# A Tough Noncombustible Material Prepared by Grafting of Poly(2-ethylhexyl acrylate) with Vinyl Chloride

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ABSTRACT: A noncombustible tough poly(vinyl chloride) (tPVC) was prepared by suspension-grafted copolymerization of poly(2-ethylhexyl acrylate) (poly-EHA; elastomer) with vinyl chloride (VC). Elastomer (poly-EHA) was prepared by emulsion, mainly homopolymerization of 2-ethylhexyl acrylate at a temperature of  $30 \pm 0.1$ °C in the presence of a redox system and with the advantage of dosing the monomer into two portions. Grafted-suspension copolymerization of poly-EHA with VC was carried out at  $54 \pm 0.1$  °C, keeping other reaction conditions only slightly modified in comparison with those for the polymerization of pure VC. An optimum content of the incorporated poly-EHA in PVC was found to be in the range 7.5-8.5 wt %, whereas notched toughness of 85–87 kJ m<sup>-2</sup> was reached. Both below and above the found range of the content of poly-EHA, the toughness decreases. A copolymer prepared by a directemulsion copolymerization of 2-EHA and VC (poly-EHA-co-VC) exhibited worse mechanical properties than the copolymer prepared by two polymerization steps. On the basis of experimental results, effects of the reaction procedure on the properties of resulting material are described. In addition to good mechanical properties, tPVC also shows its noncombustibly. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2355-2362, 2002

**Key words:** 2-ethylhexyl acrylate; homopolymerization; elastomer; grafting, vinyl chloride; notch toughness; tough poly(vinyl chloride)

#### **INTRODUCTION**

The applicability of polymer materials is predominantly influenced by their mechanical properties, and toughness is one of the most important properties. Toughness is characterized as the work applied in a drawing test which ends in the destruction (ripping) of a material. A quantitative value of this work was obtained by the integration of the stress-strain curve along the strain axis. Impact toughness is the ability to resist a force, resulting in a brittle fracture (usually breaking a hole in a specimen).<sup>1-4</sup> A special type of toughness test is represented by the treatment of notched samples<sup>1,3</sup> (notched toughness), which allows us to consider the effects of surface structure on the strength of the material.

Analysis of the stress-strain curves allows us to distinguish between brittle and tough materials. A brittle material breaks with minimal deformation. Before total cracking, small cracks (crazing) develop perpendicular to the principal direction of deformation. In contrast, a tough material

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exhibits a substantial deformation before breaking (a plateau on the stress-strain curve is very often observed).<sup>1,4,5</sup> A ratio between brittle and shear strength of the material determines the type of break. If the brittle strength is lower than the shear strength, the break will be brittle, and similarly, lower shear strength than the brittle strength contributes to elasticity and may improve toughness of the material.<sup>6,8</sup> Generally, there are two main ways to increase the toughness, as follows: (1) to increase the brittle strength (e.g., by lowering the extent of crosslinking); and (2) to increase the tendency to slipping (i.e., to lower the shear strength). Since increasing the glass transition temperature by the addition of crosslinkers and subsequent worsening, or even impossible, thermal processibility, copolymers with crosslinkers are used if the final products are prepared by block copolymerization (thermosets instead of thermoplastics are prepared). In addition, higher crosslinking increases the fragility of a polymer (low brittle strength). A special type of crosslinking uses inorganic fillers,<sup>2</sup> (e.g., metal oxides, carbonates, or silicates) of about 50-100 nm. These small particles retain their reactivity and, in part, react with polymer molecules. Of course, this type of filler also decreases shear strength; thus, both the affects are applied.

To prepare a tough poly(vinyl chloride) (*t*PVC), which is desired to process thermal-mechanical operations, the second approach is frequently used. Elastomeric nanomoieties (fillers) are incorporated into the mass of the polymer,<sup>6-10</sup> hence, condition (2) is fulfilled.

Incorporation of elastomer moieties may be attained either by mechanical mixing of powder PVC with powder particles of elastomeric polymer or by grafting of vinyl chloride (VC) on little elastomeric polymer beads. A grafting procedure usually leads to better properties of the *t*PVC; however, the used elastomer polymer must exhibit particular features to obtain not only good mechanical properties of the final copolymer, but to have also good processibility of the polymer mass.<sup>6–10</sup> Most of all, the transition glass temperature  $T_g$  must be lower than a temperature considered for application of a polymer product. Second, elastomer moieties must form a separate phase in the polymer matrix because a dissolved elastomer can act as a plasticizer. If these features are not attained, mechanical strength can be decreased and/or brittleness may occur at a certain (particularly lower) temperature.

In contrast to the requirement of the separate phase formed by the elastomer, a proper adhesion of the elastomer particles to surroundings represented by the PVC phase is necessary. The best method for attaining this feature is the grafting of VC on elastomer beads. Elastomeric features of elastomer-polymer domains must be preserved in the final polymer, but the polymer mass must be sufficiently homogeneous. These properties can be established by the size of the elastomer domains<sup>11,12</sup> of 30–300 nm, which implies the size of prepolymerized elastomer particles.

The next contradictory property with quasihomogeneous distribution of elastomeric moieties is the requirement for good weather resistance to allow good mechanical properties and treatability of the polymer mass. Window-frame profiles, facings of buildings, roof covers, and so on are typical examples of polymer goods that must fulfill these requirements. It is well known that PVC is more resistant and stable than commonly used elastomers [e.g., poly(ethylene-co-vinyl acetate), poly-(ethylene acrylate]. Thus, polymer products prepared by mechanical mixing may have shortcomings stemming from a higher concentration of the less stable elastomer particles located on the surface and/or very close to the surface of the product.

Despite the mentioned problems, the majority of products from tPVC is manufactured by mechanical mixing and partial molding (the socalled compounding process) of PVC and elastomer polymers as dispersions. Besides polyelastomers obtained from alkylvinyl acetates and alkyl acrylates, chlorinated polyolefines (e.g., chlorinated polyethylene) are of gradually increasing importance. Of course, the best method should be copolymerization (grafting on the prepolymerized beads of elastomer); this procedure has attracted our attention.

This article reports on the preparation of VC copolymers with 2-ethylhexyl acrylate eventually crosslinked with multifunctional monomers. We focused on the comparison of the polymers prepared in one polymerization step (copolymerization of VC and 2-EHA) with polymer prepared by two polymerization steps [i.e., grafting of VC on the poly(2-EHA) beads prepared by emulsion polymerization].

#### **EXPERIMENTAL**

#### Chemicals

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), 1,1dichloroethane (3), 1,2-dichloroethane (4), monovinyl acetylene (12), and water (193). 2-Ethyhexyl acrylate (EHA, Chemical Works, Sokolovo, Czech Republic), purity 99.2 wt %, with a density of 885 kg m<sup>-3</sup> and m.p. of -90°C was used. Triallyl ester of cyanuric acid (Fluka A.G.) C<sub>2</sub>H<sub>15</sub>-N<sub>3</sub>O<sub>3</sub> of 99.1 wt % purity and m.p. 25-28°C and pentaerythritol tetraacrylate (VUP, Prievidza, Slovak Republic) of 97.3 wt % purity were obtained. Potassium peroxydisulphate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) of purity 98.9 wt % with free sulfuric acid (0.04 wt %) and iron (as  $FeSO_4$ , 0.005 wt %), natrium dithionite (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> 2H<sub>2</sub>O, Lachema Brno, Czech Republic) m.p. 52°C, calcium formate (Chemko Strazske, Slovak Republic) of chemical grade purity, and demineralized water were used.

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.

Methylhydroxypropyl cellulose (Methocel F50, Dow) with 28.5% methoxyl groups and 6.1% hydroxypropyl groups was obtained. 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), a mixture of linear sodium alkylsulphonates  $C_{12}$  to  $C_{18}$  with 39% of dry weight, was also used.

#### Preparation of the Poly(2-ethylhexyl acrylate) Dispersion

Poly(2-ethylhexyl acrylate) elastomer was prepared by emulsion homopolymerization of 2-ethylhexyl acrylate in water by initialization affect of the redox system ( $K_2S_2O_8 + Na_2S_2O_4$ ) at 30  $\pm$  0.1°C. The most frequent weight ratio of water : EHA was 3 : 1.

Copolymer with triallyl cyanurate (3 wt % with respect to EHA) was prepared in water at  $80 \pm 0.1^{\circ}C$  (wt 3 : 1 = water : EHA). The amounts of initiator (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) and emulsifier (E-30) were 0.75 and 1 wt %, respectively, with respect to EHA. A copolymer with pentaerythritol was prepared similarly, but the amount of water was 2 : 1.

#### Preparation of a Suspension tPVC

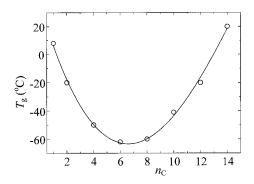
The pre-prepared polyacrylate dispersion (poly-EHA) was used for the suspension-grafted polymerization with VC which was carried out in a reactor (10 dm<sup>3</sup>) equipped with an anchor stirrer. Typical amounts of components used for the polymerization were (in  $cm^3$ ): VC (3300); water (3500); water solution with 2 wt % of Methocel 50F, 10 g of the mixed initiator EHP-80 (500), and water solution containing 20 g calcium formate (150). The amount of poly-EHA varied according to the desired content in the final product. After closing the reactor and removing the air, components of the polymerization mixture were inserted into the autoclave while the mixture was stirred. For 25 min, the autoclave was heated to a temperature of 54  $\pm$  1°C and then kept at this temperature until the pressure decreased by 0.3 MPa (taking about 5 h). The reacted mixture was cooled and nonconverted VC was released to the waste VC reservoir. The suspension was filtered, washed with water three times, and dried under reduced pressure at a temperature of 50°C.

A similar procedure was used for the preparation of copolymer of VC with EHA.

#### Analysis of Chemical and Physicochemical Properties of Copolymers

The size of the latex particles in the EHA dispersion obtained by the emulsion polymerization was evaluated by using a dynamic light scattering method. The ratio of monomers in yielding poly-(vinyl chloride-*co*-2-ethylhexyl 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. The distribution according to size of the suspension copolymer particles was determined by the sieve analysis following the procedure STN 64 0212 (equal to EN ISO 1624, 1997). The viscosity number of polymers were determined following STN 64 0325 (equal to EN ISO 1628-2, 1998).

To determine other physical and mechanical properties of the copolymer, the PVC suspension was treated as follows: The ingredients [1.5 g dibutyltin maleate, 0.5 g calcium stearate (thermostabilizers), and 0.5 g montan wax (external lubricant)] were added to 97.5 g of a suspension copolymer. After 5 min of homogenization in an isothermal mixing device at  $25 \pm 2^{\circ}$ C, the mixture was molded and either calandered or expelled. Calandering was on the double roller at a temperature of 160°C for 5 min. The samples for measurements were cut from the prepared materials. Size of specimens was  $4 \times 6 \times 50$  mm (calandered copolymer) or  $4 \times 10 \times 80$  mm (ex-



**Figure 1** Influence of the number of carbons  $(n_{\rm C})$  in the alkyl chain of poly(alkyl acrylate) on the glass transition temperature  $(T_{\rm g})$  (from data given in ref. 16).

pelled copolymer). Measurements of notch toughness were carried out following the procedure given in STN 64 0612 (equal to EN ISO 179, 1997) usually at a temperature of 20°C. According to the protocol of notch-toughness measurements, notch-toughness  $A_{nt}$  is expressed in units of kJ m<sup>-2</sup>. The next details are given in reports.<sup>4,13,14</sup>

#### **RESULTS AND DISCUSSION**

#### Elastomers as Filler for Improvement of Toughness

Three methods are commonly used for the preparation of copolymers by grafting a polymer A with monomer/oligomer units of a polymer B:

- 1. Grafting by transition of polymer chains of the monomer B on polymer A;
- 2. After activation of reactive groups and/or fragments of macromolecules of polymer A;
- 3. Grafting with exploitation of functional groups attached to polymer A.

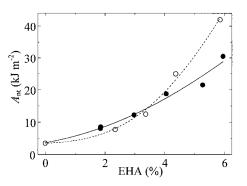
From this list, procedure 2 was mainly used in our work. The tendency to graft vinyl polymers is proportional to reactivity of their radicals and is given by the sequence<sup>15</sup>: vinyl chloride > vinyl acetate > ethyl acrylate > methyl methacrylate > styrene. Judging from the effect of molar weight on the reactivity and steric obstacles, 2-ethylhexyl acrylate could have lower reactivity than methyl methacrylate.

In the past, we realized<sup>4</sup> that suspension homopolymerization of alkyl acrylates (e.g., poly-EHA) did not give an appropriate elastomer for the preparation of *t*PVC. One of reasons for such a behavior may be a low compatibility (homogenization) of poly-EHA with VC; a homogeneous sol not is obtained, but only a strong swollen gel. Residues of the dispersifier Methocel F-50, which sticks to particles of poly-EHA and restricts their solvation, probably cause this low compatibility. On the basis of knowledge about other copolymers [e.g., poly(ethylene vinyl acetate)] with good homogenization ability, we have tried to modify the procedure for the preparation of poly-EHA as described under Experimental. We have chosen 2-EHA as a good precursor of the elastomer because of the very good value of the glass transition temperature (Fig. 1) and its commercial availability.

#### **Preparation of EHA Elastomers**

At the first stage of our investigation, crosslinked copolymers of 2-EHA either with triallyl cyanurate or with pentaerythritol (both 3 wt %) were prepared. The size of the dispersion particles was 100–200 nm. Figure 2 documents a positive effect of the added elastomer on the notch toughness, but crosslinkers present in the elastomer increase  $T_g$ , which is not desired for final utility properties of the copolymer.

A preparation of elastomers based on the pure 2-EHA was the next stage of our investigation. In this case, the size of particles was slightly lower than in the case of crosslinked ones: 80-160 nm. The limit viscosity number ( $\eta$ ) was the value for characterization of different batches of elastomers. To determine this quantity, we directly treated water dispersion of poly-EHA with toluene under vigorous mixing and heating, whereas the formed water was separated after cooling of toluene–water vapors. This procedure is faster



**Figure 2** Notch toughness  $(A_{nt})$  of *t*PVC versus the content (EHA) of incorporated poly-EHA, prepared with 3 wt % of crosslinker: (•) Triallyl cyanurate; (O) pentaerythritol triacrylate.

	Initialization System (wt % to EHA)				tPVC <sup>a</sup>		
Entry	$K_2S_2O_8$	$\mathrm{Na_2S_2O_4}$	Dosing of EHA	Elastomer $\eta \ (\mathrm{cm}^3 \ \mathrm{g}^{-1})$	$w_{\rm EHA}^{\rm \ b}(\%)$	$A_{\mathrm{nt}}^{}\mathrm{c}}(\mathrm{kJ}\;\mathrm{m}^{-2})$	
1	1	0.7	$\mathrm{batch}^{\mathrm{d}}$	360	7.0	14.6	
2	0.6	0.4	batch	320	6.7	18.8	
3	0.6	0.4	cont. <sup>e</sup>	400	5.6	7.1	
4	0.3	0.2	cont.	350	6.0	19.6	
5	0.3	0.2	1/2 + 1/2	250	6.9	62.0	
6	0.3	0.2	1/2 + 1/2	180	6.7	60.7	
7	0.3	0.2	1/2 + 1/2	200	5.5	48.6	
8	0.05	0.035	1/2 + 1/2	450	8.0	3.0	
9	0.1	0.07	1/2 + 1/2	350	8.0	3.7	
10	0.3	0.2	1/2 + 1/2	250	7.4	66	
11	0.6	0.4	1/2 + 1/2	150	8.1	67	

Table I Influence of Dosing of 2-EHA to the Reaction Mixture of Its Emulsion Polymerization (wt  $H_2O$  : EHA = 2 : 1, Content of the Emulsifier 1.5 wt % to EHA, 30 ± 0.1 °C) and Amount of Initialization System, on Viscosity ( $\eta$ ) of the Elastomer, and Properties of the *t*PVC

<sup>a</sup> Tough PVC prepared from the poly-EHA and VC.

<sup>b</sup> Content of poly-EHA in the *t*PVC.

<sup>c</sup> Notch toughness of the *t*PVC.

<sup>d</sup> Batch polymerization.

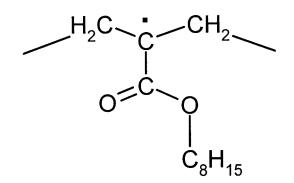
<sup>e</sup> Continuously during 5 h.

and simpler than dissolution of isolated poly-EHA in toluene. Depending on the reaction conditions, poly-EHA with the limit viscosity number ( $\eta$ ) up to 800 cm<sup>3</sup> g<sup>-1</sup> were prepared, but polymers with  $\eta > 300$  cm<sup>3</sup> g<sup>-1</sup> are not suitable for copolymerization with VC due to their bad compatibility. This phenomenon is illustrated by Table I, where copolymers prepared from poly-EHA with a low value of  $\eta$  exhibited the best toughness.

## Branch and Linear Elastomers—Effect of Dosing 2-EHA

The viscosity number of poly-EHA, as well as properties of the subsequently prepared *t*PVC, strongly depend on the preparation protocol of the poly-EHA, as reported in Table I. When the whole amount of 2-EHA is dosed at the start, then the notch toughness  $10-20 \text{ kJ m}^{-2}$  is obtained for the *t*PVC, containing about 7 wt % of elastomer (e.g., entries 1 and 2 in Table I). However, if 2-EHA is added in two portions (the initiator is added at the start), the resulting *t*PVC exhibits the notch toughness of  $60-70 \text{ kJ m}^{-2}$  (entries 5, 6, 10, and 11 in Table I).

Elastomers with a significant positive influence on the notch toughness of copolymers are also typical with a relatively low viscosity and a very low concentration dependence of viscosity in the concentration range 0.02-0.5 wt % (the slope is close to zero). On the contrary, elastomers with higher viscosity-concentration dependence do not allow the production of *t*PVC with a good toughness. It is well known that macromolecules with a branched structure contribute less to the increase of the viscosity than macromolecules with the same molar weight but with a linear structure. This statement explains why neither the batch nor the continuous addition of 2-EHA to the polymerization mixture resulted in good elastomers. In both cases, mainly linear chains grow. On other hand, when 2-EHA is dosed in two aliquot portions (the second half after reaching about 55-70% conversion of 2-EHA), probability for branching is increased. This is due to partial consumption of components of the initiator system, as well as low concentration of 2-EHA in the polymerization mixture. Initialization of both the end and the inner parts of macromolecules may arrange continuation in polymerization, whereas activation of alpha-carbon in the macromolecule is supposed. This assumption is based on the activation by the carbonyl group and consequent lowering of strength of the C-H bond on the alpha-carbon in comparison with other C-H bonds in the macromolecule. In addition, this kind macroradical (Fig. 3) is stabilized by the effect of the ester



**Figure 3** Fragment of the macroradical formed from poly(2-ethylhexyl acrylate).

group. Monomers can enter a reaction with this activated carbon (or radical) more easily because of a higher mobility than oligomers, or even macromolecules; therefore, a branched structure of the macromolecule may start to develop. We denote this branched (grafted) macromolecule as the poly-EHA-g-EHA.

To obtain a good elastomer, components of the initiator system cannot be totally consumed. This is illustrated by experiments with low concentration of the initiator system (i.e., entries 8 and 9), in which only 0.05 and 0.1 wt % of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, respectively, related to 2-EHA were used. The best tPVC ( $A_{nt} = 67 \text{ kJ m}^{-2}$ ) was obtained with middle and higher concentrations of the initiator: 0.6 wt % related to 2-EHA (entry 11 in Table I) and the two-step addition of 2-EHA. It is important to stress once more that dosing of the initiator in two portions, together with 2-EHA, always resulted in tPVC of worse quality than when all amounts were charged at the start. This again implies a different behavior of the fresh and partially consumed (deactivated) initiator.

#### Compatibility of Poly-EHA with VC versus Emulsifiers

Besides its positive effect in the suspension polymerization of VC with poly-EHA, emulsifier also has a negative effect, because it lowers compatibility of VC with poly-EHA. This negative effect is suppressed by divalent metal cations [e.g., Ca(II), Mg(II), Ba(II), etc.].<sup>12</sup> As a complication of the addition of inorganic salts, coagulation of elastomer dispersion may appear. We searched for a proper solution of the outlined problems using calcium formate as a modifier of the polymerization system. First, we determined a precipitate curve [reaction (1)] expressing the amount of the

precipitate versus the amount of calcium formate added to the solution with the same concentration of emulsifier (Mersolat) and dispersifier (Methocel F50) as used in the polymerization,

$$2 C_{15}H_{31}SO_3Na + (HCOO)_2Ca \rightarrow (C_{15}H_{31}SO_3)_2Ca + 2HCOONa \quad (1)$$

Despite the fact that two- or threefold of the amount of calcium formate predicted by the precipitation curve was used in our experiments (precise figures are in Experimental), we have not observed any problems in the polymerization of VC with 2-EHA or 2-EHA-g-EHA. No negative effect on properties of the final *t*PVC is not surprising if no coagulation dispersion was observed by visual investigation of the elastomer stirred for a few hours in polymerization mixture without VC. Thus, we can assume that after proceeding of the reaction (1), preservative-colloidal properties of the emulsifier-dispersant system are sufficiently strong to prevent coagulation of the dispersion. A similar ratio of components may be also advised for industrial application of the preparation of this kind of *t*PVC.

## Effect of Dispersifier and Stirring on the Granulometric Properties of *t*PVC

As given in Table II, a lower or higher concentration of dispersant (Methocel F50) shifts distribution of particles to bigger or smaller beads. Good processing of the suspended *t*PVC requires the narrowest distribution of particles between 0.25 and 0.063 mm. The portion bigger than 0.25 should be zero; the portion lower than 0.063 mm should be close to zero. This requirement is mainly for handling and optimizing (shortening) residence time in a processing device. Laboratory tests showed similar properties of products (e.g., foils; see Experimental) not significantly dependent on the granulometric composition.

Better distribution of suspended tPVC particles was obtained at lower rotations of anchor stirrer. This effect could be prescribed to lower hydrodynamic disturbances in the surroundings of developing tPVC particles. However, these observations and statements are only valid for our laboratory reactor. A larger industrial reactor requires further step-by-step optimization.

### Poly-EHA-g-EHA and poly-EHA-g-VC Elastomers versus Toughness

To increase compatibility of elastomer dispersion with VC, we prepared the EHA-g-VC elastomer

		Distribution (wt %) of Powder <i>t</i> PVC According to Amount of Hold up on the Sieve with the Size (mm)						
$c_{ m disp.}$ (wt % to VC)	$rpm (min^{-1})$	0.25	0.20	0.18	0.10	0.063	Throughs	
0.24	250	0.4	0.4	0.4	9.2	38.4	51.2	
0.24	200	0.4	1.0	1.4	36.2	41.0	20.0	
0.18	300	0.2	0.8	21.2	20.3	24.3	33.2	
0.18	250	0.6	9.6	16.6	28.6	23.6	21.0	
0.18	200	0.3	8.0	10.5	32.1	32.9	16.2	

Table II Influence of the Concentration of the Dispersifier  $(c_{disp.})$  and Rotations (rpm) of the Anchor Stirrer on Glanurometric Composition of the Formed *t*PVC (8 wt % of poly-EHA Prepared According to Entry 10 in Table I)

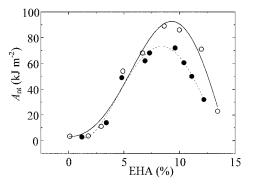
containing 8.3 wt % of incorporated VC. This elastomer was prepared by emulsion copolymerization of 2-EHA with VC carried out similarly as the previously described homopolymerization of 2-EHA with dosing all amounts of monomers at the start. Both these elastomers were used for the preparation of tPVC and results from notch toughness tests are reported in Figure 4. The value of about 8 wt % of poly-EHA seems to be optimal for both elastomers. Evidently, the pure poly-EHA-g-EHA manifests higher improvement in toughness than poly-EHA-g-VC. The wide range of applicability of poly-EHA-g-EHA (from 7 up to 10 wt %) is important for processing the prepared *t*PVC; fewer inhomogeneities in the distribution of elastomer cause a lower negative effect than would be the case of poly-EHA-g-VC elastomer.

A decrease in toughness above 9.5 wt % of the content of EHA shows an increase of elastic properties of *t*PVC due to the nature of elastic properties of poly-EHA. When elastomeric filler particles are present as filler, they stretch under ap-

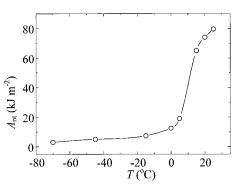
plied strength, thus dissipating much of the energy necessary to develop the new surfaces of the crack. If a higher amount of filler is applied, shear strength (tendency to slipping of polymer domains) is decreased so much that a brittle appearance of *t*PVC can totally turn out to be elastic. To summarize, elastomeric fillers act as toughness improvers up to a certain content; then there is a transition region in which toughness is similar to the original material. Next, elastomer increases elasticity and softness of a polymer (e.g., well reflected by ductility). Recently,<sup>13,17</sup> we reported on intrinsically softened PVC containing 12-60 wt % of butyl acrylate, which prepared under a special protocol, proved to be well processible, and products exhibited very good properties (nonleaching of plasticizer, shape stability, good aesthetic appearance, etc.).

#### Notch Toughness of tPVC versus Temperature

Figure 5 shows the highest toughness of tPVC around 20°C. Lowering the temperature has a



**Figure 4** Notch toughness  $(A_{nt})$  at 20°C of *t*PVC versus the content (EHA) of incorporated poly-EHA. (O) Elastomer prepared only from 2-EHA; ( $\bullet$ ) Elastomer prepared from 2-EHA and VC.



**Figure 5** Notch toughness  $(A_{nt})$  versus temperature (T) of the *t*PVC containing 8 ± 0.3 wt % of poly-EHA elastomer.

dramatic effect on the notch toughness; products begin to be more fragile. A higher content of elastomer could increase the notch toughness even at lower temperature. Because handling of products from *t*PVC is carried out mainly at the temperature close to 20°C, after positioning these products on or at an aim place, they are not strained so much. Consequently, the temperature decrese in toughness may not be evaluated negatively. In any case, PVC materials modified with elastomeric fillers exhibit better toughness than nonmodified ones also at lower temperature.

#### Industrial Applicability of the Developed tPVC

The developed elastomeric poly-EHA-g-EHA filler enables us to prepare *t*PVC, which has more than 10-fold higher notch toughness at room temperature than the original PVC. In comparison with rigid inorganic filler, this elastomeric filler does not worsen processibility. On the contrary, at higher temperatures, the elastomer nature of elastomer particles makes tPVC treatment better. All common techniques can be applied for the manufacture of products from thermoplastics (e.g., pressing, calandering, but also injection). Additional tests showed that PVC containing a higher content of poly-EHA-g-EHA can be processed together with commercial suspension and emulsion types of PVC. Of course, thermal treatment of *t*PVC must be minimized to avoid dissolution of elastomeric particles in the bulk volume of PVC. The final product manifests increased notch toughness depending on the content of EHA (Fig. 4). Moreover, final products from this *t*PVC are practically noncombustible.

### CONCLUSIONS

We developed a procedure for the preparation of tough poly(vinyl chloride) by grafting vinyl chloride on the dispersion of poly(2-ethylhexyl acrylate) acting as an elastomer filler. The best results were obtained with poly(2-ethylhexyl acrylate) prepared by the emulsion polymerization with two-step dosing of aliquot portions of 2-ethylexyl acrylate to the polymerization mixture. On the basis of viscosity measurements and reactivity, a hypothesis concerning branched macromolecules resulting from grafting of monomer units of 2-ethylhexyl acrylate on the poly(2-ethylhexyl acrylate) was suggested. These branched macromolecules have better filler properties and consequently higher improvement in toughness is reached.

With respect to good mechanical properties, compatibility with commercially available emulsion, and suspension PVC, the developed tPVC is a good candidate for the production of tough, noncombustible, nontoxic goods applicable in civil engineering, furniture, agricultural equipment, and others. Results reported in this article offer a basic design of an industrial reactor for the production of the described tPVC. More detailed information is available from the corresponding author.

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