

Simultaneous Statistical Suspension Copolymerization of Vinyl Chloride with Butyl Acrylate and Grafting on Poly(butyl acrylate)

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ABSTRACT: An intrinsically softened poly(vinyl chloride–butyl acrylate) was prepared by the suspension statistical polymerization of vinyl chloride (VC) with butyl acrylate (BA) using oil-soluble initiators, dispersants, and a buffer agent, at the temperature $59 \pm 1^\circ\text{C}$ (procedure A). The polymer obtained was sufficiently soft and elastic, depending on the ratio of VC and BA; however, the polymer was hard to process. It stuck to metal parts of an assembly line. The properties of the polymer were slightly modified, mainly by addition of crosslinking agents, and improved treatability was obtained in this way. Acceptable treatability was obtained only after preplastification. Similar features were exhibited by a polymer prepared by grafting of a fine dispersion of polybutyl acrylate (PBA) with VC (procedure B). The dispersion of PBA was prepared separately via the emulsion polymerization of BA at $75 \pm 1^\circ\text{C}$ (the weight ratio $\text{H}_2\text{O} : \text{BA} = 2$; a mixture of sodium alkane sulfonates 0.95 w/w % and $\text{K}_2\text{S}_2\text{O}_8$ 0.4 w/w % with respect to BA). An intrinsically softened polymer with elasticity derived from the amount of incorporated BA was obtained; unfortunately, as with case A, the polymer was difficult to work up, and preplastification was necessary. The best procedure for the preparation of intrinsically softened poly(vinyl chloride–butyl acrylate) proved to be simultaneous statistical copolymerization of VC and BA, and grafting on PBA (procedure C). The principle consists of gradual addition of VC and BA to the fine dispersion of PBA. A shape stable, aesthetic looking, and well readily processible material was obtained. The ductility of foils prepared from the polymer increases with the increasing amount of BA, while the temperature stability, hardness, and mechanical strength decrease. A hypothesis expressing the morphology of a polymer with good properties has been proposed. Significantly different values of copolymerization parameters of BA (approx. 5) and VC (approx. 0.1) are responsible for irregularities in a copolymer when all amounts of monomers are added at the start of the reaction. The rate of addition of monomers to the polymeric reaction mixture ought to be at such a rate as to allow the formation of relatively regular alternated chains of homopolymers and copolymers of BA and VC that start to grow mainly from the core represented by PBA chains. At the end of copolymerization, an excess of VC is useful for making a PVC hydrophobic cover of particles, and, in consequence, low stickiness to metal surfaces. This may be used for the description of a good polymer, as well as to account for bad properties of other copolymers of BA and VC. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 649–656, 1998

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INTRODUCTION

An important portion of PVC production is processed with plasticizers to give flexible products. The amount of plasticizer (softener) determines ductility, flexibility, and freezing resistance of the product. However, migration of the plasticizer to the surface is an undesirable property of this kind of product. The plasticizer is gradually lost from the surface due to evaporating or washing with liquids that are in contact with the product. Consequently, the product starts to be more rigid, shrinks, and cracks. In addition, the leached plasticizer pollutes the environment. The problem of softening may also be solved in different ways, usually by the substitution of softened PVC by another polymer, or by creating a protective surface layer, nonpermeable for the plasticizer. The latter can be done using coextrusion of softened PVC with other suitable plastics, which ensure the protective function. Other possible surface modifications, such as ultraviolet or γ -irradiation, treatment in plasma may be used to form a cross-linked surface layer that is a barrier to the exudation of plasticizer. The exudation of plasticizer can also be reduced by using more bulky molecules, i.e., higher molecular, or even polymeric plasticizers.¹ Finally, intrinsically softened PVC prepared by copolymerization of vinyl chloride (VC) with comonomers or polymers with low value of the glass transition temperature, T_g , can be used. Copolymers of VC with acrylates and other comonomers such as vinylidene chloride, vinyl benzoate, isobutylene, styrene, dialkyl maleate or dialkyl fumarate, acrylonitrile, acrylic acid, vinyl acetate, and hydroxyacrylate have such properties.¹⁻⁶ During copolymerization, all comonomers are added together, or alkylacrylate and the other comonomer are added gradually to obtain a homogeneous product. A statistical thermoplastic copolymer is obtained in this way. These thermoplastics have mechanical properties comparable to those of commonly softened PVC, but in addition, they can be used over a wider temperature range, and possess shape stability. However, there are some problems in their processing due to high stickiness and low stability at lower temperatures. The copolymer of acrylic acid with VC and magnesium oxide seems to be attractive as a biocompatible plastic prepared by grafting VC and 2-ethylhexyl acrylate on the ethylene-vinyl acetate copolymer.⁷

Similarly, PVC may be intrinsically softened by polyester blocks, or with ethylene-vinyl acetate copolymer, and occasionally, by polyfunctionalized

copolymerized comonomers as triallyl cyanurate.⁸ The latter-mentioned procedure is complicated by the requirement of a broader assortment of comonomers. Recently, we described the preparation of intrinsically softened product based on poly(vinyl chloride-alkyl acrylate)-grafted copolymer.⁹ However, the procedure given in ref. 9, gives barely processible material, sticking to metal parts of the assembly line. The foils produced had nonaesthetic surfaces of the "orange peel" form. This problem was solved by preplastication at a temperature of 165°C for 5 min and calendering at a temperature of 195°C. Using this two-stage process, smooth foils were obtained.

In the context of the above-mentioned facts, the aim of this article is to explain observed discrepancies in properties of a polymer vs. the procedure of preparation, and to find a way to prepare intrinsically softened modified suspension copolymer that should be easily processed by common one-stage procedures.

EXPERIMENTAL

Chemicals

Vinyl chloride (VC) (Nováky Chemical Works, Nováky, Slovak Republic) contained the following impurities (in ppm): acetylene (1), propylene (3), 1,3-butadiene (11), methyl chloride (49), ethyl chloride (7), 1,1-dichloroethane (3), 1,2-dichloroethane (4), monovinyl acetylene (12), water (193).

Butyl acrylate (BA) of purity 99 wt % was distilled in an inert atmosphere prior to use.

The polymerization initiator was EHP-80 (Nováky Chemical Works, Nováky, Slovakia) and consisted of 50 wt % xylene, 35 wt % bis(2-ethylhexyl) peroxydicarbonate, 14 wt % benzoylperoxy-2-ethylhexyl carbonate, and 1 wt % dibenzoyl peroxide.

Dilauroyl peroxide of purity 98.5 wt %; the content of active oxygen 3.95 wt %.

Potassium peroxydisulphate $K_2S_2O_8$ of purity 98.9 wt % with free sulfuric acid 0.04 wt % and iron (as $FeSO_4$) 0.005 wt %.

Methylhydroxypropyl cellulose (Methocel F50); with 28.5% of methoxyl groups, 6.1% of hydroxypropyl groups, the viscosity of water solution (2 wt %) was 55 mPa s (all data were determined according to ASTM D 2363).

The emulsifier E-30 (Mersolat-Leuna Werke, Germany) mixture of linear sodium alkylsulphonates C12 to C18 with 39% of dry weight.

All other chemicals were of analytical grade.

Preparation of the Poly(butyl acrylate) Dispersion

Deionized water (3900 g), 97.5 g aqueous solution of emulsifier E-30 of concentration 19 wt %, and 50 g of BA were added to a glass autoclave (8.5 dm³) equipped with paddle wheel stirrer (300 rpm). After removing air and heating to 75 ± 1°C, 7.8 g of K₂S₂O₈ was added to the reaction mixture. Then, for 2 h, 1900 g of BA was gradually added to the stirred mixture and the polymerization was continued an additional hour at 75 ± 1°C. The content of autoclave was cooled, isolated, and weighed. The obtained dispersion of poly(butyl acrylate) (PBA) had a concentration of 33 wt %.

Preparation of Copolymers of VC with BA

Three basic types of copolymers of VC with BA were prepared: (A) a statistical copolymer of VC with BA (without addition of the PBA dispersion at the start of the procedure); (B) a copolymer of VC and BA prepared by grafting VC on PBA; (C) a copolymer prepared by simultaneous statistical copolymerization of VC and BA, and grafting of these monomers on PBA.

Procedure A (a Statistical Copolymer of BA and VC)

The copolymerization was carried out in a stainless steel autoclave (10 dm³) with the paddle wheel stirrer (300 rpm). At the start, 2500 g of deionized water, 750 g of water solution of methylhydroxypropyl cellulose (2 wt %), and 1 g of 50% xylene solution of EHP-80 initiator, 3000 g of a mixture of VC and BA, and 10 g of dilauroyl peroxide were added to the reactor. After closing and removing air, 2500 g of VC and 250 g of water solution of calcium formate (10 wt %) were introduced into the autoclave while the mixture was stirred. For 25 min the autoclave was heated to the temperature of 59 ± 1°C and kept at this temperature until the pressure decreased by 0.5 MPa (taking 5 h). The reacted mixture was cooled, and nonconverted VC was released to the waste VC reservoir. The suspension was filtered, washed three times with water, and dried under reduced pressure at 50°C. We obtained 2601 g of the copolymer of VC and BA mixed with homopolymers of VC and BA.

Procedure B (VC Grafted on PBA)

This copolymerization was carried out in the same reactor as used for the copolymers A. Differences

in the procedures consisted in the addition of an amount of the PBA dispersion to the reactor at the start (usually 1000 g), and in continuous addition of VC to the polymerization mixture. The amounts of the dispersant and initiators varied according to the amount of the applied monomer.

Procedure C (VC and BA, a Statistical and Grafted Copolymer)

The same reactor as above was used for this procedure. A certain amount of the PBA dispersion, for example, 1000 g, was placed in the reactor together with 2500 g of deionized water, 750 g of water solution of methylhydroxypropyl cellulose (2 wt %), 1 g of 50% xylene solution of EHP-80 initiator, 6.5 g of dissolved dilauroyl peroxide, and 250 g of a water solution of calcium formate (10 wt %) while the mixture was slowly stirred. The reactor was closed, the air removed, and the autoclave was heated to 59 ± 1°C. After reaching the desired temperature, a continuous feed of VC (2500 g) and BA (500 g), in which 3.5 g of dilauroyl peroxide were dissolved, was started. The reactor was fed during 3.5 h, and then, the copolymerization continued at the same temperature (59 ± 1°C) until the pressure dropped by 0.5 MPa (usually 1.5 h). The next steps of procedure were the same as in A. The ratio of VC and BA was changed, keeping the total amount of comonomers equal to 3000 g, and the weight of the PBA dispersion was 1000g, i.e., the weight ratio of the PBA dispersion to monomers was constant.

Analysis of Chemical and Physicochemical Properties of Copolymers

The ratio of monomers in the resulting poly(vinyl chloride–butyl acrylate) copolymers was calculated on the basis of the amount of chlorine, supposing the content of vinyl chloride to be proportional to the amount of chlorine. Portions of statistical and grafted copolymer were approximately determined from solubility measurements in benzene, butyl acetate with acetone, and tetrahydrofuran.

The size of latex particles in the PBA dispersion obtained by the emulsion polymerization was evaluated using a dynamic light-scattering method using a Laser goniometer BI-200 SM, Brookhaven Instrument Corp.

The distribution, according to size of the suspension copolymer particles, was determined by sieve analysis, bulk density, and the other measurements as described earlier.¹⁰ The pouring

ability was measured using a funnel 114 mm height with opening diameter 9.5 mm.¹¹ The thermal stability was evaluated by the current resistance¹² of foils prepared from the suspension.

To determine physical and mechanical properties of the copolymer, the suspension was treated as follows: the ingredients; 1.5 g of dibutyltin maleate, 0.5 g of calcium stearate (thermostabilizers), and 0.5 g of montan wax (external lubricant) were added to 97.5 g of a suspension copolymer. After 5 min of homogenization in an isothermic mixing device at $25 \pm 2^\circ\text{C}$, the mixture was molded and, afterwards, calendered on a double roller at the temperature of 160°C for 5 min. The samples for measurements were cut from the such prepared foil.

Stability to leaching of plasticizers was evaluated by extraction in a Soxhlet apparatus using diethyl ether.

RESULTS AND DISCUSSION

The dispersion of PBA prepared by the emulsion polymerization consisted of very fine particles with size in the range 60–120 nm.

Textural and mechanical characteristics of suspension copolymers obtained from procedures A–C did not differ significantly. The bulk density was in the range $520\text{--}600\text{ kg m}^{-3}$, pouring ability (see Experimental) $0.2\text{--}0.3\text{ g s}^{-1}$. The portion of particles above 0.25 mm was less than 6 w/w % in all cases, and the portion of particles that passed through sieve, less than 0.063 mm, was in the range 14–30%, i.e., a higher inhomogeneity of the particle size in comparison to particles from industrial processes was observed. This inhomogeneity is probably caused by the relatively small volume of the polymerization autoclave used in our experiments. We suppose that inhomogeneity does not significantly affect workability and properties of products prepared from the copolymers.

We examined the effects of incorporation of BA in the preparation procedures A–C. Before discussing results, it is worthwhile to add a few comments concerning copolymerization of VC and BA alone and in the presence PBA “nanoparticles” of which the dispersion consists.

A Difference Between Copolymerized and Incorporated Amount of BA

The word “incorporated” expresses the total amount of BA involved in a copolymer without distinguishing if the BA is incorporated into the

chains of the copolymer, grafted on PBA, or in chains of the homopolymer. The term “statistical” also has its particular meaning for copolymers of VC with BA. Due to the great difference in reactivities of VC (M_1) and BA (M_2), which are represented by copolymerization parameters^{13,14} $r_1 = 0.07$ and $r_2 = 4.4$ (ref. 13) and $r_1 = 0.1$ and $r_2 = 5.5$ (ref. 14), the amount of the monomer M_1 incorporated is very low with respect to the amount of monomer M_2 in a macromolecule, and a similar statement is valid for M_2 with respect to M_1 . There can even exist homopolymeric chains formed from M_2 if the concentration of M_2 is high and homopolymeric chains of M_1 when the concentration of M_1 is high and the concentration of M_2 is practically negligible. Therefore, the term “statistical” needs to be considered as slightly exaggerated in the context of meaning in polymerization theory.

Penetration (“Diffusion”) of Monomers into the PBA “Nanoparticles”

Affinity between BA and PBA is very high; BA dissolves PBA. It is possible that, due to this high affinity, BA penetrates into the PBA particles easily and can be grafted on the polymeric chains even near the core of particles (the size is very low; 60–120 nm). VC has a lower affinity for PBA than BA, but it also dissolves PBA. Moreover, the rate of polymerization of VC is lower than that of BA. Thus, homopolymeric chains of Pba are formed first and grafted to the basic PBA chains; copolymers of BA and VC are formed slower, and homopolymeric chains of PVC are formed at the end of copolymerization.

Emulsion and Suspension Polymerization

The PBA dispersion was prepared by the emulsion polymerization using the emulsifying agent E-30 (see Experimental). A part of this emulsifying agent remained in the PBA dispersion. To suppress emulsion polymerization, calcium formate was added to the reaction mixture. Hence, mainly suspension copolymerization was expected.

We studied the effect of an amount of incorporated BA in VC copolymer products and the effect of the procedure on physical and mechanical properties. We also evaluated the potential processing possibility for intrinsically softened products.

The effect of the amount of incorporated BA and the effect of the procedure on ductility of prepared foils are shown in Figure 1. The results (A; full circles) represent the foils from copolymer prepared basically by statistical copolymerization

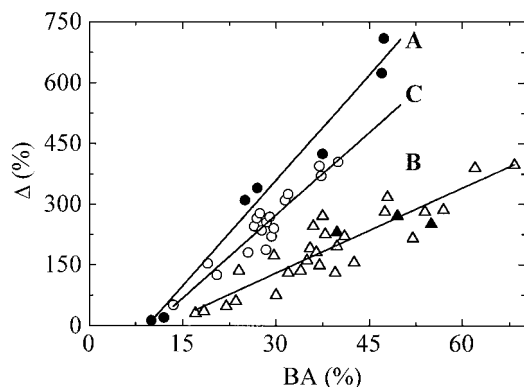


Figure 1 Influence of the amount and way of incorporating BA (BA, w/w %) into the copolymer on the ductility (Δ) of the foil. (A) Full circles: statistical copolymerization of VC and BA. (B) Open triangles: PBA grafted by VC, full triangles: results of samples prepared following ref. 9. (C) Open circles: combined grafting and statistical copolymerization.

of VC with BA prepared by the procedure (A). The suspension of this copolymer was hard to process on the double roll calender. Despite sufficient amounts of outer lubricants, the foil with a sharp skin could hardly be moved out from the rollers due to sticking. On the other hand, after pressing such preplastificated foils, transparent, smooth foils with good ductility were obtained.

The results (B) in Figure 1 (open triangles) represent ductility measurements of foils prepared from the powder of modified copolymer from grafting VC on the PBA homopolymer. Three measurements (full triangles) belong to the samples prepared by the known procedure described in the literature.⁹ The product obtained was also difficult to process on the double-roll calender and the surface of the prepared foils was rough (sharp skin). After pressing at the temperature of 190°C, we gained smooth but opaque foils.

The empty circles in Figure 1 describe the set (C) and represent results of grafting of PBA with VC and BA by the procedure C, as well as simultaneous statistical copolymerization of VC with BA. This modified copolymer processed well without sticking on the double-roll calender. A very good quality, smooth, transparent foil was easily removed from the roll and it was not necessary to treat the foil by pressing.

To evaluate the ratio of statistical and grafted copolymer of BA with VC, extraction experiments were carried out. Benzene was used to dissolve PBA. A statistical portion of the copolymer and then a grafted portion of the copolymer were dissolved in the mixture of butyl acetate and acetone.

Viscosity measurements were performed for evaluation of relative macromolecular size. A nonsoluble residue (mainly homopolymer of VC) was dissolved in tetrahydrofuran. Taking into account properties of foils prepared by procedure C, the optimum ratio of grafted to statistical copolymer of BA with VC should be 1 : 1.5–4, i.e., the amount of statistical copolymer may be in an excess with respect to that grafted. As seen from Figure 1, the ductility of foils increases linearly with the content of incorporated BA in the case of basically statistical copolymer VC-BA (procedure A). A similar effect is also observed in the case of statistically and grafted copolymerization of VC and BA (procedure C). A comparable tendency of ductility was also observed for grafted copolymers of PBA by VC (procedure B) but it was not as unambiguous.

We suppose that grafting of the PBA dispersion takes place on α -carbons of BA where, due to the mesomeric effect of carbonyl or ester groups and partly alkyl and alkylene parts of copolymerized BA, the strength of C—H groups is weakened. PBA chains in the presence of peroxides, generate radicals and play a role of “quasi-functionalized” polymeric chains. Radicals formed from decomposition of peroxides or other free radicals fragments can create a macroradical, or even a “macro-polyradical,” by elimination of hydrogen radicals or several hydrogen atoms from α -carbons.

Figure 2 shows the thermal stability (according to Vicat) and the hardness of samples prepared by procedure C) with different contents of incorporated BA. Values of both these quantities decrease with the increasing content of the incorporated BA. The results obtained for samples from the pure statistical (procedure A) and from, in principle, grafted copolymerization (procedure B) were similar, they differed in the range $\pm 5\%$ with respect to the values given in Figure 2.

A decrease of the tensile strength was observed for samples from modified copolymer of VC with increasing content of incorporated BA (Fig. 3). A difference is not seen between statistical (full circles in Fig. 3), statistical, and grafted copolymer (open circles) and, in principle, grafted copolymer of VC with BA on PBA (empty triangles) or copolymer prepared according to the procedure⁹ (full triangles). However, to obtain foils of good quality, calendering was a sufficient procedure only for the copolymers prepared by the statistical-grafted route (procedure C), while, to reach the desired processibility, the other samples needed a two-stage process, i.e., preprocessing by

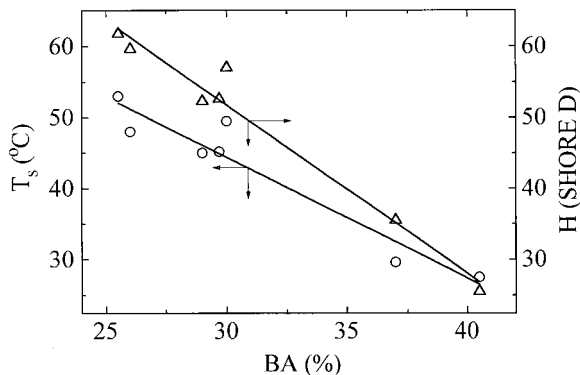


Figure 2 Effect of the amount of incorporated BA (BA, w/w %) in the copolymer of VC and BA prepared by procedure C on the thermal stability (T_s , circles) and hardness (H, triangles).

preplastification and pressing at the temperature of 190°C for 5 min.

The products from suspension copolymer of VC with BA prepared by statistical and simultaneously grafted copolymerization on dispersed PBA elastomer (procedure C) have given, in comparison to purely grafted copolymerization (procedure B), foils with a higher ductility and lower adhesion to smooth metal surfaces of the processing line. On the contrary, the copolymers, prepared by statistical or purely grafted copolymerization, were hard to process.

Finally, we compared extractivity of four foils prepared by the "classical" procedure from softened PVC with K-value 68 (Sloviny S-683) using 25 wt % of dioctylphthalate as the plasticizer, with four foils prepared from modified suspension statistical-grafted VC with BA containing 25 wt % of incorporated butylacrylate according procedure C. The samples were extracted with diethyl ether in a Soxhlet apparatus over 6 h. The foils softened with dioctylphthalate decreased in weight by 20.1–20.4 wt % and their size was reduced by 10.9–11.2%, after extraction. The weight of the foils intrinsically softened by copolymerized BA decreased only by 2.6–2.8 wt % mainly due to extraction of stabilizer and lubricants and diminished in size by 3.3 to 3.5%.

Using the results described in previous paragraphs, we tried to develop a hypothesis concerning the morphology of a copolymer with respect to its properties and the procedure of preparation. This hypothesis was set up under the following observations and assumptions: (1) Poly(butyl acrylate) exhibits relatively strong adhesivity to metal parts of an assembly line, probably mainly due to its hydrophilic features. On the other hand,

PBA has very good elastic properties. (2) In the contrast to PBA, PVC is more hydrophobic, but it is more "fragile." (3) From (1) and (2) we infer that good aesthetic and mechanical properties should be exhibited by a copolymer that is represented by relatively regularly distributed chains of PBA and PVC and copolymers of VC and BA to avoid formation of large "hydrophilic domains" and large "hydrophobic domains." (4) Reactivity of BA in polymerization, as well as in copolymerization with VC, is much higher than that for VC (see reactivity factors discussed above). From the latter statement, it can be expected that, in copolymerization of BA with VC, polymerization of BA proceeds predominantly, and VC is incorporated only to a very low extent ("statistical" copolymerization). After consumption of practically all the BA, the polymerization of VC proceeds and the rest of BA is incorporated by grafting on original and new formed branches of macromolecules of the copolymer, with homopolymeric chains of PVC formed as well.

We believe that a good copolymer of VC and BA with proper aesthetic and mechanical features has the morphology that is represented by a relatively regular alternating of polymer chains of PVC, PBA, and copolymers of VC and BA, which are chemically or physically fixed to the bulk of the polymer. A graphical representation is given by Figure 4. The straight chain in the middle of Figure 4 represents a basis of PBA homopolymer prepared by the emulsion polymerization. Side chains of PBA and PVC develop the structure during grafted or statistical copolymerization. In the

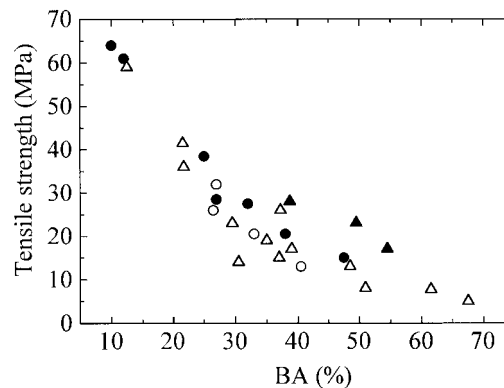


Figure 3 Influence of the amount and way of incorporating BA (BA, w/w %) into the copolymer on the tensile strength. (A) Full circles: statistical copolymerization of VC and BA. (B) Open triangles: PBA grafted by VC, full triangles: results of samples prepared following ref. 9. (C) Open circles: combined grafting and statistical copolymerization.

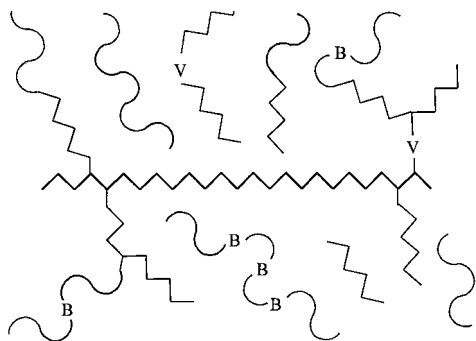


Figure 4 The morphology of a copolymer prepared by partially grafted and statistical copolymerization of VC with BA added to the dispersion of PBA (procedure C). The broken and wavy lines represent chains of PBA and PVC, respectively. Letters B and V represent BA and VC, respectively. The thicker broken line in the middle represents PBA added to the reaction mixture at the start. The length of polymeric chains does not reflect the relative molar weight.

left upper corner, a PBA chain bound to the basic PBA chain and prolonged by a PVC chain is depicted. Going to the right of this chain, the PVC homopolymer chain, a chain of the copolymer of BA with VC, and isolated PBA chains are indicated. The more complicated structure is in the right upper corner of Figure 4, where VC is incorporated on the chain of PBA, continuing as two chains with one of these prolonged by the PVC chain. A similar situation is shown in the bottom left corner of the picture. The isolated copolymer chain in the middle of the lower part of Figure 4 represents what is probably the most frequently occurring situation, i.e., isolated macromolecules of VC with BA. A less probable regular statistical fragment of the copolymer chain of BA with VC is shown in the upper part of Figure 4. Side polymeric chains (both bound chemically and physically) fragments of polymers and copolymers are formed under the properly carried out procedure, i.e., adding VC and BA with the proper flow rates to the mixture of finely dispersed PBA with dispersant (procedure C). If the rate of dosing and the rate of polymerization of the less reactive monomer differ significantly, the resulting polymer does not maintain the desired aesthetic and mechanical properties. A pure grafting of PBA by VC (procedure B) is not a good way to obtain copolymers of good quality. Due to the low reactivity of VC, PBA is not grafted extensively, and chains of homopolymers of VC are formed mainly. This results in formation of large "hydrophilic" and "hydrophobic domains," and, in the consequence, the processibility of such copolymer is bad. An

even worse case can happen if the whole amounts of BA and VC are placed in the polymerization reactor at the start. Moieties of PBA are formed very quickly; they remain isolated as "hydrophilic domains," and later, they are complemented by PVC "hydrophobic domains." An unattractively looking and very poorly processible polymer is obtained in the latter case (procedure A). If there is no sufficient alternation of PBA and PVC chains, and copolymers of VC and BA in the copolymer, preprocessing by mechanical mixing ought to precede the main treatment as was illustrated for copolymers denoted as A and B. Of course, such good-looking products as obtained by procedure C cannot be obtained by procedures A and C.

In spite of the fact that we do not have direct proof of the morphology suggested by Figure 4, we suppose this scheme to be very close to reality. We reach this conclusion based on the theoretical considerations described above and practical results of repeated experiments following procedures A–C (about 3×50 runs). The copolymers prepared by procedure C were always the best ones for processibility, lifetime, and aesthetic features of products obtained.

CONCLUSIONS

A procedure enabling preparation of a high-quality intrinsically softened copolymers of VC with BA has been developed. A principle of this procedure is based on the proper rate of continuous simultaneous dosing of individual monomers to the polymerization mixture, in which a finely dispersed PBA together with dispersant is present. This procedure has its nature in the reactivity of individual monomers. The rate of dosing needs to be sufficiently slow to enable step-by-step formation of a relatively homogeneous structure of PBA and PVC macromolecular fragments (both homopolymers and copolymers of VC and BA) bound chemically (grafting) or physically, starting by grafting on the basic PBA homopolymer chains. Especially at the end of polymerization, the rate ought to allow formation of a surface layer consisting of PVC fragments predominantly. This ensures low adhesivity to metal surfaces during processing of the copolymer. Foils prepared following the best procedure are transparent and sufficiently temperature stable, with very good mechanical processibility. Moreover, they do not stick to metal parts of the assembly line.

The stability of elasticity of the copolymer pre-

pared by the suggested procedure was also tested by extraction with diethyl ether. No significant changes of the outer look of material and good mechanical properties proved a perfect fixation of "the plasticizer" (PBA chains in the copolymer). In comparison with materials prepared from PVC softened with "classical" plasticizers, for example, dioctylphthalate, the polymers intrinsically softened with PBA are much less harmful to human health because of not leaching and releasing plasticizers to their surfaces and environment. Therefore, they are suitable not only for technical purposes but also for goods, involving personal contact, for example, food packing foils, floor and wall covering, etc. Another advantage of the described intrinsically softened polymers is the shape stability of products manufactured from these kind of copolymers.

On the basis of the hypothesis describing a morphology of a desired copolymer, also the morphology of a copolymer with undesirable features may be inferred. Taking into account the reactivity under conditions in which the polymerization is performed, this can help to analyze problems occurring during certain technological processes.

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