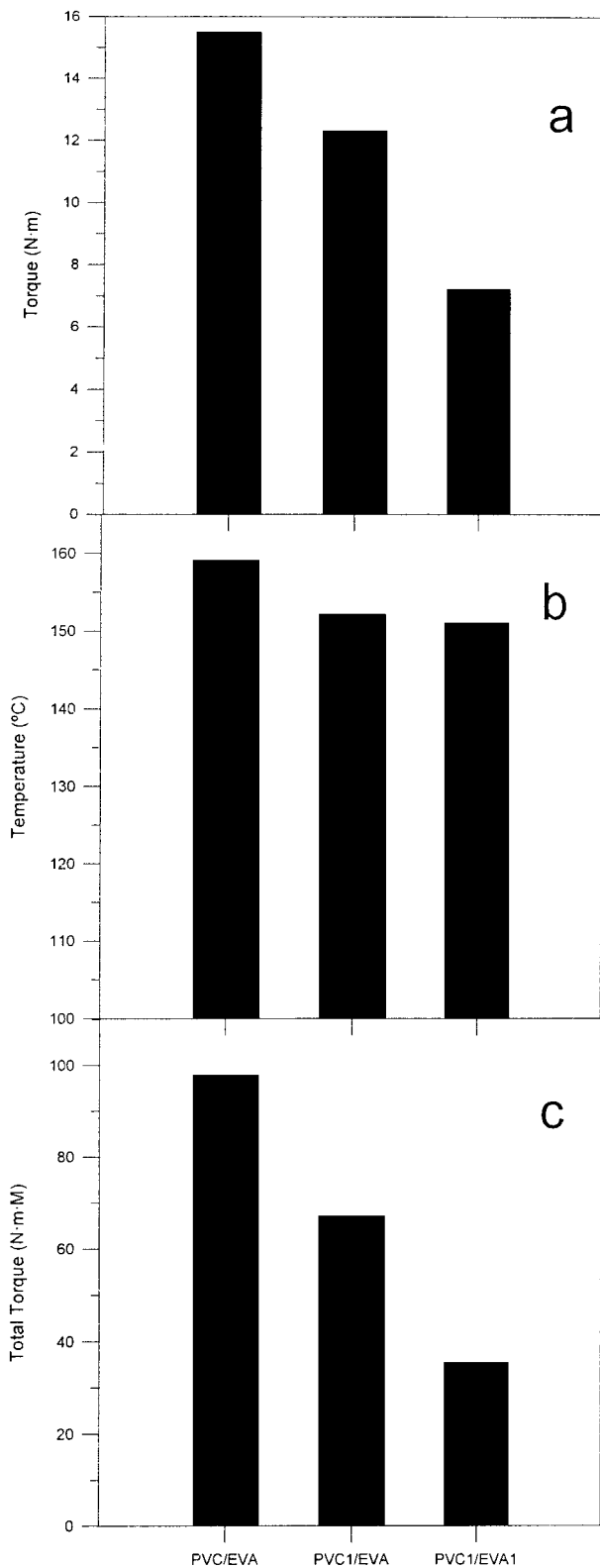


Figure 4 Dependence of processing parameters on the VA content of the polymeric components in PVC/EVA (70:30) blends processed at 150°C and 40 rpm for 5 min. (a) Final torque; (b) final melt temperature; (c) total torque.

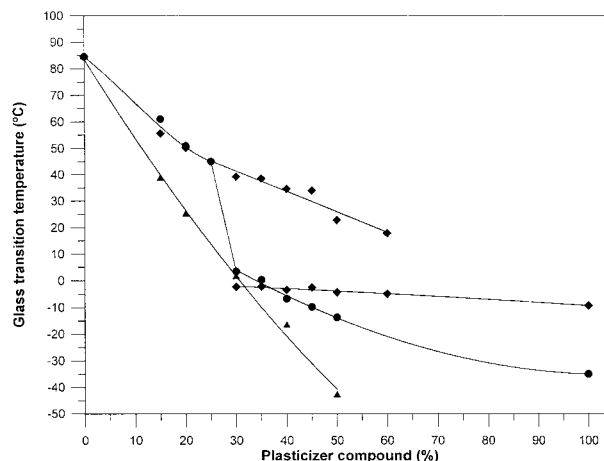


Figure 5 Glass transition temperatures of blends as a function of blend composition. ♦ PVC/NBR1; ● PVC/NBR2; ▲ PVC/DOP.

blends at concentrations lower than 30% of NBR, a single T_g value is found, thus indicating miscibility. However, for higher values in the NBR concentration, the behavior of blends with NBR1 or with NBR2 is different. In the case of PVC/NBR1 blends, two T_g values were observed, indicating phase segregation. Both T_g values are located between the corresponding values of the raw polymers, in agreement with the existence of interactions between phases and their partial miscibility. On the other hand, for PVC/NBR2 blends, the miscibility is maintained at concentrations of NBR2 above 30%, with T_g values close to that of those NBR2. This fact can have some

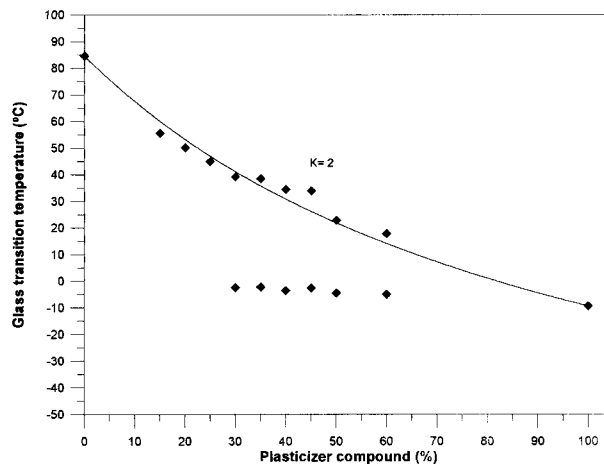


Figure 6 Glass transition temperatures of blends as a function of blend composition. ♦ T_g PVC/EVA; ● T_g PVC/E-Acry; ▲ T_g PVC/DOP; T_m PVC/EVA (Y axis at right).

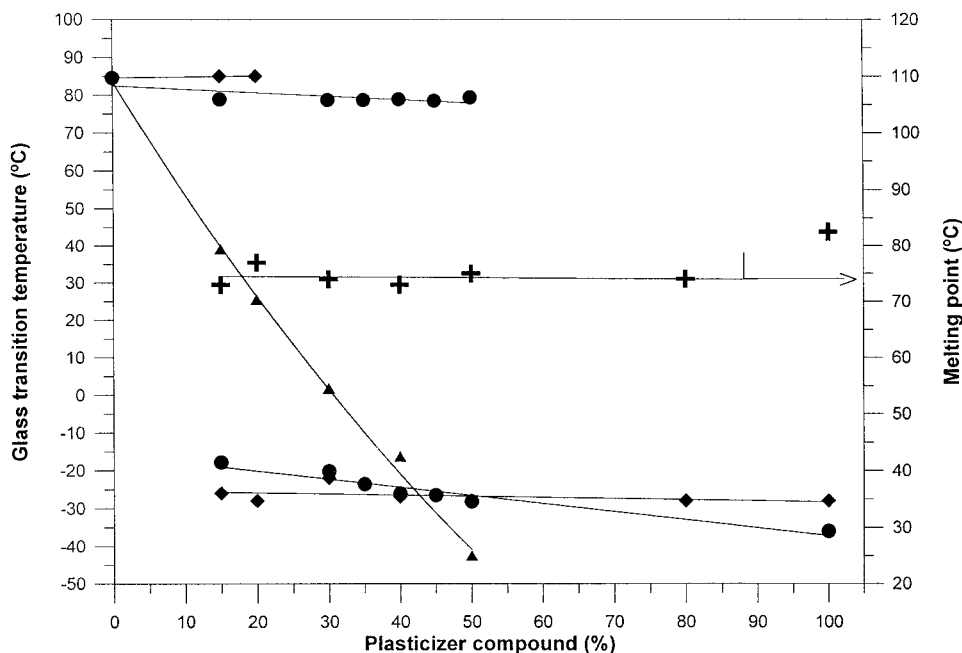


Figure 7 Glass transition temperature of PVC/NBR1 blends as a function of blend composition. \blacklozenge Experimental points. — Gordon-Taylor equation plot ($k = 2$).

consequences on mechanical properties, as will be seen below. Finally, for the PVC/DOP system, a drastic decrease in T_g can be observed as the concentration of plasticizer increases.

The T_g -composition behavior has been modeled in the case of PVC/NBR1 blends. Shown in Figure 6 are comparisons of the experimental results with those predicted by the Gordon-Taylor equation. It can be observed that the experimental values fit those of a miscible blend (also shown in Figure 6 is the second T_g corresponding to the immiscible phase).

PVC/Ethylene Copolymer Blends

In Figure 7 evolution of the thermal transitions of PVC/EVA and PVC/E-Acry blends as a function of

their composition is shown. Although not illustrated here, it was observed that the peak corresponding to the melting of crystalline sequences in EVA overlaps with the glass transition of PVC. Thus, only for blends with a low content in EVA was it possible to measure the T_g of the PVC domains. The existence of two T_g values in the whole range of compositions studied can be clearly appreciated for both systems, corresponding to values close to those of the raw polymers compounded in the blend, thus indicating the complete immiscibility of these blends. In the case of PVC/EVA blends, the melting point of EVA, plotted in Figure 7, is invariant at all compositions, thus supporting the conclusion of the immiscible character of the blends.

Table III Glass Transition Temperatures and Melting Points of PVC/EVA Blends

Blend	T_g PVC (°C)	T_g EVA (°C)	T_m EVA (°C)	ΔH_m EVA (Cal/g)
Raw PVC	84.6	—	—	—
Raw PVC1	81.7	—	—	—
Raw EVA	—	-27.8	82.5	130
PVC/EVA (70 : 30)	?	-21.7	73.6	100
PVC1/EVA (70 : 30)	?	-17.5	73.4	99
PVC1/EVA1 (70 : 30)	?	-13.0	65.1	57

To obtain a greater understanding of the miscibility behavior of PVC/EVA blends, additional investigations with different EVA and a vinyl chloride-co-vinyl acetate copolymers were carried out. Data for the thermal transitions of blends prepared are shown in Table III. These results suggest two different methods to improve the miscibility of PVC/EVA blends. First, comparing PVC1/EVA and PVC1/EVA1 blends, it can be observed that by increasing the VA content in EVA from 27% (molar) to 33% (molar), a decrease in crystallinity takes place (T_m and ΔH_m decreases) because of the diminishing size and number of ethylene sequences. On the contrary, the increase in the T_g EVA value could be explained in terms of the increase of the polymer blend interaction. Second, comparing the PVC/EVA PVC1/EVA blends, it can be concluded that the presence of 5% (molar) of VA in PVC does not affect the crystalline fraction of EVA, but the amorphous increases its interaction with PVC, leading to an increase in T_{gEVA} .

Mechanical Properties

The mechanical properties of the blends were evaluated using a traction test, performed as described in Experimental. From these experiments, the Young's modulus, ultimate tensile strength (UTS), and elongation at break were determined for the blends and compared with the results for the PVC/DOP system.

PVC/NBR Blends

The evaluation of the mechanical properties as a function of blend composition is shown in Figure 8. For Young's modulus [Fig. 8(a)] and UTS [Fig. 8(b)], it can be observed that the behavior of the PVC/NBR blends is similar to that of the PVC/DOP system, although for PVC/NBR1 blends, the Young's modulus for determined composition is significantly higher than for PVC/NBR2 or PVC/DOP, because of the high content of acrylonitrile in NBR1. For elongation at break [Fig. 8(c)], differences in behavior of PVC/NBR blends and PVC/DOP are clearly shown. The elongation for PVC/NBR blends is much lower than for PVC/DOP, being shorter with increasing acrylonitrile content in NBR. It can be concluded from the mechanical properties that the general behavior of PVC/NBR blends is similar to that of the PVC/DOP systems, but it is possible to improve some of the properties, such as toughness, as a function of the nature of the blend.

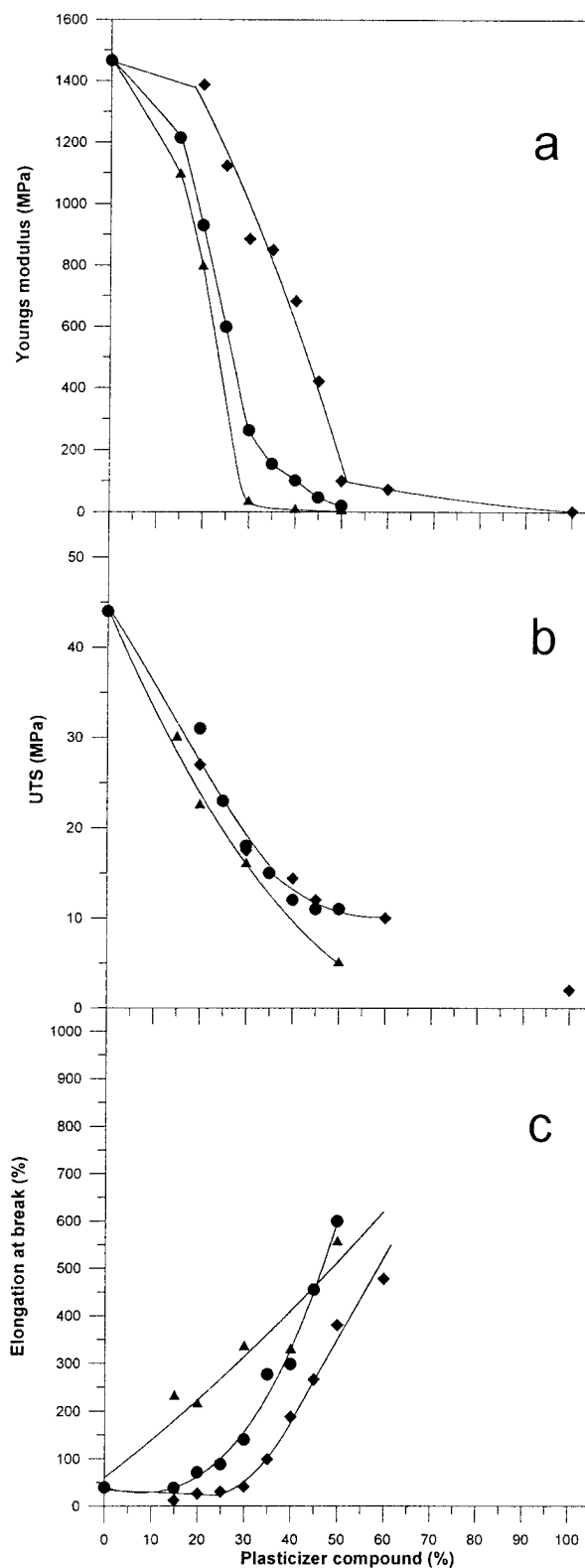


Figure 8 Mechanical properties of blends as a function of blend composition. (a) Young's modulus; (b) ultimate tensile strength; (c) elongation at break. \blacklozenge PVC/NBR1; \bullet PVC/NBR2; \blacktriangle PVC/DOP.

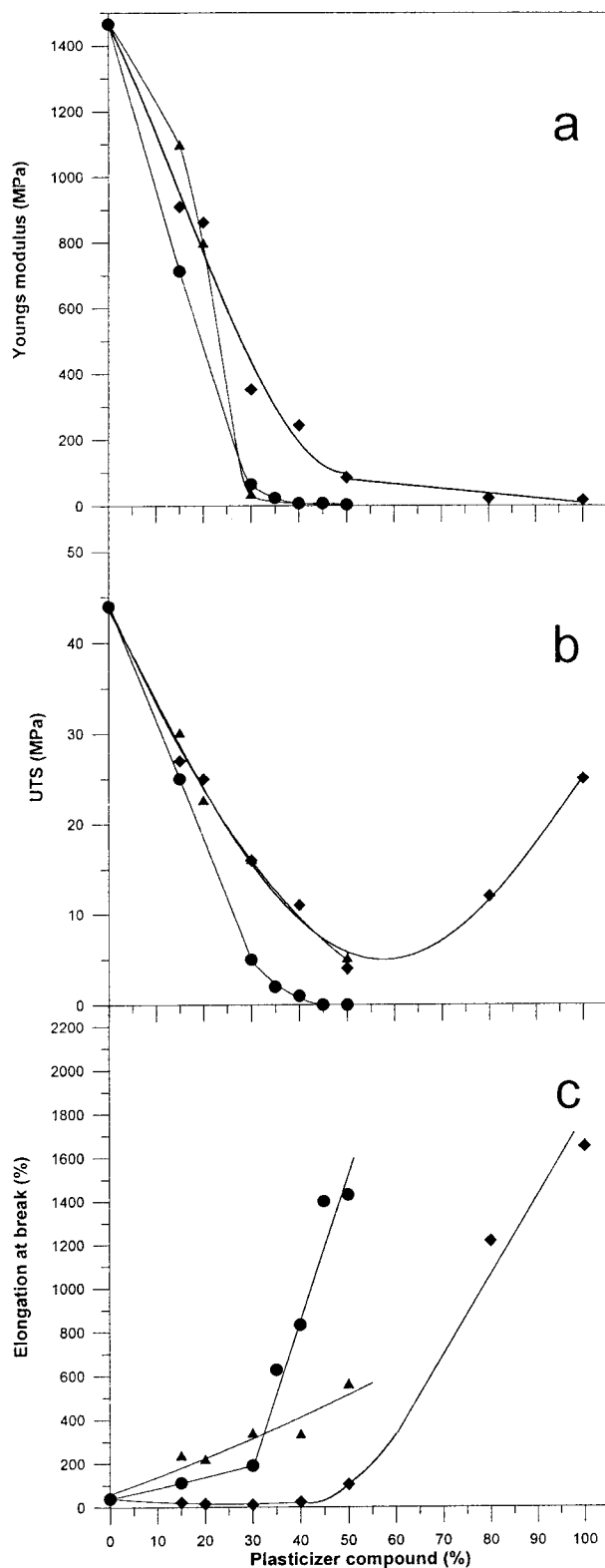


Figure 9 Mechanical properties of blends as a function of blend composition. (a) Young's modulus; (b) ultimate tensile strength; (c) elongation at break. \blacklozenge PVC/EVA; \bullet PVC/E-Acry; \blacktriangle PVC/DOP.

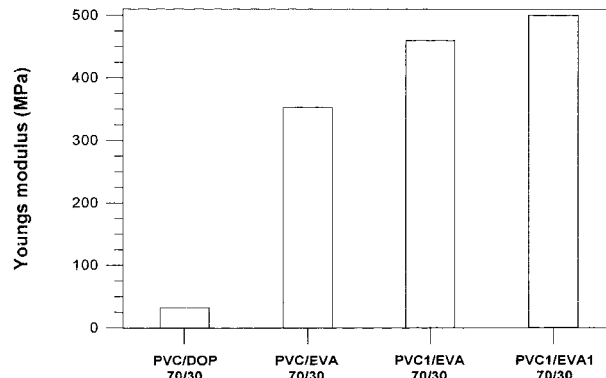


Figure 10 Dependence of the Young's modulus on VA content of the polymeric components in PVC/EVA (70:30) blends.

PVC/Ethylene Copolymer Blends

The evolution of the mechanical properties of PVC/EVA and PVC/E-Acry blends as a function of composition is presented in Figure 9, and compared with that of PVC/DOP. For PVC/E-Acry blends, a highly plasticizing effect of E-Acry can be observed, which leads to a sharp decrease in the Young's modulus and UTS, and to large elongations, even for low E-Acry contents. The solution to this undesirable effect will be discussed below. On the other hand, the PVC/EVA blends show a different behavior, fundamentally in the evolution of the UTS [Fig. 9(b)], where it can be observed that the values for the blends are significantly lower than those for the raw polymeric components of the blend, thus indicating the incompatibility of these blends.

As in the case of the study of the thermal behavior, the study of the mechanical properties of the PVC/EVA blends has been extended to blends prepared with polymers with a varying VA content. The most relevant differences in the mechanical properties were found in the values of the Young's modulus. These results are plotted in Figure 10, where it can be observed that the Young's modulus increases as the VA content is higher in any of polymeric blend components. This could be considered in some way as a compatibilizing effect, being more apparent when VA is present in PVC than when the VA content in EVA is increased. These results are interesting from a technological viewpoint because they indicate the possibility of increasing the compatibility of PVC/EVA blends without decreasing crystallinity of EVA, which could be useful in some applications.

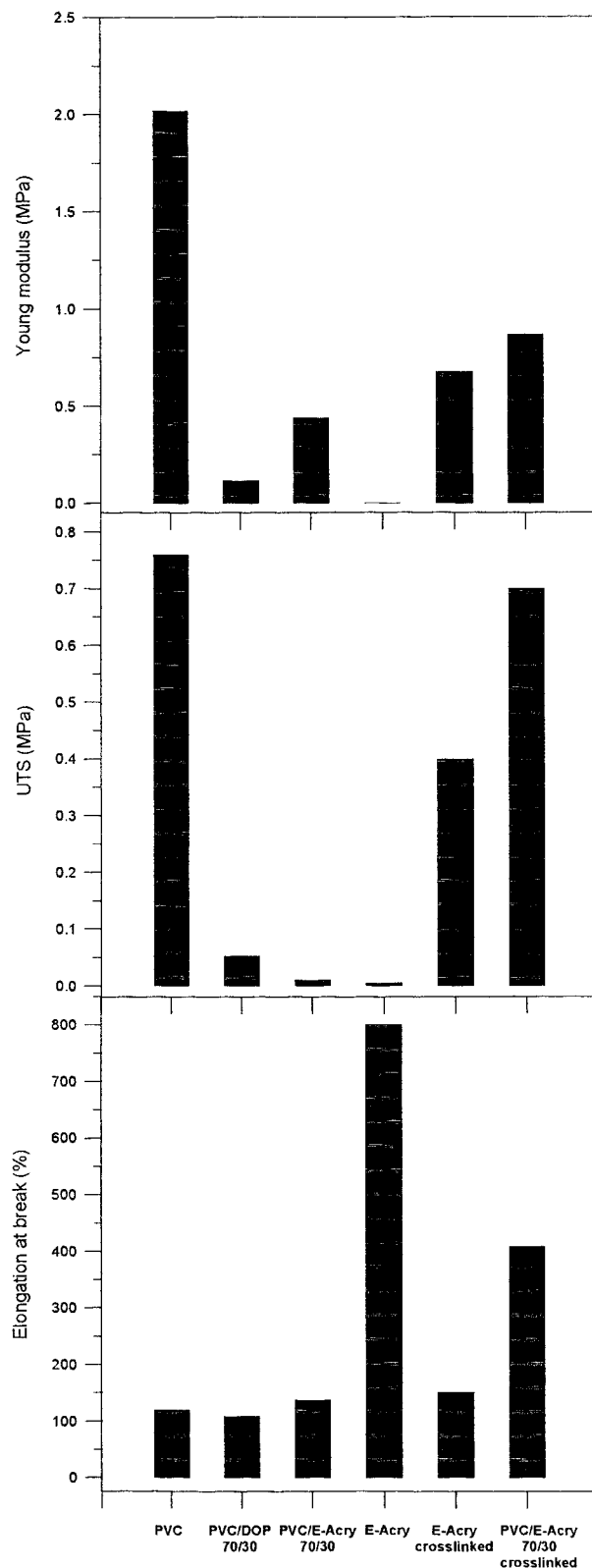


Figure 11 Comparison of mechanical properties of crosslinked and uncrosslinked PVC/E-Acry blends. (a) Young's modulus; (b) ultimate tensile strength; (c) elongation at break.

Crosslinked PVC/E-Acry Blends

As explained above, PVC/E-Acry blends are characterized by a high plasticizing effect, greater than that of DOP, very large elongations, and poor values in Young's modulus and UTS. As described in Experimental, E-Acry is in fact a terpolymer in which one of the monomers allows the crosslinking of the polymer. The concentration of this third monomer is approximately 1% (molar), thus the reticulation of the blends leads to the formation of a weak network. As shown in Figure 11, where results of the traction test at 140°C are plotted for this system, together with those of the uncrosslinked polymers and the PVC/DOP system, crosslinking leads to an improvement in the mechanical properties. In the case of the results from UTS, the values are similar to those for raw PVC. We can conclude that the behavior of the crosslinked blend corresponds to that of a highly plasticized PVC matrix reinforced by the presence of a network of crosslinked E-Acry microdomains.

CONCLUSIONS

The aim of this study was to test the use of specific polymers as plasticizers for PVC. In the case of PVC/NBR blends, the results show that the processing parameters are similar to that of PVC. The miscibility of these blends depends on their composition and on the acrylonitrile content in NBR. Thus, it is possible to obtain plasticized PVCs with higher moduli and shorter elongations in comparison with the PVC/DOP system.

On the other hand, for PVC/ethylene copolymer blends, processing is almost the same as that for PVC/DOP, although immiscibility is found for all the blends studied. In the particular case of PVC/EVA blends, the study of the mechanical properties demonstrates incompatibility in these blends. Additional studies have permitted the improvement of compatibility, by increasing the VA content in EVA or using vinyl chloride-co-vinyl acetate copolymers in the blend preparation. Finally, for PVC/E-Acry blends, excessive plastification is observed. However, it can be resolved by crosslinking the blend, leading to a typically plasticized material with quite good mechanical properties.

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