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Crosslinking of binary blends of ethylene/vinyl acetate copolymer and low density polyethylene or metallocene polyolefin elastomer as heat-shrinkable materials

Summary — The results of investigation of selected properties of peroxide crosslinked binary blends of ethylene/vinyl acetate copolymer and low density polyethylene or metallocene polyolefin elastomer as candidates for production of heat-shrinkable materials were presented. Analytical methods used — *i.e.* gel content, hot set test and rheometric investigations — as the measures of crosslinking degree, oxidation induction time and tensile properties measurements, before and after accelerated degradation, proved that the tested recipes were good starting points for further technological work. Some aspects of analytical determination of crosslinking degree are discussed.
Key words: heat-shrinkable materials, polyolefins, crosslinking, thermal stability, tensile properties.

SIECIOWANIE DWUSKŁADNIKOWYCH MIESZANIN ZŁOŻONYCH Z KOPOLIMERU ETY-LEN/OCTAN WINYLU ORAZ POLIETYLENU MAŁEJ GĘSTOŚCI LUB POLIOLEFINOWEGO ELASTOMERU, SŁUŻĄCYCH JAKO MATERIAŁY DO PRODUKCJI WYROBÓW TERMOKURCZLI-WYCH
Streszczenie — Przedstawiono wyniki badań o charakterze technologicznym, prowadzonych w celu opracowania receptur materiałów przeznaczonych do produkcji wyrobów termokurczliwych. Jako podstawowy komponent polimerowy stosowano dwuskładnikowe mieszaniny, w których użyto kopolimeru etylen/octan winylu oraz polietylenu małej gęstości bądź elastomerycznego kopolimeru etylen/okten; ponadto, badane układy zawierały stabilizatory termiczne oraz napełniacz nieorganiczny (wodorotlenek magnezowy bądź glinowy) (tabela 1). Ocenę produktów opierano na wynikach badań ich następujących właściwości: stopnia usieciowania trzema metodami (liczba żelowa, pomiar wydłużenia trwałego w podwyższonej temperaturze, pomiary reometryczne), charakterystyki wytrzymałościowej przy rozciąganiu oraz odporności termooksydacyjnej (tabele 1—3, rys. 1). Podkreślono przy tym, że wnioskowanie o stopniu usieciowania na podstawie pomiaru jedynie liczby żelowej jest dalece niewystarczające. Stwierdzono korzystny wpływ wprowadzenia kopolimeru etylen/octan winylu na osiągnięty maksymalny stopień usieciowania.
Słowa kluczowe: materiały termokurczliwe, poliolefiny, sieciowanie, stabilność termiczna, właściwości mechaniczne przy rozciąganiu.

Process of crosslinking of polyolefin materials is widely used in the industry, especially for production of insulation of electrical wires. There are three methods of crosslinking of polyolefin materials of commercial im-portance: two pure chemical methods, namely, with the use of organic peroxide or silane compounds, and third alternative method — the use of radiation (gamma or electron beam) [1]. Crosslinking is a very drastic modifi-

cation method because it completely changes the character of the thermoplastic material [2].

One of the very interesting applications of crosslinking technology, mainly with the use of electron beam radiation, is that for production of heat-shrinkable materials [3]. Formerly, the base polymer used in heat-shrinkable materials recipes was low density polyethylene (PE-LD). Then new types of polymers gained more attention, because of their advantageous balance of properties and cost. The most important in this respect are ethylene/vinyl acetate (EVA) copolymers, which are very often used as components of blends with PE-LD [4]. Different kinds of elastomers were also described as raw materials for heat-shrinkable products, *e.g.* ethylene/propylene/diene terpolymer (EPDM) [5], chlorosulfonated polyethylene (CSM) [6, 7] or ethylene-acrylic rubber [8].

Relatively new thermoplastic elastomers are copolymers of ethylene with higher olefins, synthesized with the use of metallocene catalysts. Such type of copolymers, (for example ethylene/octene) was also the subject of research work aimed at crosslinked materials recipes [9, 10]. We think that these kinds of polymers have so great potential for further development, that deserve even higher attention than present.

New applications of heat-shrinkable items — caps, sleeves, pipes, tubes, multi-way cable breakouts — are very demanding. They have to meet very rigorous specifications during both the manufacturing and application stages. Therefore there is a need to develop new materials tailored exactly to specific applications. Such detailed problems as: processability, mechanical properties (expandability, shrink ratio and temperature, flexibility, tensile properties, hardness), continuous operating temperature, thermo-oxidative resistance, copper corrosion resistance, chemical resistance, flame retardancy, electrical and dielectrical properties (dielectrical strength, volume resistivity, tracking resistance, electrical stress control) should be taken into consideration during the process of development of new materials for heat-shrinkable items. As a result the recipes of the materials contain some times more than 10 ingredients and there is the possibility of unwanted interactions between them [11].

The aim of this paper is to shed some light on selected topics of technological importance, associated with the research and development work dedicated to modern materials for production of heat-shrinkable items. Presented in the further text new materials are based on binary blends of ethylene/vinyl acetate copolymer and low density polyethylene or metallocene polyolefin elastomer.

EXPERIMENTAL

Materials

All undermentioned specifications are given according to producers' data.

— EVA-20 — ethylene/vinyl acetate copolymer Escorene Ultra EVA FL 00220, ExxonMobil Chemical [vinyl acetate content = 20 wt. %; melting point = 83 ^{o}C, density = 0.943 g/cm^3, melt flow rate (*MFR*, 190 ^{o}C/2.16 kg) = 1.8 g/10 min, tensile strength = 42 MPa; elongation at break = 600 %, 1 % secant modulus = 40 MPa];

— EVA-28 — ethylene/vinyl acetate copolymer Escorene Ultra EVA UL 00728, ExxonMobil Chemical [vinyl acetate content = 27.5 wt. %, melting point = 70 ^{o}C, density = 0.952 g/cm^3, *MFR*(190 ^{o}C/2.16 kg) = 7.0 g/10 min, tensile at 100 % elongation = 3.6 MPa, elongation at break >100 %, elastic modulus = 16 MPa];

— m-POE — ethylene/octene copolymer Engage 8003 (metallocene polyolefin elastomer), Dow Chemical [octene content = 30 wt. %, melting point = 78 ^{o}C, density = 0.885 g/cm^3, *MFR* (190 ^{o}C/2.16 kg) = 1 g/10 min, ultimate tensile strength = 21.8 MPa, elongation at break = 670 %, 2 % secant modulus = 35.1 MPa];

— PE-LD — low density polyethylene, type GGNX 18D003, Basell Orlen Polyolefins, sp. z o.o. [density = 0.921 g/cm^3, *MFR* (190 ^{o}C/2.16 kg) = 0.20—0.27 g/10 min, ultimate tensile strength = 19 MPa, elongation at break = 650 %];

— ATH — aluminium trihydrate, Martinal OL-107/C — commercial product, Albemarle-Martinswerk;

— MH — magnesium hydroxide, Magnifin H10A — commercial product, Albemarle-Martinswerk;

— DCP — dicumyl peroxide, Di-Cup R — commercial product, Hercules Inc.;

— stabilizing system: Irganox 1010 + Irganox MD1024 + Chimassorb 944 — all stabilizers are commercial products, Ciba Specialty Chemicals.

Samples preparation

All components of the sample, that is: polymer(s), peroxide, stabilizing system and metal hydroxide (in two cases, as mineral fillers) were homogenized using two roll mill at temp. of 125 ^{o}C for 10 minutes. The hot mass was taken off the rolls and pressmolded under pressure of 5 MPa at temp. 180 ^{o}C for 20 minutes; cross-

T a b l e 1. Symbols and formulations of the samples (wt. %)[*]

Sample symbols	EVA-20	EVA-28	m-POE	PE-LD	ATH	MH
E20	98.2	—	—	—	—	—
E20/POE	78.2	—	20.0	—	—	—
E20/POE/A	68.2	—	20.0	—	10.0	—
E20/POE/M	68.2	—	20.0	—	—	10.0
E28/POE	—	78.2	20.0	—	—	—
E28/PE2	—	78.2	—	20.0	—	—
E28/PE4	—	58.2	—	40.0	—	—
E28/PE6	—	38.2	—	60.0	—	—
E28/PE8	—	18.2	—	80.0	—	—

[*] Up to total content 98.2 wt. %; all formulations include moreover: dicumyl peroxide — 0.8 % and stabilizing system — 1 % (Irganox MD1024 — 0.4 %, Irganox 1010 — 0.3 %, Chimassorb 944 — 0.3 %).

linking was effected during this stage. In all samples the concentration of dicumyl peroxide was 0.8 wt. % and the concentration of ternary stabilizing system was 1 wt. %. The formulations of all samples are given in Table 1.

Methods of testing

Gel content

The gel content of the crosslinked samples was determined using a solvent extraction technique [12]. Xylene was chosen as a solvent. The gel content is expressed in the percentage of the weight remaining.

Elongation at high temperature (hot set test)

Hot set test was performed according to EN 60811-2-1: 1998 standard, at temperature 200 $^{\circ}$C for 15 minutes and load of 20 N/mm^2. Results of the test are given in Table 2 as two numbers. The first one is the percentage elongation of the sample after 15 min at given temperature, under the load. The second one is the percentage elongation of the sample after removal of the load, leaving the sample for 5 min at the test temperature and finally destressing it in natural way to room temperature. This test is widely used by cable industry [13]. The higher degree of crosslinking of the material the lower hot set test values.

Rheometric studies

The results of rheometric studies, are based on the concept presented in [12, 14, 15]. The apparatus used — after slight modification — was oscillatory rheometer Wulkametr WG-03, produced by Metalchem, Gliwice, Poland, widely used for rubber curing testing. Temperature of the test was set for 160 $^{\circ}$C, time for 15 minutes; the oscillation angle was 3°, 1.8 Hz. The result of the measurement was the time dependence of the torque. The ratio of the difference between maximal and minimal torque values to the minimal torque value (M_r) describes crosslinking degree of a polymer [12].

Thermooxidative stability

Oxidation induction time (OIT) was measured by isothermal DTA using a DSC scanning microcalorimeter, model 605M, from Unipan Thermal. The analysis was performed in isothermal conditions (230 $^{\circ}$C) [16].

Tensile properties

Tensile properties (stress and strain at break, secant modulus) were determined (also after accelerated ageing) using Instron universal testing machine, model 4466, according to EN ISO 527 standard.

RESULTS AND DISCUSSION

Crosslinking degree

The most widely used measure of crosslinking degree of polymers is without any doubt sol-gel analysis [17]. As we can see in Table 2, the values of gel content in all of the investigated samples are very high, in the range 75—93 %. The highest value was obtained for E28/POE blend. The results obtained for samples E28/PE2 to E28/PE8 support the known fact, that EVA copolymers undergo crosslinking process much easier than PE-LD [12].

T a b l e 2. Selected properties of crosslinked samples

Sample symbols (see Table 1)	Measures of crosslinking degree			OIT (230 $^{\circ}$C) min	Secant modulus MPa
	Gel content %	Hot Set Test[*] (elongation, %)	M_r[*]		
E20	88.0	132 / 12	3.54	44.3	23.0
E20/POE	90.7	200 / 24	2.95	27.6	22.7
E20/POE/A	—	128 / 24	2.52	41.8	31.8
E20/POE/M	—	108 / 12	2.41	> 300	29.8
E28/POE	92.6	140 / 8	3.32	11.6	15.6
E28/PE2	88.0	112 / 8	3.06	26.1	22.6
E28/PE4	81.0	224 / 20	1.84	44.9	43.0
E28/PE6	75.5	200 / 16	1.24	17.6	n.d.[**]
E28/PE8	78.0	180 / 12	1.45	43.4	n.d.

[*] See Experimental, methods of testing.
[**] n.d. — not determined.

There is one additional aspect of sol-gel analysis we want to discuss. The gel content analysis is used mainly to evaluate crosslinking degree of polymers, but some authors use it for composites consisting of polymers and mineral fillers as well. For example Li and Qu [18] investigated crosslinking degree of composite EVA/ Mg(OH)$_2$, Gheysari and Behjat [19] — of composite EVA/Al(OH)$_3$, Jiao and coworkers [20] — of composite EVA/hydrotalcite/red phosphorus, and Çopuroglu and Şen [21] — of composite EVA/carbon black; all these authors did not use any correction factor for the presence of filler in the investigated samples. On the other hand, Xie and coworkers [22] who investigated composite PE-LD/carbon black and Zhang and Fang [23] who investigated composite EVA/organoclay incorporated the weight of the filler into the equation for gel fraction calculation. Obviously, the difference in gel fraction values obtained by those two approaches is quite important.

In this paper we rather concentrate on two other methods for crosslinking degree evaluation, namely uniaxial tension measurements, (hot set test) and rheometric measurement. In general, it is apparent, that there is no simple correlation between the results obtained for these three analytical methods. On the basis of gel content measurement the highest crosslinking degree among investigated polymers shows E28/POE blend, according to rheometric results — E20, and according to hot set test — E28/PE2 blend. Good illustration of this is also Fig. 1. As we can see, the dependence of crosslinking degree on PE-LD content in EVA-28/PE-LD blends is completely different for three analytical method used.
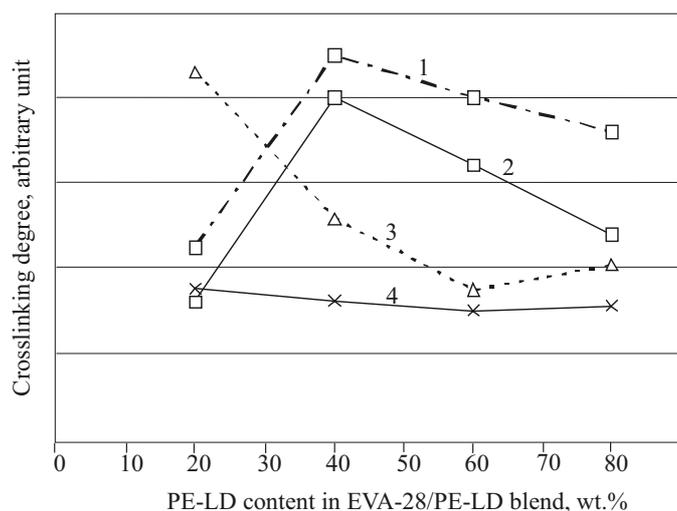
Fig. 1. Influence of PE-LD content in EVA-28/PE-LD blends on crosslinking degree determined by three different methods: 1 — hot set test (elongation under load), 2 — hot set test (permanent elongation), 3 — rheometric measurement, 4 — gel content

To sum up the discussion on crosslinking degree of polymers we believe that in order to characterize properly crosslinked network structure it is necessary to give information not only about gel content, *i.e.* so called gel index, but also about results obtained with the use of others techniques, *e.g.* hot set test or rheometric measurements [24]. As pointed out by Borealis AB research group for the case of peroxide crosslinking of polyethylene, the effective network is constituted primarily of physical crosslinks, so called "trapped entanglements", The chemical crosslinks are in minority but they play double role: they contribute to the total network and prevent the entanglements to slip under load [25]. In the case of swelling measurements (gel content) we neglect the presence of physical crosslinks, which have important input to the properties of crosslinked materials in solid state.

Thermooxidative resistance

Heat-shrinkable articles have to be resistant to aggressive environment, in particular to thermal oxidation. There are at least two reasons for that: firstly during application heat-shrinkable articles are subjected to severe heating, very often by open fire and the second reason is high working temperature, frequently above 100 °C. Additional harmful aspect for thermostability of heat-shrinkable materials is contact with copper, commonly used in electro-technical applications. This metal is well known as a catalyst of polyolefin degradation.

There are known many stabilizing systems for polyolefin materials, including grades for heat-shrinkable materials. In our work we used a combination of three commercially available stabilizers: Irganox 1010 — gene-

ral purpose phenolic antioxidant, Irganox MD 1024 — metal deactivator and antioxidant for wire and cable applications and Chimassorb 944 — HALS stabilizer (Hindered Amine Light Stabilizer), known as light stabilizer as well as long-term thermal stabiliser. All our formulations contained 1.0 wt. % of above mentioned system; the ratio of particular stabilizers was: 3:4:3, respectively.

As we can see in Table 2, all investigated compositions showed high thermo-oxidative resistance. The values of oxidation induction time at temperature 230 °C were above 10 minutes. Special attention has to be paid to the composition E20/POE/M for which the value of *OIT* considerably exceeded 5 hours. The effect is quite surprising and was not observed when aluminium hydroxide was used instead of magnesium hydroxide [26] (sample E20/POE/A, *OIT* = 41.8 min).

Secant modulus

Secant modulus at 2 % strain in the case of heat-shrinkable materials is the measure of force needed for expansion of crosslinked item, *e.g.* pipe or sleeve. The higher the modulus value the more difficult is the process of expansion carried out with the use of compressed air or mechanical force. As we can see in Table 2, the most desirable, *i.e.* the lowest of the modulus (15.6 MPa), was obtained for the E28/POE blend. On the other hand, the highest value of the modulus (43.0 MPa) was for the E28/PE4 blend. So, it is evident, that variation of the composition of blends under consideration results in remarkable differences in secant modulus value. Furthermore, the addition of 10 wt. % of mineral fillers to the E20/POE matrix caused increase in secant modulus value by roughly 7 MPa (MH) and 9 MPa (ATH).

Influence of accelerated ageing on tensile properties

As mentioned earlier, heat-shrinkable materials are very often designed for production of heavy-duty items, which have to work long time without any significant failure. They have to maintain their properties despite of severe conditions in which they will be used. One of the ways of testing resistance of heat-shrinkable materials against such harmful conditions is the measurement of tensile properties before and after accelerated ageing. Different standards describe various conditions for such accelerated processes, namely the temperature of the process and its duration. In this paper we described the results of the ageing tests with the following sets of parameters: long-term test — 168 hours at 160 °C and high--temperature test — 4 hours at 250 °C.

In Table 3 the values of tensile properties (stress at break σ_B and strain at break ε_B) of the investigated samples, before and after ageing, are given. As we can see, for the non-aged samples the values of stress at break are in the limits of 13.3 to 30.5 MPa, whilst strain at break — 402 to 589 %. The worst results have been obtained for

the blend E28/PE8. The blends in which m-POE was used have significantly better tensile properties (samples E20/POE and E28/POE). It is clearly seen that the addition of ATH extremely deteriorates the properties (sample E20/POE/A); on the other hand the effect of magnesium hydroxide is practically neutral (sample E20/POE/M).

T a b l e 3. The effect of ageing on tensile properties of investigated samples[*]

Sample symbols (see Table 1)	Before ageing		Ageing 160 °C / 168 h		Ageing 250 °C / 4 h	
	σ_B MPa	ε_B, %	σ_B MPa	ε_B, %	σ_B MPa	ε_B, %
E20	30.4	579	25.0	571	6.61	408
E20/POE	28.8	589	20.0	553	5.23	351
E20/POE/A	14.5	435	18.3	572	7.00	427
E20/POE/M	30.5	568	21.4	549	4.74	140
E28/POE	29.4	580	18.8	560	5.93	454
E28/PE2	22.3	541	19.2	540	6.02	402
E28/PE4	25.9	571	19.5	550	4.69	199
E28/PE6	18.7	526	15.3	539	5.05	113
E28/PE8	13.3	402	15.0	546	4.85	85

[*] σ_B — stress at break, ε_B — strain at break.

It was quite surprising for us that for the two samples (E20/POE/A and E28/PE8), which had the worst properties when non-aged, the ageing process conducted at 160 °C for 168 hours showed very beneficial effect. The increase in σ_B value was 26 % and 13 % and of ε_B value — 31 % and 36 %, respectively. Generally speaking, the stabilizing system used shows very good protective effect against degradation of investigated materials at 160 °C for 168 hours.

The degradation process carried out at 250 °C for 4 hours had much more harmful effect. Stress at break maintains only 16—48 % of its initial value, and strain at break — from 21 % to 98 %. In this case we can clearly see again, that the addition of ATH helps to keep the tensile properties of the E20/POE blend after ageing on relatively high level. For the blends EVA-28/PE-LD, we can observe worst tensile properties after ageing at 250 °C for 4 hours, especially with higher content of PE-LD (samples E28/PE6 and E28/PE8).

CONCLUSIONS

Crosslinking of polyolefin materials is a very important industrial process, and its use is the way to obtain heat-shrinkable items. Modern plastic materials designed for manufacture of such products have to meet several rigorous requirements. Thanks to commercial availability of new sorts of thermoplastic polymers, we have the opportunity to design the tailor-made materials, meeting various specifications. Among the sam-

ples investigated the most prone to crosslinking process was the blend composed of 78 % of EVA-28 and 20 % m-POE (E28/POE). The next step is the proper selection of functional additives (*e.g.* stabilizer, elastomer). The results presented by us could be useful for the development of new materials designed for commercial production of heat-shrinkable products.

The right selection of analytical methods is of great importance, too. In particular, in order to properly assess crosslinking degree of polymers, especially at higher values of this parameter and for polymer composites, the gel content analysis itself is far from completeness. The use of others methods, such as hot set test or rheometric analysis, is in this case a necessity.

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