

Free-Radical Grafting of *trans*-Ethylene-1,2-Dicarboxylic Acid onto Molten Ethylene-Vinyl Acetate Copolymer

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ABSTRACT: Distinctive features of free-radical grafting of *trans*-ethylene-1,2-dicarboxylic acid (TEDA) onto macromolecules of molten ethylene-vinyl acetate copolymer (EVA) in the course of reactive extrusion have been investigated along with structure, mechanical characteristics, and high-elastic properties of molten functionalized products (EVA-*g*-TEDA). It is shown that EVA-*g*-TEDA yield depends on both the peroxide initiator concentration and content of vinyl acetate units in the copolymer molecular structure. At functionalization, acid grafting is accompanied by secondary reactions of macromolecular degradation and crosslinking. With a low-peroxide initiator concentration (0.1 wt %), degradation prevails; with a higher (0.3 wt %) concentration, crosslinking of macromolecules prevails. It is reported that monomers being grafted attach mostly over secondary carbon atoms in the polymer chain. EVA-*g*-TEDA appears to have a less perfect crystal structure with a lower-melting temperature and crystallinity as against the starting polymer. The functionalized products display enhanced rigidity and lower deformability in comparison with the initial copolymer. Variations in the swelling ratio and melt strength of EVA-*g*-TEDA depend on the course of competing secondary processes of macromolecular degradation and crosslinking. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

The grafting of polar unsaturated monomers onto polyolefin (PO) macromolecules in melt in the extrusion mixer–reactor has been widely used to achieve new functional properties.^{1–4} PO containing grafted-polar monomers (functionalized PO) have been used as compatibilizers to improve compatibility of blends consisting of polar and nonpolar polymers, to intensify interphase interactions between macromolecules and filler surface, to increase adhesion to solid surfaces, to control high-elastic properties of polymer melts, to produce concentrates of various additives to be used in polymer composites.^{3–5} PO-macromolecules have most often been functionalized in melt by the reactive extrusion method (RE); the material cylinder of the extruder serving as a continuously acting reactor.^{1–3,5,6}

It had to be noted that most researches of fundamental importance for the development of notions about reactions—occurring during macromolecular functionalization in melt—have been devoted to nonpolar PO such as polyethylene (PE), polypropylene (PP), and ethylene–propylene copolymers.^{1–12}

One of the most important representatives of the PO family is ethylene-vinyl acetate copolymer (EVA).^{13,14} A relatively high strength, resistance toward aggressive media, elasticity at low temperatures, adhesion to different materials, and a number of other specific properties allow to use EVA for making technical parts, electrically insulating cable sheathings, films, compounds and blends with other polymers, and various fillers. Besides, EVA has been used to prepare hot-melt adhesives for footwear, furniture and other industries, protective coatings for hard surfaces, metal pipes with protective polymeric envelopes, intermediate adhesive layers in multilayer articles, films, etc.^{13–15}

The high adhesiveness of EVA is explained by carbonyl groups present in side chains of macromolecules. Their concentration increased by higher amounts of vinyl acetate (VA)—used to synthesize EVA—leads to higher adhesiveness of the copolymer.^{14,16} However, the set of rheological, thermal, and stress–strain properties undergoes changes, which in fact somewhat limits the choice of copolymer for a specific application.

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Table I. Test Materials and Their Properties

Material	Symbol	VA content (wt %)	T_m (°C)	T_{cr} (°C)	MFI* (g/10 min)	δ ((J cm ⁻³) ^{0.5})
EVA 11306-075	EVA (113)	12.0	97.0	72.0	12.4	17.1
EVA 12306-020	EVA (123)	17.5	91.0	68.0	3.5	17.4
EVA 12508-150	EVA (125)	28.0	82.6	54.6	12.7	17.9
<i>Trans</i> -ethylene-1,2-dicarboxylic acid	TEDA	-	287.0	-	-	21.4
1,3-Bis-(<i>tert</i> -butylperoxyisopropyl) benzene	Perk-14	-	40.0	-	-	16.4

*Determined at $T = 190^\circ\text{S}$, $R = 21.6\text{ N}$, capillary diameter, 2.095 mm.

Besides, it is often impossible to control EVA adhesiveness within required limits only by varying the VA concentration. The presence of only side VA pendants in copolymer macromolecules does not ensure satisfactory compatibilizing activity of the copolymer in polymer blends.^{17,18} That is why EVA is being modified, also by free-radical grafting of adhesion-active groups (anhydride, carboxyl, isocyanate, etc.) in polymer melts using extrusion mixers-reactors.

Several authors^{19,20} have reported a possibility of grafting polar monomers onto EVA macromolecules in the presence of initiators of free-radical reactions. Particularly, maleic anhydride (MA) was grafted onto EVA macromolecules in Haake mixing unit at 110–140°C during 8 min in the presence of different peroxide initiators.¹⁹ It was shown that vinyl acetate units in the EVA structure favor more efficient grafting of MA in comparison with LDPE. A major secondary process that accompanies grafting of MA onto EVA is macromolecular crosslinking, which also proceeds more intensively in comparison with LDPE.

In study,²⁰ MA was grafted onto EVA in the twin-screw extruder at 200°C; dicumyl peroxide being the initiator. It was also found that VA fragments present in the macromolecular structure stimulate grafting of MA onto EVA. It was shown that crosslinking of macromolecules and disproportionation of macroradicals occur side-by-side with grafting.

The data of study^{19,20} are important for understanding the grafting rules for MA onto EVA. However, detail understanding of functionalization in melt of this copolymer requires accumulation and generalization of experimental data on grafting carried out with different monomers and initiating systems. It is also necessary to clarify the influence of VA-fragments in the EVA macromolecular structure on the grafting-reaction progress and concomitant processes when monomers of various chemical structures are used. Because at RE-regimes the grafting reaction and concomitant chemical transformations can be influenced by both the chemical activity and mutual dissolution of the reagents,⁴ it may be of interest to estimate the efficiency of EVA functionalization from the solubility viewpoint. And it is not clear from the analysis of the researches performed to what types of carbon atoms in EVA chain macromolecules the grafted monomer gets attached. It was reported in^{19,20} that MA was mainly grafted to tertiary carbon atoms of the main chain belonging to the methine group (>CH-). It was reported in,²¹

however, that in MA grafting as well as in crosslinking reactions there participate, mostly, methyl groups (–CH₃) belonging to VA fragments. It seems important to study the functionalization effect of EVA macromolecules and the set of concomitant reactions on the structure and properties of grafted products.

The present work is aimed at analysis of special features of EVA functionalization by grafting *trans*-ethylene-1,2-dicarboxylic acid (TEDA) during RE; at studying the structure, rheological and high-elastic properties of melts, and deformation behavior of EVA-g-TEDA.

EXPERIMENTAL

Materials

The objects of investigation were EVA with different VA-concentrations as produced by JSC “NefteHimSevilen,” Russia. The monomer-grafted TEDA, pure grade, was supplied by Kamtex, Russia. The initiator was 1,3-bis(*tert*-butylperoxyisopropyl) benzene (Perk-14) produced by Akzo Nobel, Holland. The properties of these products are listed in Table I. EVA-grades in Table I were chosen for investigation based, first of all, on the fact that these copolymers differ in VA-group concentration, which permits estimating of how their amount influences the TEDA-grafting efficiency, as well as the course of secondary reactions. Besides, these EVA are produced commercially, which predetermines a possibility of immediate using the results obtained for practical purposes.

Preparation of Functionalized EVA

The functionalization of EVA (TEDA grafting) was performed by RE using the extrusion-granulating line based on the twin-screw extruder TSSK 35/40 (China; screw diameter, 35 mm; L/D = 40; the number of heating zones, 10); the screws were equipped with special mixing elements. EVA granules, powders of TEDA and Perk-14 were separately measured on weight-dose meters and loaded into the main zone of the extruder TSSK. The zone temperatures in the materials cylinder were, °C: I—60; II—120; III—150; IV–VIII (main zones of the reaction)—180; IX—170; X—160. Having passed through the material cylinder, molten EVA-g-TEDA appeared from the dies in the form of four strands; the latter were water-cooled, hot-aired, and granulated on the rotor-type granulator. The granulate obtained was then dried at 60–70°C up to a residual humidity not higher than 0.02%, and used for analysis.

In all of the experiments, the concentration of TEDA grafted onto EVA was constant, 1.0 wt %; the Perk-14 content was varied from 0.1 to 0.3 wt %.

Estimation of Grafting Efficiency, MFI, and Gel-Fraction

The monomer content grafted onto EVA macromolecules was determined by titration. To do this, film samples of the functionalized EVA were placed in Soxhlet apparatus and the ungrafted monomer was extracted in acetone for 18 h. An EVA-g-TEDA sample of 1.0 g was dissolved in *p*-xylene, 100 mL at $95 \pm 5^\circ\text{C}$. The prepared solution was quickly titrated with 0.1 N KOH alcohol solution. The indicator was 1.0% alcohol solution of phenolphthalein. The grafted acid was calculated in terms of acid number values (AN)²²:

$$\text{AN} = \frac{V \times T \times 1000}{g} \quad (1)$$

where *V* is the 0.1 N KOH-solution, mL, spent for sample titration; *T* is the KOH solution titer; *g* is the weighed sample, g, of the product being investigated.

The grafting efficiency (α) was found from Expression 2²²:

$$\alpha(\%) = \frac{\text{AN} \times E_{\text{ac}}}{561}, \quad (2)$$

where AN is the acid number, E_{ac} is the equivalent acid weight.

The calculated results were averaged over three parallel measurements. The melt viscosity of the polymer materials was found from the melt flow index (MFI) values determined at 190°C , load 5 kg, and capillary diameter 2.095 mm using IIRT-AM instrument (Ukraine).

The gel-fraction in functionalized EVA samples was determined as described elsewhere^{19,20}; the solvent being *p*-xylene.

FTIR Analysis

The FTIR spectrophotometer Nicolet 5700 (USA) was used to record IR-spectra of the extracted film samples of both initial and functionalized EVA. The spectra were recorded with 0.4 cm^{-1} resolution; the scan number was 60.

The absorption band at 1372 cm^{-1} methyl groups contained in VA-fragments was analyzed.²³ The absorption band with maximum at 4325 cm^{-1} (skeletal vibrations $-\text{CH}_2-$) was used as the internal standard.

The mathematical treatment of IR-spectra was performed using the OMNIC (Version 7.1) computer program that contains functions to build base lines and calculate integral intensities of absorption bands. The arithmetic mean values of optical densities were obtained by analyzing the results for nine samples (relative error of a single measurement being below 0.8%).

Estimation of Component Solubility

The mutual solubility of components in the reaction mix was estimated from their solubility parameters (δ) that were calculated using the group contributions following the procedure from this study.²⁴

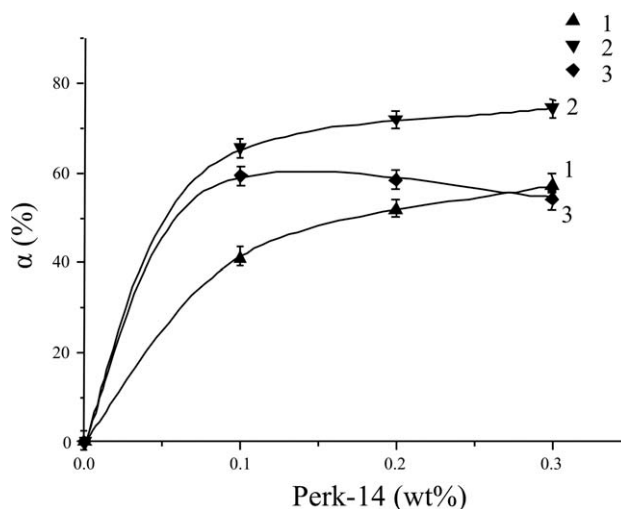


Figure 1. Effect of peroxide initiator concentration on grafting efficiency TEDA onto EVA macromolecules, 1—EVA (113); 2—EVA (123); 3—EVA (125).

DSC Analysis

The differential scanning calorimetry technique (DSC) was used to determine the thermal properties and structure of the materials. The study was performed using microcalorimeter Perkin Elmer Diamond DSC (Shelton, USA); the weighed sample being 5 mg; heating/cooling rate, $16^\circ\text{C}/\text{min}$. To exclude the effect of sample, thermal prehistory on the structure, the measurements were conducted on samples, which had been first preheated up to 160°C in calorimeter cells, controlled thermostatically at this temperature for 60 s, then used for analysis.

Measurements of Mechanical Properties

The mechanical properties of the materials were determined on injection-molded samples (machine EN-30, Taiwan; injected volume, 30 cm^3 ; molding temperature, 170°C). The test samples were bars; the neck measuring $45 \text{ mm} \times 5 \text{ mm} \times 2 \text{ mm}$. The tensile tests were performed on machine Instron 5567 (UK); the loading rate being $50 \text{ mm}/\text{min}$. The arithmetic mean value of five parallel tests was taken as mechanical property value.

Characterization of High-Elastic Properties

The high-elastic properties of molten initial EVA as well as those of functionalized EVA, were estimated from their melt strength (σ_m) and jet swell ratio (*K*) as determined following the procedure described elsewhere.^{5,25,26}

RESULTS AND DISCUSSION

Grafting Efficiency and MFI of Materials

It can be seen in Figure 1 that the grafting efficiency of TEDA onto EVA macromolecules depends not only on the peroxide concentration but also on the VA content in the copolymer as well. The mode of peroxide influence depends on the EVA type: with a relatively low VA content [EVA (113), [VA] = 12% and EVA (123), [VA] = 17.5%; Table I] the concentration dependences α are ascending curves with saturation, while with a relatively high VA content [EVA (125), [VA] = 28%] the α -values decrease with increasing Perk-14 concentrations (Figure 1). On the whole, it can be stated that with higher VA-contents

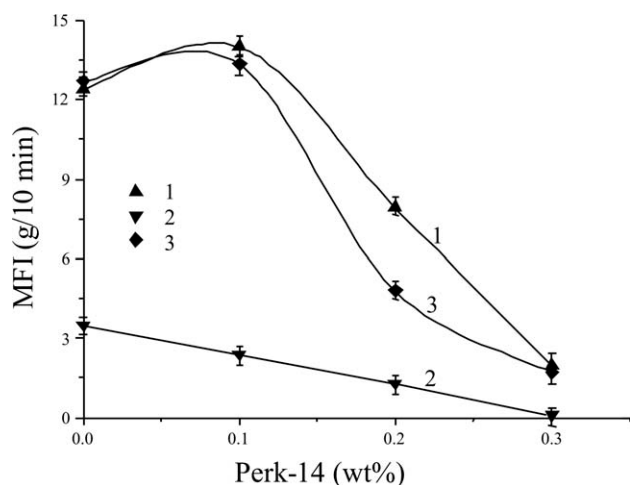


Figure 2. Dependence of melt flow index of EVA and EVA-g-TEDA on peroxide concentration, 1—EVA (113); 2—EVA (123); 3—EVA (125).

α -values increase regardless of initiator concentrations. Only with 0.3 wt % of the peroxide that α -values for EVA (125) are lower than those for EVA (113) (Figure 1).

When polar monomers are grafted onto PO macromolecules, secondary reactions—mostly crosslinking and degradation of macromolecules—were found to occur.^{2,4} Various secondary reactions usually take place simultaneously; one or another process prevails depending on the PO nature and concrete functionalization conditions.^{1,2,4} The PO whose main chain contains a tertiary carbon atom bound to hydrogen, e.g., PP, suffers chiefly degradation if functionalized in melt,²⁷ whereas PE and its several copolymers undergo crosslinking.^{2,4} The course of secondary reactions happening at PO functionalization can be judged by melt viscosity variations (flow index) and gel-fraction content variations.^{1,4,27}

Figures 2 and 3 show large variations in the MFI values as well as in the gel-fraction content disregarding the EVA used. The extent of these variations, however, depends on the copolymer type; this fact proved that VA-content influences the course of secondary reactions. It is clear, in general, that crosslinking (or some other events, e.g., increased molecular weight, higher degree of macromolecular branching) prevails leading to higher melt viscosity (lower MFI) of EVA-g-TEDA against the initial copolymer. A sharp increase in gel-fraction content occurs at an increased peroxide concentration (0.3 wt %; Figure 3). At a low Perk-14 concentration (0.1 wt %), EVA (113), and EVA (125)—unlike EVA (123)—showed some rise in MFI; this is indicative of prevailing degradation over crosslinking.

Below is a detail discussion of variations in the yield of functionalized product, in the course of secondary processes, taking into consideration the present-day ideas about free-radical reactions running in PO during RE.

One of the important factors to be taken into consideration at functionalization is mutual dissolution of components in the reaction mix.^{28–30} To reduce oligomerization of the monomer grafted and raise the yield of grafted products, it is advisable that initiator for free-radical reactions had to be a peroxide that

has thermodynamic affinity to the polymer being functionalized.²⁹ It is shown in Table I that Perk-14 solubility parameter values are close to that of EVA. It was reported elsewhere³¹ that without strong-specific interactions between materials blended their thermodynamic miscibility (mutual molecular dissolution) can be achieved with a difference in $\delta \leq 2$ (J cm^{-3})^{0.5} values. Therefore, Perk-14 must satisfactorily be dissolved in molten EVA; the better, the lower VA concentration in macromolecules. This fact evidently explains possibility of a relatively high yield (over 40%) of grafted product, EVA-g-TEDA (Figure 1). It is hardly possible that TEDA can undergo oligomerization—during functionalization—because of a great difference in the solubility parameters of the acid and peroxide. If an initiator dissolves well in the polymer during peroxide break down, the radicals formed detach mobile hydrogen from macromolecules; the macroradical formed interacts with the monomer and forms a grafted product.^{27–29}

It had to be noted that of the copolymers tested, EVA (113) must have a better solubility—in respect to Perk-14; its solubility parameter values are closest to that of peroxide. However, the grafting efficiency of TEDA to this copolymer is generally much lower than for EVA (123) over the whole concentration range of the peroxide, and for EVA (125)—with Perk-14 concentrations of 0.1 and 0.2 wt % (Figure 1). One of the causes may be an activating effect of VA-fragments on radical breakdown of the peroxide.^{19,20} Besides, it is quite possible that specific-polar interactions with peroxide become more intensive after increasing the VA-content in EVA macromolecular structure; these interactions favor compatibilization.²⁹

The description of concentration dependence of grafting efficiency for TEDA onto EVA (125)—which unlike that for other copolymers drops on increasing peroxide concentration within limits tested (Figure 1)—requires separate consideration. It also had to be taken into account that α -values for EVA (125)-g-TEDA are significantly lower than those for EVA (123)-g-TEDA with a lower VA-concentration (Figure 1). It also had to be mentioned that during functionalization the MFI values of EVA

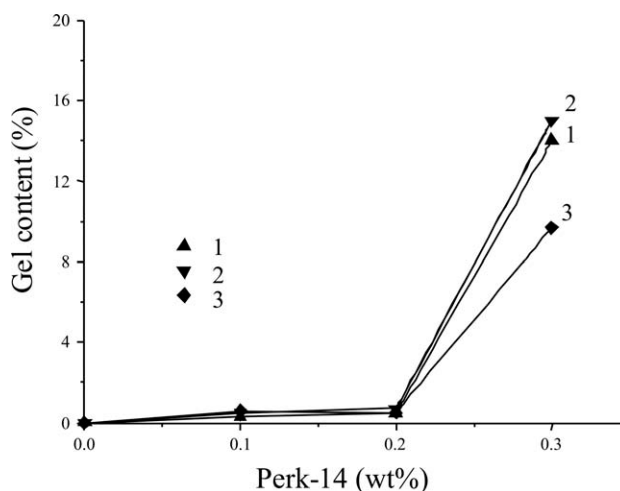


Figure 3. Variations in gel-fraction content in EVA-g-TEDA depending on peroxide concentration, 1—EVA (113); 2—EVA (123); 3—EVA (125).

(125) decrease more sharply in comparison with EVA (113), but in spite of this, a minimal quantity of gel-fraction is typically formed with EVA (125)-g-TEDA (Figures 2 and 3).

VA high concentrations in EVA (125) macromolecules help to stimulate specific interactions with peroxide leading to better dissolution and activating thermal decomposition of the latter, thus raising the free-radical concentration in EVA (125) as against other copolymers. This is probably the main cause of higher α -values for EVA (125)-g-TEDA when compared with EVA (113)-g-TEDA (Figure 1). On the other hand, VA high concentrations in EVA side chains create steric hindrance to interactions between macroradicals formed on the main chain of macromolecules and monomer molecules. Probably because of this, α for EVA (125)-g-TEDA is lower than for EVA (123)-g-TEDA (Figure 1). Numerous researchers^{1-4,11,12,27} indicated an important role of steric factor in the PO-functionalization process. Macromolecular recombinations may be accompanied by molecular weight growth, formation of branched or spatially crosslinked products. These processes lead to a higher-polymer melt viscosity; in the case of intermolecular crosslinking, a gel-fraction is formed. Because the gel-fraction yield is minimal for EVA (125), the sharp reduction in MFI values during functionalization can probably result from increased molecular weight and greater branching of macromolecules. As the Perk-14 concentration is increased, free radicals are formed in a greater number and owing—probably mostly—to steric hindrances they are spent in secondary reactions that are indirectly revealed from the data of rheological measurements and gel fraction variations (Figures 2 and 3). Therefore, for EVA (125)-g-TEDA—unlike for other copolymers— α reduces with higher peroxide concentrations (Figure 1).

The tertiary carbon atoms bound to hydrogen in the main chain of EVA macromolecules pre-determine formation of tertiary macroradicals and their subsequent β -break down that leads to macromolecular degradation. According to Ratzsch et al.,²⁷ the reactivity of hydrogen bound to tertiary carbon is much higher than that of the hydrogen bound to secondary carbon in free-radical transformations. Probably, therefore at a low-peroxide concentration (0.1 wt %), there is observed somewhat higher MFI-values for higher graded EVA (113) and EVA (125) during functionalization (Figure 2). This effect is not shown during functionalization of EVA (123) that has high initial viscosity (Figure 2). As a result, RE creates higher shear stresses in molten EVA (123), and probably more free macroradicals are formed owing to mechanochemical transformations in macromolecules. Recombination of the macroradicals formed favors a higher viscosity and larger gel-fraction during functionalization. This explains the highest gel-fraction value in EVA (123)-g-TEDA and a steady drop in MFI of the melt, while peroxide concentration being raised (Figures 2 and 3).

Proposed Mechanism for EVA Grafting with TEDA

Some possible reactions that follow the free-radical mechanism in molten EVA during RE are shown in Figure 4. Primary free radicals are generated at homolytical decomposition of peroxide macromolecules (Scheme 1). At their further interaction with macrochains, different types of macroradicals are formed and

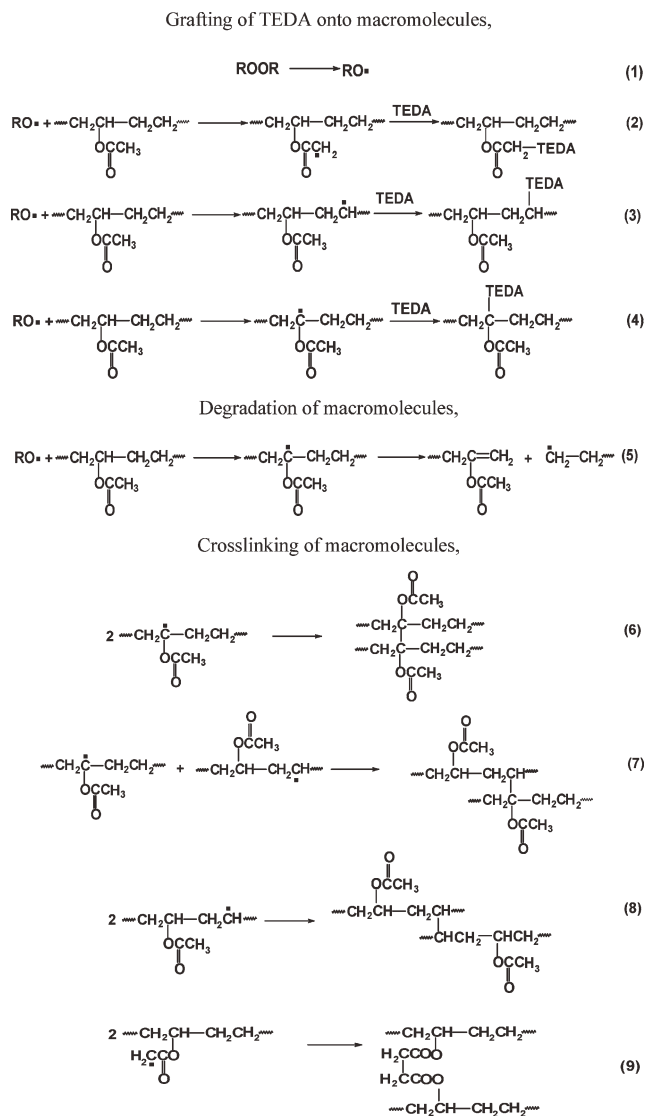


Figure 4. Possible chemical transformation at free-radical grafting of TEDA onto EVA macromolecules in the course of reactive extrusion.

participate in TEDA grafting by Schemes 2–4. Macromolecular degradation that follows the β -scission mechanism (Scheme 5) unavoidably causes molecular weight reduction of the copolymer resulting in higher MFI values determined at a low-peroxide concentration (Figure 2). Macromolecular crosslinking that causes MFI decrease and formation of gel-fraction may proceed by several schemes (Schemes 6–9). The most debatable question—in the discussion of monomer grafting onto EVA macromolecules—concerns types of carbon atoms, by which monomer is attached and which participate in secondary reactions.

It had to be noted in this connection that the carbon—hydrogen bond strength in PO macromolecules weakens in the sequence: methyl ($-\text{CH}_3$), methylene ($-\text{CH}_2-$), methine ($>\text{CH}-$) groups.^{1,4} That is, hydrogen detaches most easily from a tertiary carbon atom in the methine group. One may believe that a higher-formation rate of macroradicals must be characteristic of tertiary carbon atoms and that methine groups must mainly participate in the monomer-grafting reaction. When analyzing

Table II. Grafting Effect of TEDA onto EVA Macromolecules on Relative Optical Density of Absorption Band (at 1372 cm⁻¹) of Methyl Groups —SN₃ belonging to vinyl acetate fragments

Copolymer	Average concentration of VA (wt %)	TEDA concentration (wt %)	Peroxide concentration (wt %)	D ₁₃₇₂ /D ₄₃₂₅
EVA (113)	12.0	1.0	-	7.76 ± 0.06
			0.1	7.35 ± 0.05
			0.2	7.51 ± 0.05
			0.3	7.42 ± 0.05
EVA (123)	17.5	1.0	-	9.66 ± 0.07
			0.1	9.54 ± 0.07
			0.2	9.69 ± 0.08
EVA (125)	28.0	1.0	-	16.68 ± 0.13
			0.1	16.20 ± 0.12
			0.2	16.30 ± 0.12
			0.3	16.67 ± 0.13

probable grafting mechanisms, a number of complementary circumstances had to be considered.

It is known, first of all, that free-radical reactivity is inversely proportional to their formation rate.⁴ In the case of tertiary macroradicals, the efficiency of their interaction with monomer molecules also decreases because of steric hindrances created by the macromolecular side chain. Besides, some role is played by the kinetic factor:³² β -scission of tertiary radicals produces an equivalent quantity of macroradicals with a reactive center at the secondary carbon atom (Figure 4, Scheme 5). The analysis of maleic anhydride grafting onto polypropylene showed that it also contains tertiary carbon atoms in the macromolecules, no grafting was detected over these centers.³³ This observation can be explained by fast loss of polypropylene secondary macroradi-

cals. Higher rates of tertiary macroradical β -scission and loss of secondary macroradicals in comparison with attachment rates of the monomer can cause a reduction in the monomer-grafting efficiency. It had to be mentioned that monomer-grafting efficiency toward PO macromolecules also depends on —CH₂— chain length. Some researchers³⁴ analyzed dibutylmaleinate grafting—initiated by dicumyl peroxide—onto ethylene–propylene copolymer and found the grafting rate onto —CH₂— fragments to increase with their distance from the tertiary macroradical.

The IR-spectral analysis showed, in our experiments, the relative optical densities of absorption bands of methyl groups —CH₃ belonging to vinyl acetate fragments of the initial and functionalized EVA to be in fact identical (Table II). This fact indicates that —CH₃ methyl groups do not, practically, participate in

Table III. Melting and Crystallization Temperatures of Initial EVA and EVA-g-TEDA

Copolymer	Perk-14 concentration (wt %)	T _{cr} (°C)	ΔT_{cr} (°C)	T _m (°C)	ΔN_m (J/g)	ΔI_{cr} (rel.unit)
EVA (113)	0	72.0	17.8	97.0	50.0	1.00
	0.1	72.7	19.2	91.0	48.4	0.97
	0.2	71.9	19.8	92.1	49.0	0.98
	0.3	71.3	29.5	90.2	40.9	0.81
EVA (123)	0	72.5	16.1	91.0	48.6	1.00
	0.1	67.5	23.1	90.1	41.5	0.85
	0.2	68.3	24.3	87.9	40.9	0.84
	0.3	66.9	27.0	88.6	36.8	0.76
EVA (125)	0	54.6	16.7	82.6	24.8	1.00
	0.1	57.0	20.0	76.8	19.7	0.79
	0.2	56.0	20.8	75.2	18.5	0.75
	0.3	56.9	21.2	74.8	20.1	0.81

Notes, $\Delta I_{cr} = \frac{\Delta H_{m,f}}{\Delta H_{m,i}}$ is the relative variation in EVA crystallinity at functionalization; $\Delta N_{m,i}$ is the melting heat of initial EVA; $\Delta N_{m,f}$ is the melting heat of EVA-g-TEDA (for initial EVA $\Delta N_{m,f} = \Delta N_{m,i}$).

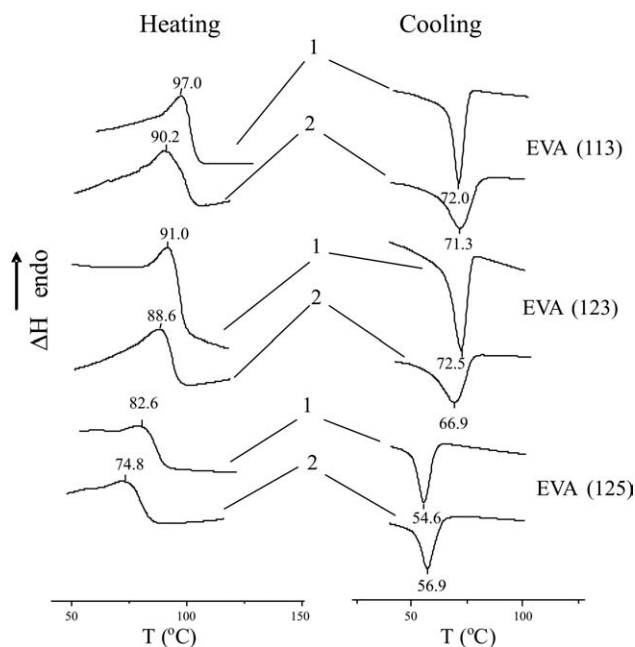


Figure 5. DSC-curves of initial (1) and functionalized (2) EVA; EVA-g-TEDA was prepared with peroxide concentration of 0.3 wt %.

grafting reactions or secondary processes. All this allows to assume that monomers being grafted become attached over secondary carbon atoms in the main polymer chain. It is most probable that secondary reactions of macromolecular degradation, as well as crosslinking, occur with their participation.

Results of DSC Analysis

The effect of EVA functionalization on its melting and crystallization depends on the type of copolymer used and peroxide concentration (Table III, Figure 5). For example, the melting temperature (T_m)—irrespective of EVA type—drops during functionalization; the reduction is the greater, the greater the Perk-14 concentration. The reduction degree of T_m —as against the initial EVA—is minimal for EVA (123)-g-TEDA (by 3.1°C) and maximum (by 7.8°C) for EVA (125)-g-TEDA. The material crystallinity drops simultaneously; the decrease is greatest for EVA (123)-g-TEDA. This fact is explained by formation of less perfect crystallites—during crystallization of functionalized EVA—in comparison with the initial EVA. The crystallization temperature (T_{cr}) varies in a more complicated manner. For EVA (123), T_{cr} drops by 4.2–5.6°C through functionalization; for EVA (113), it varies in an extreme mode with a maximum at Perk-14 concentration of 0.1 wt %; for EVA (125), T_{cr} increases by 1.4–2.4°C (Table III). An obvious reason for T_{cr} reduction is a lower regularity of macrochains at functionalization and also higher melt viscosity that create kinetic obstacles when fragments of macromolecular chains make folds. The growth of T_{cr} results from lower melt viscosity and easier crystallization. This effect is typical of EVA (113)-g-TEDA prepared with 0.1 wt % of Perk-14 (Table III). Higher T_{cr} for EVA (125)-g-TEDA made with higher peroxide concentrations—as against the starting copolymer—may be associated with a low degree of macromolecular crosslinking at functionalization and reduced rate of intermolecular interactions,

which must help to accelerate crystallization.³⁵ It is worth noting that regardless of T_{cr} values, EVA-g-TEDA of any composition crystallizes over a wider temperature range when compared with the source copolymer, which results from kinetic hindrances and is indicative of less ideal crystal formations in the functionalized product.

The data in Table III and Figure 5 show the variations in T_m , T_{cr} , and crystallinity of functionalized EVA to result from chemical macromolecular transformations taking place during TEDA grafting.

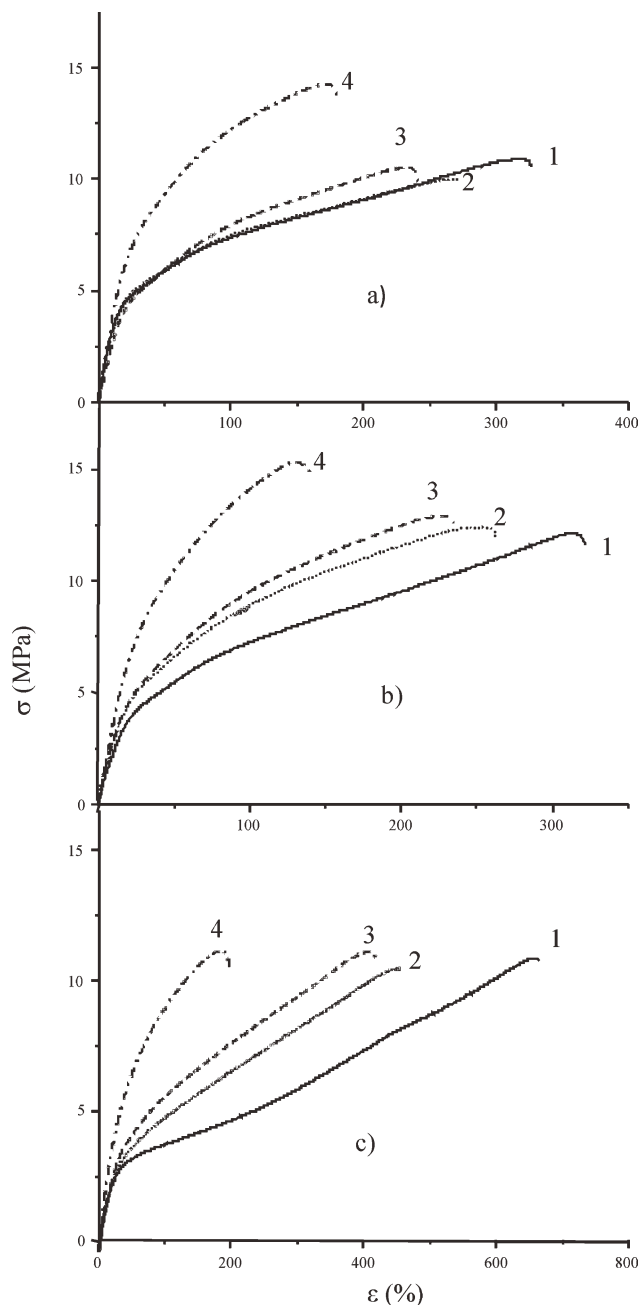


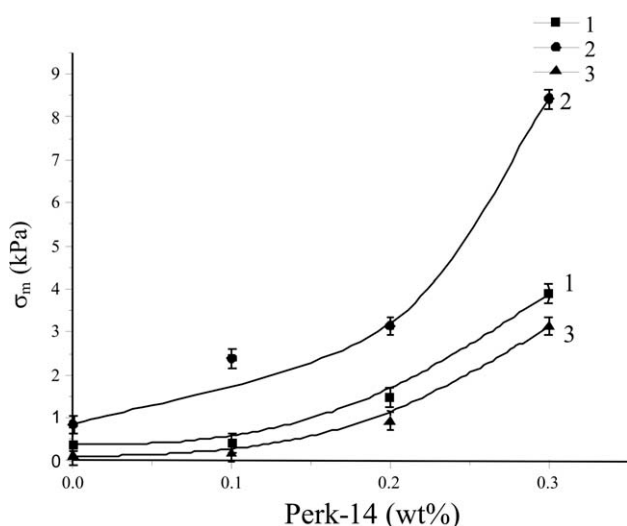
Figure 6. Deformation curves of initial and functionalized EVA, a—EVA (113); b—EVA (123); c—EVA (125). Peroxide concentration at functionalization, 1—0 wt %; 2—0.1 wt %; 3—0.2 wt %; 4—0.3 wt %.

Table IV. Effect of Peroxide Initiator Concentration on Mechanical Properties of EVA-g-TEDA

Copolymer	Perk-14 concentration (wt %)	σ_r (MPa)	$\sigma_{50\%}$ (MPa)	ϵ_r (%)	E_t (GPa)
EVA (113)	0	10.8 ± 0.8	5.8 ± 0.3	326.0 ± 30	0.043 ± 0.003
	0.1	10.2 ± 0.7	5.8 ± 0.3	279.0 ± 26	0.041 ± 0.003
	0.2	10.5 ± 0.7	6.3 ± 0.4	246.0 ± 23	0.041 ± 0.003
	0.3	14.2 ± 1.1	9.3 ± 0.5	179.0 ± 17	0.044 ± 0.004
EVA (123)	0	12.1 ± 0.9	5.5 ± 0.3	313.0 ± 31	0.031 ± 0.002
	0.1	12.4 ± 1.0	6.6 ± 0.3	253.0 ± 25	0.034 ± 0.002
	0.2	12.9 ± 1.1	7.0 ± 0.4	227.0 ± 23	0.038 ± 0.003
	0.3	15.3 ± 1.2	10.4 ± 0.7	130.0 ± 13	0.042 ± 0.004
EVA (125)	0	11.3 ± 0.9	3.6 ± 0.1	657.0 ± 67	0.020 ± 0.001
	0.1	10.9 ± 0.7	4.1 ± 0.2	453.0 ± 43	0.019 ± 0.001
	0.2	11.5 ± 0.9	4.5 ± 0.2	410.0 ± 38	0.022 ± 0.001
	0.3	11.6 ± 0.9	6.8 ± 0.3	184.0 ± 18	0.027 ± 0.002

Mechanical Properties of the Materials

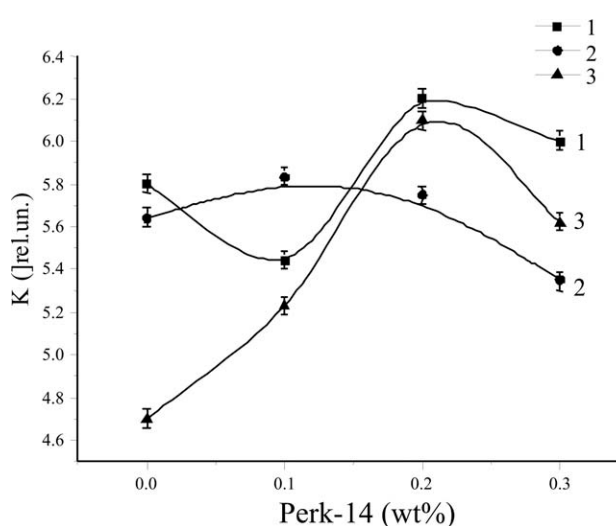
The deformation behavior and strength features of the materials can be understood from the tensile graphs in Figure 6(a–c) and data in Table IV. The mode of deformation depends on the VA amount in the copolymer. On raising the VA concentration, the tensile strength (σ_r) of EVA rises ($\sigma_r = 12.1$ MPa, maximum for EVA (123) containing 17.5% of VA), then it falls up to 11.3 MPa for EVA (125). The relative elongation at rupture (ϵ_r) increases. For example, for EVA (125) ϵ_r values are twice as high as those for EVA (113). These variations can be explained by that on introduction of VA into the macromolecular structure, the polymer crystallinity reduces, intermolecular and intramolecular interactions become, at the same time, more intensive. The mutual influence of these two factors manifests itself in an extreme dependence of strength on VA concentration in the EVA macromolecular structure.

**Figure 7.** Variations in melt strength of EVA-g-TEDA versus peroxide concentration, 1—EVA (113); 2—EVA (123); 3—EVA (125).

For EVA-g-TEDA, regardless of the EVA grade, with increasing the peroxide initiator concentration, σ_r and elastic modulus E_t become higher, while the deformability of the material reduces (Figure 6a–c; Table IV). This mode of behavior is particularly pronounced at a higher peroxide concentration (0.3 wt %). A reason for it is that intermolecular crossbonds are formed during a secondary reaction of EVA, i.e., macromolecular crosslinking. This is supported by a higher gel-fraction content in the samples with increasing the peroxide concentration (Figure 3). It also had to be mentioned that the grafted-carboxyl groups can add to the strength of intermolecular interactions, which also favors the strength and reduces the deformability of EVA-g-TEDA.

High-Elastic Properties of EVA-g-TEDA Melt

As articles (films, coatings, etc) from EVA are usually fabricated by continuous extrusion method, it is of interest to understand

**Figure 8.** Swell-ratio dependence of EVA-g-TEDA extrudate on peroxide concentration, 1—EVA (113); 2—EVA (123); 3—EVA (125).

the effect of functionalization on the high-elastic properties of molten functionalized products.

Figure 7 shows dependence of melt strength on EVA nature and peroxide concentration. It also had to be noted that initial EVA samples of different molecular weights determined from MFI values and VA-concentrations have different melt strengths. The higher the melt viscosity and the lower the VA-concentration, the higher the melt strength. In the course of free-radical grafting of EVA with TEDA—when the peroxide-initiator concentration is increased—melt strength values grow considerably regardless of EVA type. This is explained by the fact that greater peroxide contents stimulate macromolecular crosslinking leading to a branched structure and higher molecular weight of the copolymer.^{19,20,25}

The tendency to swelling of initial EVA extrudates also depends on melt viscosity and VA content in the macromolecular structure (Figure 8). The higher the VA concentration and the lower the viscosity, the lower the swelling degree of the initial EVA-melt jet. A common feature for all of EVA types is that—in the course of functionalization—the dependence of swelling ratio versus peroxide concentration is of an extreme mode. Maximum swelling is typical of EVA-g-TEDA prepared with peroxide concentrations of 0.1–0.2 wt %. Since the tendency to swelling much depends on molecular weight distribution,^{5,26} it is very likely that with these peroxide concentrations—owing to competing secondary reactions (macromolecular crosslinking and degradation)—a material is formed whose polydispersity ensures maximum extrudate swelling. Further increasing the peroxide content, leads to swell reduction owing to prevalence of macromolecular crosslinking that results in a lower high-elastic deformability of the melt.

CONCLUSION

During functionalization of EVA by TEDA grafting in the process of RE and employment of 1,3-bis(*tert*-butylperoxyisopropyl)benzene as initiator of free-radical reactions a grafted product is formed with grafting efficiency $\leq 70\%$. The EVA-g-TEDA output much depends—in addition to initiator concentration—on the VA content in the EVA macromolecular structure. A lower (12%) and a higher (28 %) VA-concentrations lead to reduced grafting efficiency.

In the course of TEDA grafting onto EVA competing secondary reactions—degradation of crosslinking of macromolecules—take place. Peroxide concentration variations over a relatively narrow range (0.1–0.3 wt %) cause noticeable changes in the mode and extent of macromolecular transformations owing to secondary reactions; their progress depends on VA content in the EVA used. With a low-peroxide concentration (0.1 wt %), degradation processes prevail that reduce melt viscosity (increased MFI). This effect becomes stronger for EVA with a lower-initial melt viscosity and VA-concentration. With a higher-peroxide concentration (0.3 wt %), whatever the type of EVA, processes prevail that lead to macromolecular crosslinking and a higher viscosity of molten EVA-g-TEDA.

Probable free-radical chemical reactions are proposed as taking place at EVA functionalization. It is shown that $-\text{CH}_3$ methyl groups belonging to vinyl acetate fragments do not, in fact,

participate in grafting reactions and in secondary processes. Variations in the molecular structure and mechanical property values happen at functionalization. According to DSC findings EVA-g-TEDA has a less perfect-crystal structure with a lower T_m and crystallinity in comparison with the parent EVA. The functionalized products are characterized by an enhanced rigidity and lower deformability when compared with the initial copolymer.

It has been established that variations in melt swell ratio and melt strength depend mostly on the competing influence of such secondary processes as degradation and crosslinking of copolymer macromolecules.

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