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Modification of porous PVC particles with polyacrylate elastomers using a surfactant-free aqueous dispersion polymerization technique

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Abstract: The modification of porous suspension-type polyvinyl chloride (PVC) particles by an *in-situ* stabilizer-free polymerization/crosslinking of a monomer solution absorbed within the PVC particles is presented. The modifying polymers are polybutyl acrylate (PBA) and polyethylhexyl acrylate (PEHA) crosslinked with ethylene glycol dimethacrylate (EGDMA). The effect of the unique blending procedure on the physical and mechanical properties of PVC has been investigated. The modified PVC characterizations includes polymerization yield, transparency, fracture surface morphology, thermal stability, dynamic mechanical properties, tensile properties, impact resistance and melt rheology. The polymer chains formed are dispersed as a separate phase as observed by scanning electron microscopy (SEM), and two separate glass transitions are observed by dynamic mechanical thermal analysis (DMTA) system, typical of immiscible polymer blends. Mechanical properties of PVC/PEHA blends reveal a substantial increase in impact strength particularly when the blend is crosslinked; however, there is a decrease in the yield stress and elastic modulus. A shift from brittle failure to ductility has been observed in blends of PVC on incorporation of PEHA. SEM studies have been carried out to support these observations.

Introduction

Blending to achieve a microheterogeneous mixture of two or more polymers is a well-known method used to improve mechanical, environmental and rheological properties of polymers [1]. Accordingly, the inherent problems of poor impact strength and difficult processing of rigid polyvinyl chloride (PVC) have been reported to be overcome through the process of blending with certain other polymeric materials which are referred to as impact modifiers and processing aids [2]. Since in these blends the identity of the components is preserved, performance characteristics depend on size and shape of the component phases [1]. Efficient impact modifiers for PVC are immiscible with PVC aiming at formation of discrete domains, and having a strong interfacial bonding to the matrix to permit efficient stress transfer across the interface [3]. Impact strength has been reported to have increased by mixing under appropriate conditions of certain acrylic polymers and copolymers with PVC [2, 4, 5].

The semi-interpenetrating polymer network, semi-IPN, can be achieved by *in-situ* polymerization/crosslinking of a given monomer in the presence of a linear polymer [6]. The formation of semi-IPN is generally known to enable control of phase separation [7], promote compatibility between immiscible polymer pairs [7-10], and thus provide a method for generation of desired properties.

In the present study, a route for producing semi-IPNs based on PVC and polybutyl acrylate (PBA), or polyethylhexyl acrylate (PEHA), crosslinked with ethylene glycol dimethacrylate (EGDMA) is described. The semi-IPNs are prepared by an *in*-situ stabilizer-free polymerization/crosslinking of a monomer/crosslinker/peroxide solution absorbed within the porous commercial suspension-type PVC particles. The modification procedure is also described in a previous publication [11]. The modifying polyacrylates are well-known to be rubbery in character having glass transition temperatures T_gs well below room temperature, and thus have the potential to act as stress concentrators and induce energy dissipation by crazing and shear yielding of the matrix [12]. The *in-situ* polymerization method, thermal, physical and mechanical properties of these blends, along with the study of their morphology have been carried out.

Results and discussion

Morphology

Freeze fracture surface morphology of the neat PVC after melt compounding in a Plastograph cell (210 °C) or twin screw extruder (180 °C) is illustrated in Figs. 1a-b, respectively. The PVC smooth surface is observed with characteristic freeze fractured lines. The observed small spherical particles, about ~ 0.1 μm, dispersed in the PVC matrix are lubricant particles, in accordance with Narkis *et al.* description [8].

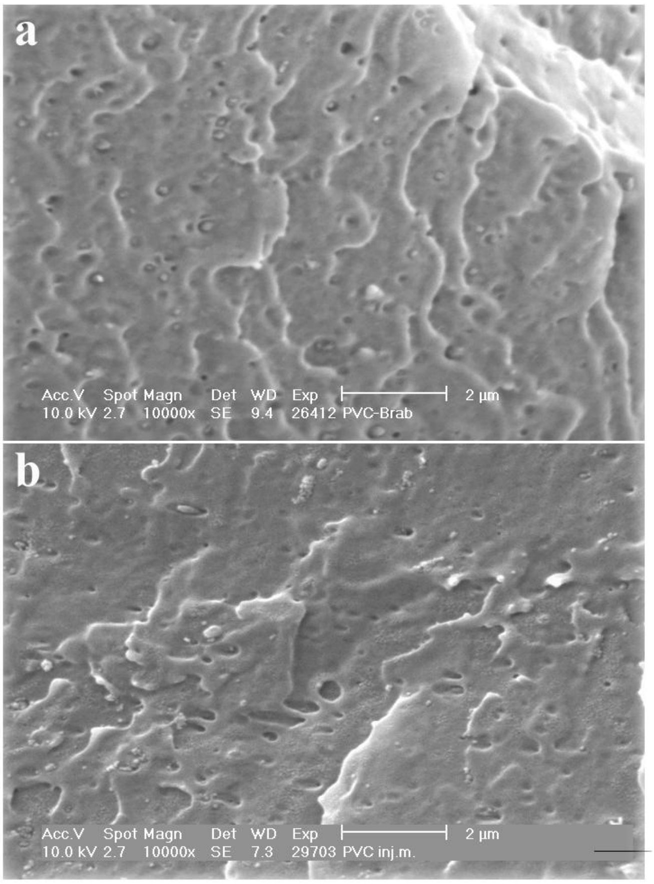

Fig. 1. SEM micrograph of freeze fractured PVC after (a) Brabender and compression molding and (b) extrusion and injection molding.

The two PVC/polyacrylate blends produced are not transparent (Table 1) and by using SEM, two phases are observed (Figs. 2-3). As shown in Fig. 2a, the PBA round particles, with an average size of about 0.3 µm, are homogeneously dispersed in the PVC matrix, in accordance with Haba and Narkis description [13]. The PVC/XPBA, 2% EGDMA blend contains dispersed round particles with an average size of 0.2-2 µm (Fig. 2b).

Tab. 1. Polymerization yields and transparency after compounding in a Brabender Plastograph cell (210 °C, 20 rpm), or in a twin screw extruder (180 °C).

System	Yield*, wt%	Transparency
PVC	-	Transparent
PVC/PBA	91	Opaque
PVC/XPBA, 0.5% EGDMA	100	Opaque
PVC/XPBA, 2% EGDMA	94	Opaque
PVC/PEHA	87	Opaque
PVC/XPEHA, 0.5% EGDMA	94	Opaque
PVC/XPEHA, 2% EGDMA	94	Opaque

* Yield is calculated by the weight gained divided by the weight of the monomer solution (monomer, crosslinker and initiator).

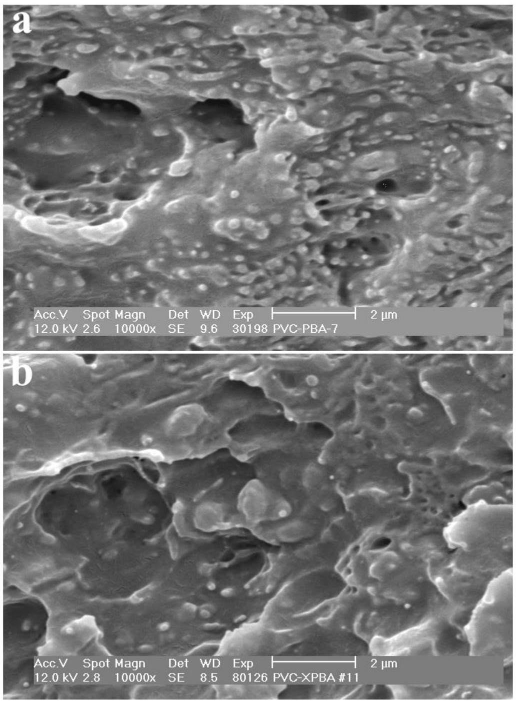

Fig. 2. SEM micrographs of freeze fractured (a) PVC/PBA and (b) PVC/XPBA, 2% EGDMA blend after Brabender and compression molding.

PVC/PEHA blends depict a very smooth freeze fractured surface morphology. The irregularly shaped dispersed PEHA and XPEHA, 2% EGDMA particles have an average size of about 2 µm (Fig. 3a) and 4 µm (Fig. 3b), respectively.

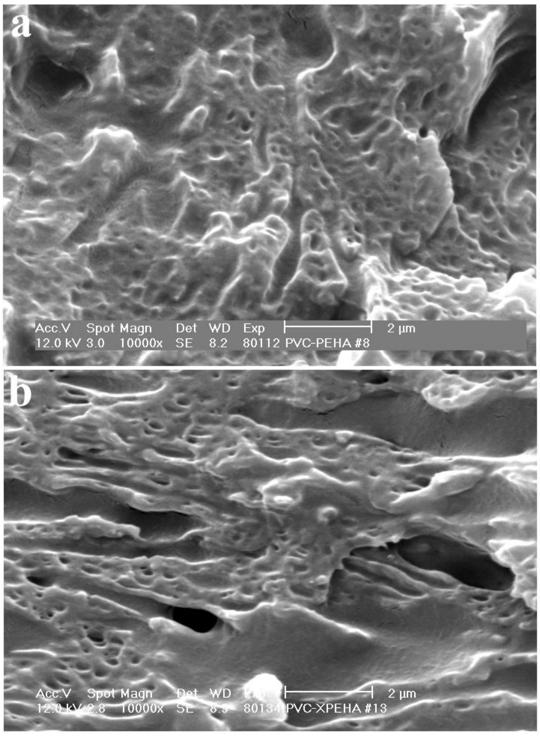

Fig. 3. SEM micrographs of freeze fractured (a) PVC/PEHA and (b) PVC/XPEHA, 2% EGDMA blend after Brabender and compression molding.

SEM micrographs of injection molded PVC/PEHA and PVC/XPEHA, 2% EGDMA blends are depicted in Figs. 4a-c. The PVC/PEHA blend exhibits a distinct skin region (Fig. 4a), different in appearance from the core (Fig. 4b). The presence of skin/core morphology in injection molded parts has been described for several immiscible blends [14-16]. In the PVC/PEHA blend, the PEHA dispersed domains at the rim are elliptically shaped (0.3-2 μm), while spherical PEHA particles (0.3-1 μm) appear in the core of the PVC/PEHA blend. These observations follow the general tendency for a skin/core morphology and can be described by the Tadmor flow model [17].

The PVC/XPEHA, 2% EGDMA blend, however, does not exhibit skin/core morphology. In the injection molded blend of PVC/XPEHA, 2% EGDMA, fiber-like XPEHA domains parallel to the flow direction appear, having dimensions of ~ 0.2 μm diameter and ~ 2 μm length (Fig. 4c). The oriented XPEHA phase in the PVC/XPEHA, 2% EGDMA blend may be attributed to a higher yield strength compared with that of PVC/PEHA blend [18].

In order to better understand the blends behavior, further SEM analyses of the Izod fracture surface were performed. Figure 5, where the micrographs of Izod fracture surface of neat PVC perpendicular to the flow direction are presented shows cavitation and void formation in the polymer skin (Fig. 5a). The cavitation and void formation are, however, barely noticeable in the PVC core (Fig. 5b). The relatively flat, smooth surfaces without any sign of plastic deformation, along with the absence of yielded zone, observed in Fig. 5, are typical characteristics of a brittle failure [19].

The morphology of fracture surfaces of the impact specimen for PVC/PEHA blend is demonstrated in Figs. 6a-b (skin and core, respectively).

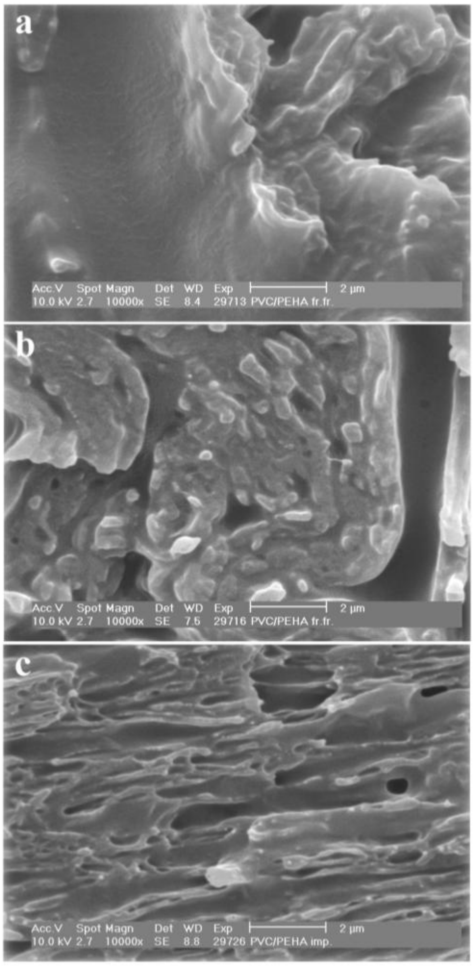

Fig. 4. SEM micrographs of freeze fractured surfaces injection molded PVC/PEHA blend (a) skin and (b) core, and (c) PVC/XPEHA, 2% EGDMA blend.

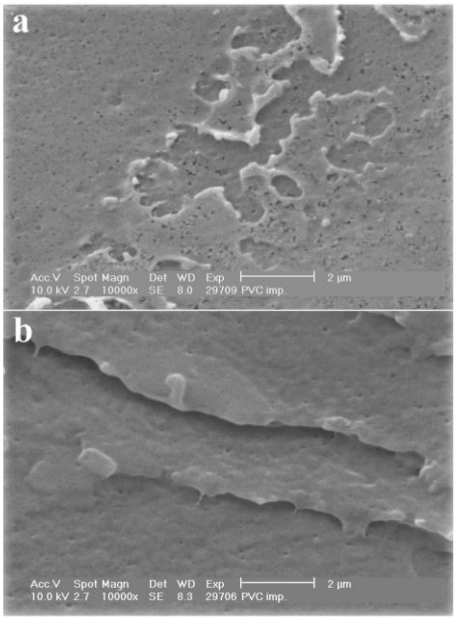

Fig. 5. SEM micrographs of the Izod impact fracture surface of PVC (a) skin and (b) core.

A beard like pattern is observed in the skin, suggesting that the impact specimen fails by a shear yielding mechanism, in accordance with Peng *et al.* description of PVC modified with elastomers and rigid organic particles [20] and Takaki *et al.* description of PVC modified with methyl methacrylate-butadiene-styrene (MBS) [21, 22]. The pattern diminishes in the core.

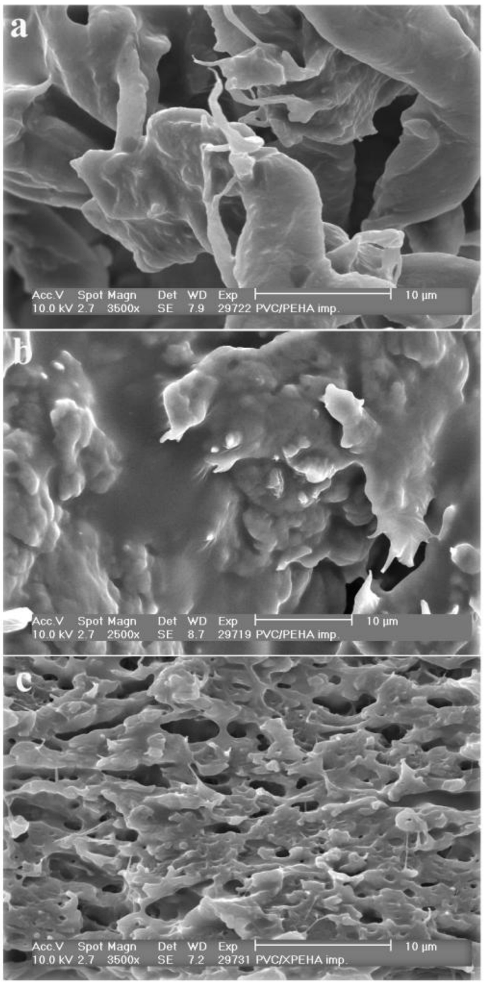

Fig. 6. SEM micrographs of the Izod impact fracture surface of PVC/PEHA blend (a) skin and (b) core, and (c).of PVC/XPEHA, 2% EGDMA.

In the case of PVC/XPEHA, 2% EGDMA blend, the lightly crosslinked rubber is well dispersed in the matrix and under stress forms a three-dimensional network structure within the PVC (Fig. 6c). Some small voids are formed, and crazing, if any, is minimal. The SEM micrograph indicates that the energy dissipation and possibly shear banding mechanism is more likely in this case. When impacted, the energy is dissipated down the branches of the network structure. The crack, if formed, grows along the branches until it cannot travel any more in that direction. Then it changes direction and travels down another branch. Thus, the crack can only propagate through the material in the zigzagging manner until the material breaks, in accordance with Rabinovitch *et al.* description [23].

This mechanism of crack propagation and shear banding appears to be responsible for the superior impact performance of the PVC/XPEHA, 2% EGDMA blend.

Izod fracture surfaces of PVC modified with PEHA and XPEHA, % EGDMA rubbers are rough and show extensive drawing of the matrix material, as typical of ductile failure [19]. The extensive plastic deformation implies that the modifiers induce the shear yielding of the PVC matrix.

Thermal Gravimetric Analysis

Figures 7-8 depict TGA thermograms of XPBA and XPEHA modified PVC, respectively. The XPBA and PBA modified PVC show similar thermal resistance compared with the neat PVC up to ~ 360°C, followed by increased thermal stability of the crosslinked blends compared with the uncrosslinked PVC/PBA blend in the temperature range of 360-700°C. The thermal decomposition temperature increases with increasing the content of the crosslinker. The PVC/XPBA 0, 0.5, 2% EGDMA blends show improved thermal resistance compared with the neat PVC up to ~ 390, 400 and 410°C respectively, followed by a decreased thermal resistance up to 700°C.

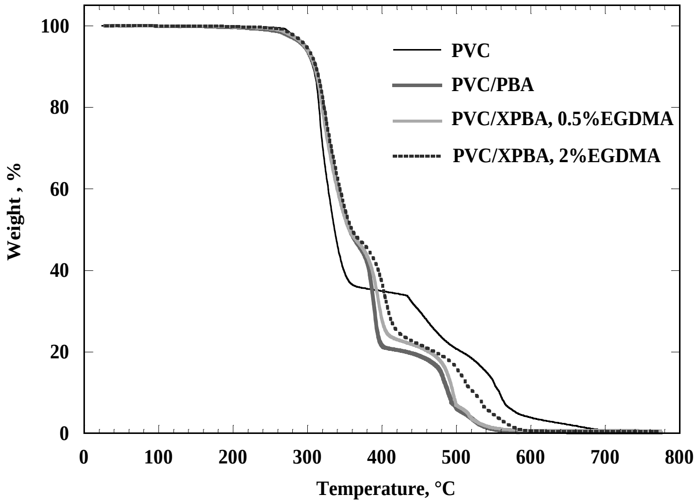

Fig. 7. TGA thermograms of PVC/PBA blends.

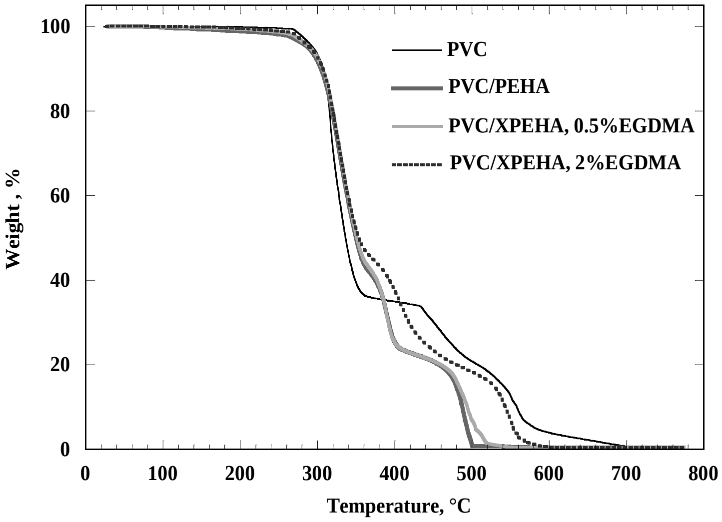

Fig. 8. TGA thermograms of PVC/PEHA blends.

The XPEHA and PEHA modified PVC show similar thermal resistance compared with the neat PVC up to ~ 340 °C, followed by increased thermal stability of the 2% crosslinked blend compared with the PVC/PEHA and PVC/XPEHA, 0.5% EGDMA blends in the temperature range of 340-600 °C. The thermal decomposition temperature increases with increasing the content of the crosslinker. This increase is more significant for the PVC/XPEHA, 2% EGDMA. The PVC/XPEHA, 2% EGDMA blend shows improved thermal resistance compared with the neat PVC up to ~ 410 °C, followed by decreased thermal resistance up to 700° C. The PVC/PEHA and PVC/XPEHA, 0.5% EGDMA blends show improved thermal stability compared with the neat PVC up to ~390 °C, followed by decreased thermal resistance up to 700 °C.

Mechanical Properties

The loss modulus curves for PVC/PBA and PVC/PEHA systems show that both PVC and PBA, or PEHA, preserve their peaks (Figs. 9-10, respectively), as in typical immiscible polymer blends [24]. The T_g peaks of PBA are at about -22 °C, and of PEHA -56 °C, similar to literature reports [9, 25-27]. The neat PVC has a distinct T_g at 64 °C and a wide β relaxation transition from -78 to 10 °C, attributed to the hindered segmental rotation about its main-chain axis [8, 27]. The observation of two T_g peaks in these blends is supported by Shach-Caplan *et al*. observation of two peaks in PVC/XPBA and PVC/XPEHA, 0, 0.5 and 5% EGDMA blends produced by *in-situ* polymerization of the absorbed acrylate monomer solutions (25 %wt) within commercial porous PVC particles [8]. Also, Walsh and Sham (1984) showed that homogeneous blends of PVC/PBA were formed by *in-situ* polymerization up to 10% BA, whereas at higher BA concentrations inhomogeneous blends resulted in [25].

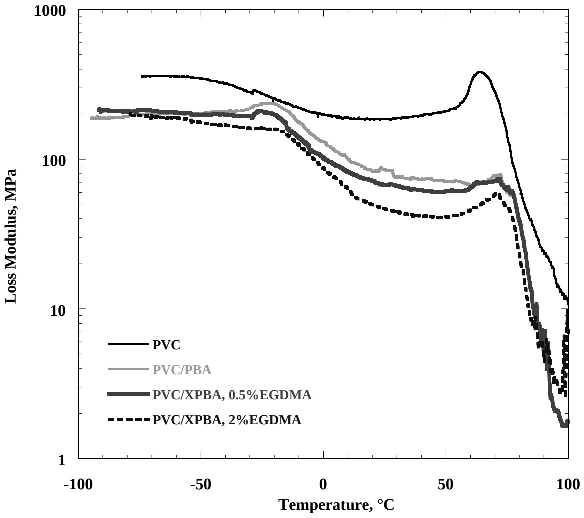

Fig. 9. Loss modulus as function of temperature of PVC/PBA blends.

A shoulder-like behavior is observed between the peaks, presumably caused by partial mixing of PBA or PEHA with PVC, which reduces the PBA or PEHA segmental mobility. The broadening of the peaks of PBA and PEHA with 2% EGDMA, can be ascribed to a broad range of semi-IPN concentrations [24, 28] and further suggests that partial mixing of the modifying polymers with PVC has taken place owing to EGDMA presence. The foregoing broadening of the PVC peaks for all the modified PVCs may reflect a flexibilization effect generally known to broaden a thermal transition region [28].

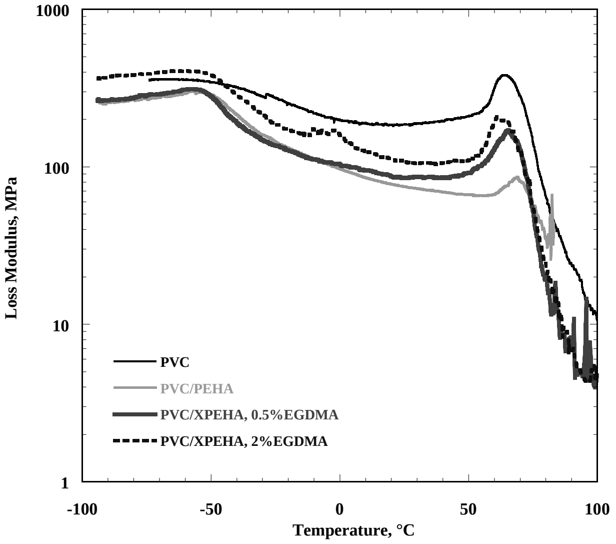

Fig. 10. Loss modulus as function of temperature of PVC/PEHA blends.

The loss modulus peak heights for PVC/PBA and PVC/PEHA systems are lower compared with the neat PVC loss modulus peak height reflecting the reduction in PVC content, in agreement with Shach-Caplan *et al.* description [8]. In addition, the peak heights of the PVC/PBA are lower as the crosslinker content increases, reflecting the increase in restriction imposed by the presence of crosslinked network in the semi-IPN morphology, which limits segmental motion and phase separation [27, 28].

In a previous publication [10], 13C Solid State NMR studies have not provided any indication of chemical interactions between the modifying polymers and PVC in the systems described in the present article.

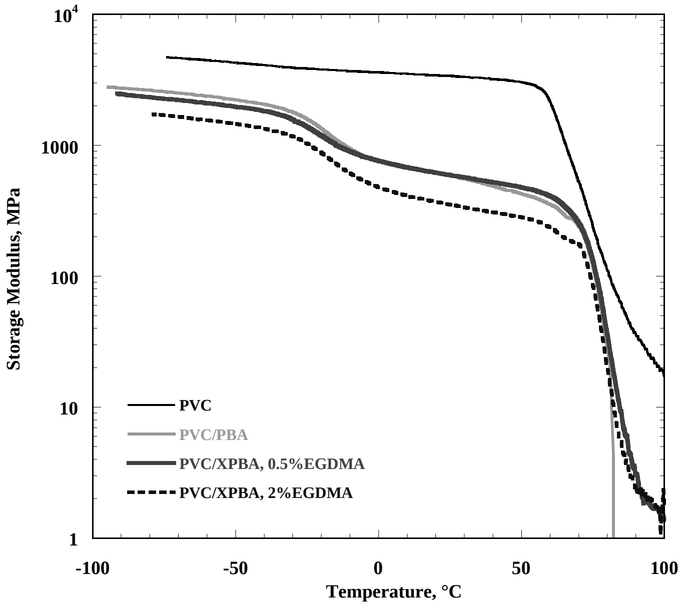

Fig. 11. Storage modulus as function of temperature of PVC/PBA blends.

The storage modulus curves of PVC/PBA blends and PVC/PEHA blends (Figs.11-12, respectively) show modulus reduction, compared with the neat PVC, for all the studied blends throughout the entire temperature range (-100 – 100 °C), due to a dominant flexibilization effect. Two storage modulus reductions are observed representing the T_g transition of each of the components, in accordance with typical immiscible or partially miscible amorphous blends [29]. Because of the presence of the PVC stiff matrix the material does not soften dramatically above the lower glass transition. The new mobility of the acrylate region causes reduction of the modulus, but the material exhibits useful solid-state properties until it approaches the PVC glass transition, about 80-120°C above the first glass transition.

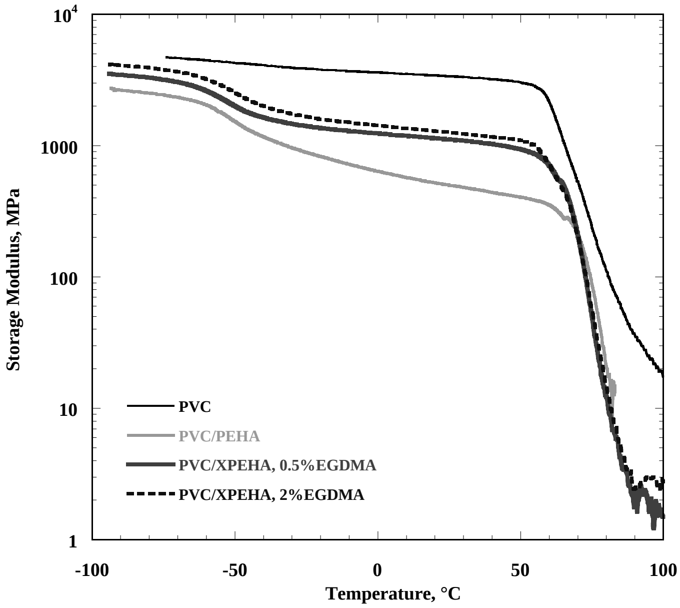

Fig. 12. Storage modulus as function of temperature of PVC/PEHA blends.

Haba and Narkis have shown that reactive extruded PVC/XPEHA (15 phr), 0.5% DVB blends produce high elongation at break compared with the neat PVC, ~90% and ~7%, respectively. The elastic modulus and tensile strength of these systems, however, were reduced [13]. Accordingly, there is a considerable decrease in the yield peak and tensile modulus in the *in*-situ polymerized PVC/PEHA blends, resulting from the incorporation of the PEHA having a rubbery character (Table 2, Fig. 13).

Tab. 2. Tensile Properties of PVC blends.

System	Elastic modulus [MPa]	Yield stress [MPa]	Yield strain %][	Ultimate strength MPa][	Elongation at break %][
PVC	2800±190	63.1±1.4	4.1±0.8	35.5±2.9	16±3
PVC/PEHA	511±98	4.2±0.60	1.5±0.1	4.72±0.90	1.6±0.2
PVC/XPEHA, 2% EGDMA	1110±11	13.2±1.6	2.0±0.3	2.12±0.46	5.5±1

Nevertheless, the PVC/PEHA and PVC/XPEHA, 2% EGDMA blends exhibit ductile behavior with low elongation at break, i.e., ~1.6% and ~5.5%, respectively. Thus, incorporation of PEHA marks a significant change in the stress-strain behavior. The crosslinked blend shows a wider yield peak compared with the uncrosslinked blend, and thus potential to show improved impact strength.

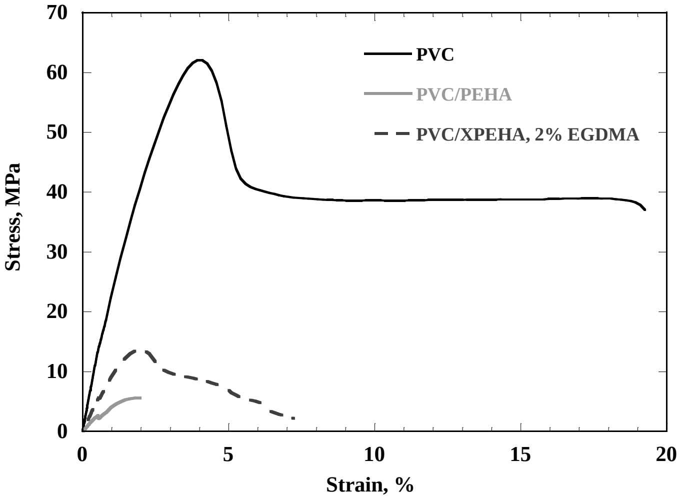

Fig. 13. Tensile stress-strain curve of PVC/PEHA blends.

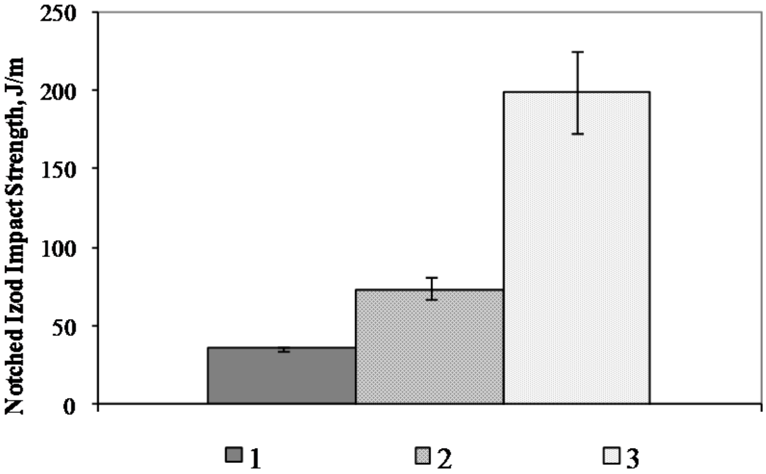

Fig. 14. Notched Izod Impact strength of (1) PVC, (2) PVC/PEHA and (3) PVC/XPEHA, 2% EGDMA blends, at room temperature.

The notched Izod impact resistance of PVC, PVC/PEHA and PVC/XPEHA, 2% EGDMA are depicted in Fig. 14. The PVC/XPEHA, 2% EGDMA and PVC/PEHA blends exhibit increased impact resistance compared with the neat PVC, namely, ~200 and ~75 J/m compared with ~35 J/m, respectively. Meaning, superior impact strength can be obtained when blending PVC and PEHA, which is supported by the tensile properties, i.e., obeying the general tendency for the impact strength to increase when yield stress decreases [3]. These results indicate that the two polymers have achieved the necessary degree of compatibility to ensure effective adhesion obtained between the discrete particles and the continuous PVC phase [3], which is in agreement with SEM results. The higher impact resistance of the crosslinked blend compared with the uncrosslinked blend can be attributed to the fine fiber-like morphology generated in the PVC/XPEHA, 2% EGDMA blend.

Zhang *et al*. found that the impact resistance of thermoplastic materials, e.g., PVC, can be improved by introducing rubbery particles with an average size of 0.3-0.7 µm [30]. Takaki *et al*. determined the Izod impact strength of PVC at different particle sizes of methyl methacrylate/butadiene/styrene (MBS). They found that when MBS's average size is below 0.2 µm the energy absorbed by crazing dominates the total energy absorption; and when MBS's average size is above 0.2 µm the energy absorbed by shear yielding dominates the total energy absorption. The energy absorption maximizes when the MBS particle size is 0.2 µm [22]. In the present work, PVC/PEHA blends have an average dispersed particles size in the range of 0.2-2 µm, accordingly, a mechanism of crack propagation and shear banding appears to be responsible for the increased impact performance.

In conclusion, in the PVC/PEHA blends the dispersed phase acts to concentrate the stresses, and thereby tends to reduce the apparent tensile strength of the material and enhances impact resistance by a toughening mechanism.

Tensile mechanical properties and impact resistance of PVC/PBA blends were not investigated and therefore are not detailed here.

Rheology

Melt rheology behavior of PVC/PBA and PVC/PEHA blends is shown in Figs. 15-16, respectively. All curves exhibit similar rheological behavior, i.e. a Newtonian region followed by shear thinning at higher levels of shear rate. Both of the PVC/polyacrylate blends exhibit a higher melt viscosity compared with the neat PVC at the lower shear rates, followed by similar or lower viscosity at the higher shear rates.

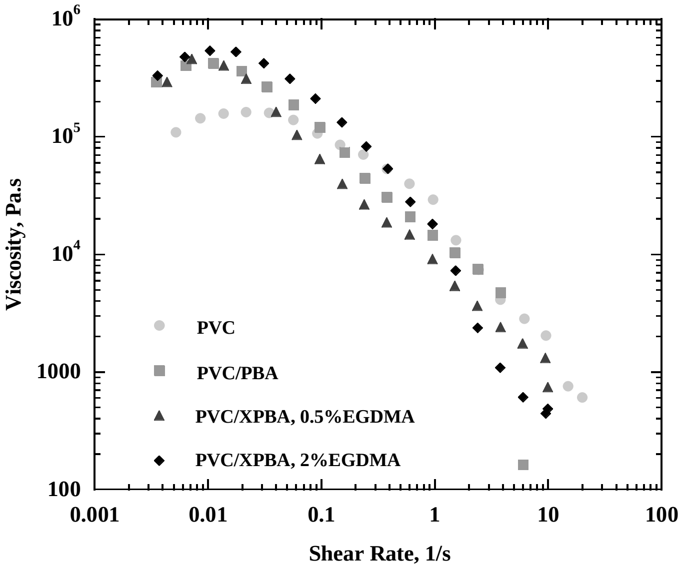

Fig. 15. Variation of viscosity with shear rate of PVC/PBA blends at 224 °C.

The PVC/PEHA blends curves extrapolate to a similar zero shear viscosity (Fig. 16*)*, indicating similar molecular weights, in agreement with the DMTA results. The rheological behavior of these blends is similar.

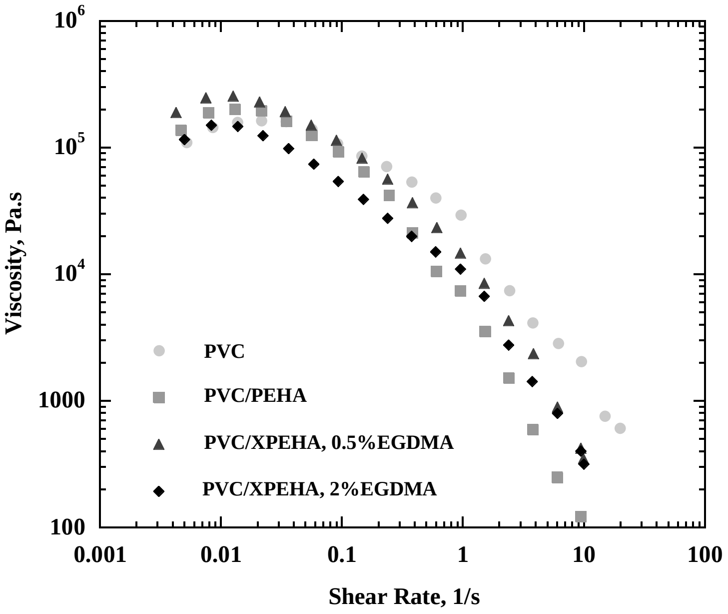

Fig. 16. Variation of viscosity with shear rate of PVC/PEHA blends at 224 °C.

Conclusions

This paper describes a modification process of porous suspension-type PVC particles by *in-situ* surfactant-free polymerization in the solid state, at 800 °C. The modifying monomers have important effect on the structure and properties of the obtained particles. Melt processing of these particles into shaped plastic products may lead to a new group of PVC materials of different structure, performance and potential applications.

Experimental part

Materials

Suspension PVC (Epivyl 40, Frutarom, Israel), porous particles, 100-150 μm diameter, (Kvalue-67) were used as received. Butyl acrylate (BA) (Fluka, Switzerland) and 2-ethylhexyl acrylate (EHA) (Fluka, Switzerland) monomers were used as received. Ethylene glycol dimethacrylate (EGDMA) (practical grade, Fluka, Switzerland), the crosslinking agent, was used as received. Benzoyl peroxide (BP) (Merck, Germany), the initiator, was purified by re-crystallization from hot ethanol. Water was deionized and distilled.

The stabilization package developed for the PVC/polyacrylate blends includes methyl tin mercaptide thermal stabilizer, epoxydized soybean oil and hydrogenated caster oil lubricants and calcium stearate stabilizer and lubricant.

Blends Preparation Procedure

PVC particles were modified by XPBA (polybutyl acrylate crosslinked with 0, 0.5, 2% EGDMA) and XPEHA (polyethylhexyl acrylate crosslinked with 0, 0.5, 2% EGDMA) using benzoyl peroxide as initiator (0.5%). The PVC/modifying polymer mass ratio was 300/100.The blends were produced in three successive steps:

Step (a): The polymerization/crosslinking step took place in a glass reactor, immersed in a water bath at a constant temperature. Dry PVC particles 300 g were placed in the reaction vessel and the monomer, crosslinker and benzoyl peroxide solution (100 g) was gradually added, at room temperature, while stirring the PVC particles. After 90 minutes, distilled water (2.4 lit) at 80 °C was added to the reactor, and polymerization proceeded for four hours. The resulting modified PVC particles were filtered and dried.

Step (b): Thermal stabilizer and lubricants were added to the modified PVC particles by a room temperature blending procedure, continued for 5 minutes, using a commercial mixer.

Step (c): The blends were processed in a batch-type Brabender Plastograph equipped with a 50 cc mixing cell, at 20 rpm and 210 °C, followed by compression molding at 195 °C and 20 ton using a $7.5\ \text{cm} \times 12.5\ \text{cm}$ mold. Some blends were produced also in a counter rotating, intermeshing twin-screw extruder, Brabender TSC 42/6 (L/D=6; D=42nm). The extruder temperature was maintained at 185 °C in all zones, and the rotation velocity was 30 rpm, corresponding to a residence time of ~5 min. Filaments of the extruder produced blends were ground and injection molded using an Arburg 220/150 injection molding machine, equipped with an ASTM standard mold. The injection molding machine temperature was 195 °C in all zones, and the mold temperature was maintained at 40 °C.

Characterization

Electron Microscopy: A Philips XX20 D816 Scanning Electron Microscope (SEM) was employed to observe fracture surface morphology of injection molded specimens. Samples were fractured in liquid nitrogen and observed parallel to the flow direction. Compression molded blends were characterized under the same conditions. Surface morphology after impact testing was also observed perpendicular to flow direction. All samples were gold sputtered prior to observation.

Thermal Gravimetric Analysis: Thermal gravimetric analysis (TGA) of the compression molded blends was carried out using a TA 2050 TGA analyzer. Samples were heated under air atmosphere, at a heating rate of 20 °C/min, monitoring their weight loss.

Dynamic Mechanical Properties: Dynamic mechanical thermal analysis (DMTA – Perkin Elmer series 7) of compression molded specimens was conducted in the three point bending mode at 1 Hz. Heating was carried out under an inert nitrogen atmosphere at a rate of 3 °C/min in a force controlled mode.

Tensile Mechanical Properties: Tensile properties of injection molded 'dog bone' specimens were determined using an Instron 5568 universal testing machine at ambient temperature using gage length 10 cm, according to ASTM D 638-72. The specimens were first extended at a cross-head speed of 1 mm/min up to an extension of 0.5%, followed by a cross-head speed of 10 mm/min. An extensometer was used at the lower extension speed to accurately measure the modulus. At least five specimens were tested for each specimen and the results averaged. The data obtained were converted into stress-strain curves and analyzed.

Impact Resistance: Notched Izod impact tests were performed at room temperature, i.e., 25 ± 1°C, according to ASTM-D256. A minimum of seven notched specimens was tested in each case.

Rheology: Melt flow studies were carried out using an AR-1000N parallel-plate rheometer (TA instruments). Compression molded samples of 2 cm diameter were heated to 224 °C and remained at this temperature for 5 minutes to get a uniform temperature. The melted samples were pressed down to a 1800 μm gap and the squeezed material was trimmed, followed by measurement of the melt viscosity as a function of shear rate. Each measurement data point is an equilibrium value with an accuracy of 5%.

Acknowledgements

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