Physico-chemical Characterization of Some Microstructured Polymeric Materials

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The behaviour of some microstructured polymers obtained in dynamic conditions using a mixture (1:1) of EPDM (ethylene-propylene-dien monomer) rubber and high-density polyethylene (in the presence of sulphur as reticulating agent) was studied. The experiments consisted in determination of swelling by maintaining the polymeric composite materials in three organic solvents (benzene, p-xylene, carbon tetrachloride) and also in recording their IR spectra. The results are useful for selection of operating conditions during preparation and for choosing the appropriate utilization of polymeric products.

Keywords: microstructural polymer, EPDM (ethylene-propylene-dien monomer) rubber, polyethylene, swelling, IR spectroscopy

The contemporary economical development is affected by the limited character of some row stock and energy resources, by the large demand for new high performance materials, used in many fieds, from the traditional ones to the top ones, as well as by the necessity to protect the environment, limiting the quantity of waste. In the polymeric materials field, some famous companies world wide recognized (Monsanto Polymer Products Company – USA, Mitsubishi Monsanto Chemical Company – Japan, Advanced Elastomer Systems – USA, Du Pont – USA etc.) have been oriented to achieve some modified polymers, having elastomeric-polyolefin structure and better physical-mechanical properties than the basis constituents ones, individually considered [1-8]. These properties lead to a longer usage in the domains where performanced characteristics materials have been required: weatherability; resistance to UV radiation, to ozone, micro-organisms and solvents; waterproof; lack of permeability to disperse systems (solid-gas, liquid-gas systems); electric insulation as far as tension of 1000 V; free of toxicity; practicability in a large temperature range etc. Properties of modified polymers are a result of both initial characteristics and some characteristics that arise from the physico-mechanical interactions that occur during the preparation process of polymeric microstructure.

Polymeric elasto-plastics materials have different behaviour, depending on the elastomer type, chemical microstructural degree of elastomer into plastics matrix, particle size, thermoplastic nature, elastomer-plastomer mass ratio etc. The study of these microstructured materials have in view the achiving of some polymers able to compete or to replace the very resistant silicone rubbers.

Microstructurating process is done simultaneously both chemically (using proper chemical agents, depending on the unsaturation degree of macromolecular chains) and technologically (running with adequate operating parameters during processing of elastomer with thermoplastic). The formation of a microstructure of elastomer in thermoplastic environment is evidenced especially by a high melt flow parameters (*i.e.,* a good machinability), thermal stability, high elasticity, high fracture resistance, tearing and impact strength, high long term thermal ageing resistance value (limit of 60…150°C temperature), stability in mineral oils, in acid or base media etc. In Romania, various products based on special rubbers (EPDM, silicon, fluoride rubber types), are marketed. Therefore, the research of thermoplastic elastomer-plastic materials based on special and polyolefine rubbers is legitimated, by studying thermodynamic compatibility in mixture with many additives for activation, crosslinking and processing. The obtained composite materials should be of high quality, due to their elastic-olefinic structure, crosslinking degree and also their ability to be processed, similar to the classical plastics one. For example, EPDM rubber based elastic-plastic materials show a good adherence to polyethylene surfaces, the mixtures being workable in melt. In this paper, the results of testing and characterization of some composites based on EPDM rubber crosslinked in a high-density polyethylene matrix are presented, by studying their behaviour at swelling in three organic solvents (benzene, p-xylene and carbon tetrachloride) and also by recording of IR spectra.

Experimental part

Rubber samples were of the ethylene-propylene terpolymers type (*Nordel IP 3745P* rubber, Du Pont Company), consisting of 70% ethylene, 29.5% propylene and 0.5% ethylene - norbonene, as either granules or made-on-roll sheets. The ethylene-norbonene terpolymer was used because it provides a low viscosity and also a low molecular distribution in this type of rubber. The microstructures achieving was performed using a laboratory mixer, by mixing the elastomer with a high-density polyethylene (*PEID B 084* type, as granules or plate), with mass ratio of 1:1. The curing of mixtures was performed using the classical curing system of sulphur and accelerators.

The elasto-plastic polymeric materials analyzed are complex mixtures, due to the existence of additives and filling materials beside the main polymer. The hydrodynamic operating conditions were selected, so that temperature required for melting the polyolefine tried on

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Table 1
THE ANALZED SAMPLES WITH POLYMERIC MICROSTRUCTURES

No.	Sample code	Mixture types	Curing system	Accelerator/Sulphur ratio in curing step	Shearing rate in preparation (rpm)	Bearing curing time (min.)
1	S1–11	-	conventional	0.75	80	1
2	S12–16	-	conventional	0.40	80	1
3	S17 – 21	-	semi - EV	1.85	80	1
4	S22 – 26	-	EV	6.34	80	1
5	SM 18	S 18 T1 S 18 T2	semi – EV	1.85	80	2 3
		S 18 R2 S 18 R3	semi – EV	1.85	100 120	1
6	SM 20	SM20T1 SM20T2	semi – EV	2.50	80	2 3
		SM20R2 SM20R3	semi – EV	2.50	100 120	1
7	SM 24	SM24T1 SM24T2	EV	5.83	80	2 3
		SM24R2 SM24R3	EV	5.83	100 120	1

to be reached, to avoid thermal degradation of both row stock and composite product, to achieve the dynamic crosslinking of elastomer within polyolefine matrix and, finally, to get an homogeneous mixture, containing crosslinked elastomer microparticles.

In table 1 some data about the samples analyzed (having polymeric microstructures) are given, the samples symbols being also included. The *EV* notation refers to the efficiently curing, whereas the others symbols are not having technological significance.

A control sample was also investigated, consisting in the same mixture having elasto-plastic structure, but without sulphur curing of rubber phase.

For the behaviour of the row stocks and composite materials in three organic solvents the gravimetry method was used, by measuring the mass variation before and after immersion. Thus, the solvent storing percentage (swelling) G_M was determined, using the formula:

$$G_M = \frac{m_g - m_i}{m_i} \times 100 \qquad (1)$$

where:
m_g – the sample mass with the absorbed solvent;
m_i – the initial mass of sample.
The result is expressed as average of values achieved on the three samples.

The rectangular shaped samples, punched out from 2 mm thickness foil, have been immersed in the following solvents (Merck reagents): benzene, p-xylene and carbon tetrachloride. The measurements were done to the following immersion times: 1, 2, 3, 24, 48 and 72 hours, at room temperature.

IR spectra were also recorded in 4-400 cm⁻¹ range using a *SPECORD IR 75* (Carl Zeiss Jena) spectrophotometer in the following conditions:
-control film with thickness below 1mm (0.496 and 0.630 mm, respectively) on the KBr window;
-alternative work state at slit, enhancement and recording rate, for obtaining a good resolution and precision;
-solvents: benzene, p-xylene and carbon tetrachloride.

Results and discussion

It is known that during preparation of elasto-plastic polymer materials, different types of reactions could occur: finalization of polymerization or crosslinking, chemical changes of polymeric chain, grafting on polymeric chain, chain transfer, forming of some interpenetrable networks, changing of molecular mass distribution [6,7]. In our work the analyzed structures include a plastic material of high-density polyethylene type with a low degree of chain branching, which provides hardness and high crystallizing ability and is consistent with processing of the selected ethylene-propylene terpolymer elastomer.

Behaviour of raw stocks and polymeric composites at swelling in solvents

Generally, the action of an organic solvent on a polymeric material should lead to the liquid uptake, extraction of soluble constituents from material, and even to a chemical reaction between polymer and surrounding liquid. In our cases, the overall result is usually named *swelling*, consisting in an enlargement of polymer volume, mainly by the organic liquid absorption. Obviously, incorporating the liquid in the polymer material could deeply change the physico-mechanical properties, as mechanical resistance, tensile strength and hardness, respectively. The effect of absorbed solvent on the composite material is depending on manufacturing and processing conditions, the presence of atmospheric oxygen, testing temperature, as well as on the nature and magnitude of internal pressures within material.

The kinetics of the swelling process could proceed in many ways: 1- a simple swelling with different rates during immersion time, till a certain limit is reached; 2- a limited swelling with simultaneous extraction of a (or some) soluble fraction (s) from polymer composite; 3- swelling followed by dissolution (totally or partially) of all constituents. The mechanism 1, and also the first stage from the mechanisms 2 and 3 are represented by first-order kinetic equations.

In many cases, the swelling is not accompanied by noticeable dissolution, due to the limited solubility of

composite which leads to the forming of two equilibrium phases: the solution containing the polymer dissolved in solvent and the swelled solid composite polymer. Another reason of the limited swelling could be the change of macromolecules flexibility due to solvation. The crosslinking with forming of chemical and physical intermolecular links could also lead to limiting of swelling. As a result of volume increasing by swelling, some stresses appear in the network, which brake and, finally, could stop this process; this is the case that occurs at the elastomeric cured materials.

Introducing the stiffened additives within a cured mixture has as effect an apparent increasing of crosslinking degree, which increases with curing intensity; obviously, the crosslinking degree is depending on the nature and structure of melting stock, this process being not correlative with particle size or particle surface.

The extraction of soluble constituents of polymer composite, especially of plasticizers and antioxidants, could change both physical and chemical properties after the evaporation of absorbed liquid (supposing that this is a volatile liquid). That is why, for a good reproducibility, the physical and chemical tests must be renewed after the immersion and drying.

The results of investigation at room temperature are shown in tables 2-4.

As a general observation, it comes out a lower swelling in benzene, medium G_M values in p-xylene and high values G_M (sometimes very high values) in carbon tetrachloride. For immersing times longer than 24 h (or, sometimes over 48 hours), the beginning of polymer material dissolving in all solvents was noticed.

The results for raw stocks and control polymers pointed out the followings:

-the PEID polyethylene shows a low swelling in all solvents. For example, in the first 3 h of immersion a mass increasing of maximum G_M of 3.44% in p-xylene and of about 2% in the other solvents has been scored; after 72 h, the maximum of swelling was of 14.05% in carbon tetrachloride as solvent;

- from the previously studies [7] we found out that EPDM elastomer increases twice its volume in benzene in the first hour of immersion, after which a meaningful dissolving of rubber was noticed. Our present results show that in p-xylene the EPDM has an intermediate behaviour, whereas in carbon tetrachloride this rubber dissolves even in the first hour of immersion.

- the control mixture is swelling substantially in the first hour of contact with all solvents.

The investigation of chemical microstructuring has leaded to the following observations:

- after maintaining one hour in benzene, the lowest swelling was recorded for S20 sample, whereas the highest swelling was for S6 sample; after 48 h, the S20 sample shows also the lowest swelling, but for this period of time S24 sample exhibits the highest swelling;

- in p-xylene solvent, in first hour after contact with composites sample the lowest swelling value has been scored for S24 sample and the highest swelling value for S6 sample; after a long immersion period (48 h), the lowest swelling was for S20 sample, followed by S24 sample; the highest one was for S18 sample;

- after one hour of immersion in carbon tetrachloride, the S20 sample has shown the lowest swelling and the S6 sample has shown the highest swelling; after 24 h of immersion, the lowest swelling value was for S6 sample and the highest value for S16 sample.

Increasing the accelerator/sulphur mass ratio from 0.4 to 0.74 during previous curing process, the corresponding swelling values in benzene and p-xylene solvents have remained close; in contact with carbon tetrachloride the samples obtained with accelerator/sulphur ratio of 0.4 have shown high swelling values, even over 100% (for example, after 24 h), by comparing with the behaviour in the other solvents and the swelling diminished for higher accelerator/sulphur ratios. It results the following order of solvents action refering to the magnitude of swelling values:

benzene H" p-xylol < carbon tetrachloride

Table 2
THE SWELLING DATA (G_M, %) FOR POLYMER SAMPLES IMMERSED OVER TIME IN BENZENE

No.	Sample code	Immersion time (h)					
		1	2	3	24	48	72
	CONTROL POLYMERS						
1	**PEID**	1.21	1.63	2.44	4.47	6.91	10.97
2	**EP**	12.46	20.42	24.57	24.91	32.18	48.10
	CHEMICAL MICROSTRUCTURING						
3	**S 6**	8.80	18.05	20.58	25.63	22.38	15.52
4	**S16**	7.53	9.81	16.21	22.00	26.25	21.68
5	**S18**	5.38	19.36	15.76	25.54	27.74	22.56
6	**S20**	4.76	9.27	13.78	20.30	21.30	17.79
7	**S24**	6.77	9.88	13.55	28.53	29.66	25.42
	TECHNOLOGICAL MICROSTRUCTURING						
8	**SM 18 T1**	4.92	17.80	20.45	26.52	28.41	40.15
9	SM 18 T2	9.09	19.89	22.16	27.84	30.11	38.64
10	SM 18 R2	8.61	18.35	20.60	25.47	27.34	37.83
11	SM 18 R3	10.14	15.94	19.57	19.57	26.09	35.51
12	**SM 20 T1**	11.27	17.82	20.73	26.18	28.73	20.36
13	SM 20 T2	7.94	14.29	16.27	26.59	27.38	20.63
14	SM 20 R2	10.40	16.83	20.30	22.77	24.75	16.83
15	SM 20 R3	9.37	15.63	18.74	23.13	27.50	18.75
16	**SM 24 T1**	7.45	13.73	16.47	25.49	27.06	25.10
17	SM 24 T2	7.50	13.13	15.63	22.50	28.13	25.63
18	SM 24 R2	12.70	19.05	22.22	31.22	27.51	25.40
19	SM 24 R3	8.54	14.63	26.83	29.27	29.27	26.83

Table 3

THE SWELLING DATA (G_M, %) FOR POLYMER SAMPLES IMMERSED OVER TIME
IN *p*-XYLENE

Nr.crt.	Sample code	Immersion time (h)					
		1	2	3	24	48	72
CONTROL POLYMERS							
1	PEID	1.53	2.30	3.44	6.88	7.27	8.43
2	EP	22.45	34.70	43.27	57.96	58.78	35.51
CHEMICAL MICROSTRUCTURING							
3	S 6	17.33	23.67	30.67	39.67	48.00	21.33
4	S16	14.28	20.71	31.42	40.00	50.00	42.38
5	S18	15.66	21.08	29.71	40.76	51.00	47.99
6	S20	12.87	18.68	29.29	35.60	45.45	43.68
7	S24	8.87	19.48	30.73	39.61	47.18	44.37
TECHNOLOGICAL MICROSTRUCTURING							
8	SM 18 T1	5.02	13.62	20.07	33.33	36.92	20.43
9	SM 18 T2	22.53	34.06	43.07	59.34	62.09	44.51
10	SM 18 R2	22.96	35.20	43.37	61.74	64.80	42.86
11	SM 18 R3	20.90	34.33	41.80	58.21	61.19	48.51
12	SM 20 T1	20.15	32.84	41.04	56.71	60.07	42.27
13	SM 20 T2	15.81	30.77	39.74	55.98	57.26	42.74
14	SM 20 R2	15.88	30.04	41.20	54.51	55.36	39.49
15	SM 20 R3	20.16	34.11	42.64	60.47	59.70	35.66
16	SM 24 T1	17.95	31.20	41.03	55.56	57.69	41.88
17	SM 24 T2	15.56	27.41	34.81	55.56	58.52	39.26
18	SM 24 R2	21.79	32.40	43.02	53.63	55.31	40.78
19	SM 24 R3	25.37	32.84	55.22	65.67	62.69	37.31

The decrease of swelling by increasing the accelerator/ sulphur ratio from 0.4 to 0.75 may be explained by a better crosslinking. Values for swelling are much lower for samples produced with an accelerator/sulphur ratio of 1.85, comparing with the value of 0.75 at conventional systems; however, the swelling percentages are comparable for the 1.85 and 6.34 ratios.

For the EV systems (with sulphur and accelerators), if the accelerator/sulphur ratio increases during preparation of composite the swelling values increase in the following order of solvents:

*benzene ≈ p-xylene < carbon tetrachloride*
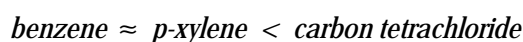
For the composite systems of "semi-EV" curing type, the swelling in all solvents increased with increasing of accelerator/sulfur ratio from 1.85 to 6.34.

As a consequence of these results, taking into account the behaviour during operating process (in regard to mixer rotors speed, time of mixing process, material braking etc.) in the investigation of the influence of technological parameters for achieving of microstructures, only the S18, S20 and S24 samples were selected and analyzed.

Further on we present some comments on technological microstructuring.

Among samples prepared by the classical curing system, denoted as SM 18, 20, 24 in tables 2-4, the best behaviour in organic solvents was evidenced for the samples: SM 24 T2 in benzene, SM 18 T1 in p-xylene and SM 24 R2 in carbon tetrachloride. The increasing of accelerator/sulfur ratio during the curing process has not generated some important variations for the swelling in benzene and *p*-xylene; however, in carbon tetrachloride a decreasing of swelling with increasing of the accelerator/sulfur ratio from 1.85 to 5.83 was noticed. This result could be interpreted by enhancing of stirring during mixing process of manufacturing (faster rotation speed of rotors, from 80 rpm to 100 rpm and 120 rpm), that produces a better crosslinking; as a consequence, a lower swelling in solvents is recorded. Moreover, the increasing of mixing time (from 1 min to 2 min) during preparation of composite, by keeping constant stirring (at 80 rpm) has also led to the swelling decreasing, indicating a better crosslinking. We

therefore can consider that the order of swelling in the three solvents is kept the same:

benzene < p-xylene < carbon tetrachloride
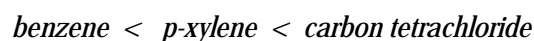
The analysis of IR spectra

In the analysis of the spectrochemical behaviour of samples we discuss about the intra- and intermolecular interactions, established as a result of participation of curing accelerators involved into the achieving of networks within elastic-plastic composites. The structural aspects of the studied composites may be evidenced by performing their IR spectra in polar and non-polar solvents that allow sufficient light transmission in the specific spectral domain.

In table 5 the spectral absorptions data and some comments for the vibration properties of structural groups within the studied elasto-plastic composites are presented.

In the analyzed IR spectra a lot of degenerations are noticed, as a result of mixtures processing at temperatures higher than 100°C. Also, many satellite bands in the chemical valence vibrations may be assigned to overlapping of some different vibrations of methyl and methylene C-H bonds with vibrations of C=O carbonyl and carboxyl bonds. These involved bonds are provided from both coupling constituents and curing agents.

In the spectral domain of chemical valence vibrations the presence of some bands that belong to νOH vibrations (associated or not by hydrogen bonds) is noticed. The absorption corresponding to vibration of non-associated groups is placed at higher values of wave number. In the range of 3100 - 2700cm^{-1} a large band occurs, as a result of vibrational combinations of either symmetric or asymmetric C-H bonds existing by the presence of some multiple methyl and methylene groups from linear chains as well as from aromatic rings.

In the spectral range of 1600 – 1400cm^{-1}, the assigning of absorption bands is difficult for the majority of benzene substitutions. Theoretically, in this domain the number of bands depends on the number and position of substitutes groups, being independent on their nature. The number of bands should be equal with the number of H atoms bonded at nucleus; unfortunately, the interpretation is

altered by the presence of a series of other bands corresponding to some combinations of vCH bond vibrations.

The crosslinking process by traditional systems induces changes within polymeric structures, by large contribution of disulphide and polysulphide intermolecular bonds, as a result of reactive attack of accelerator-sulphur couple on α-methylene hydrogen from the polymer molecules. As a consequence of crosslinking, the aromatic substitution is amplified leading to a large absorption band of overlapping of deformating vibrations outside of nucleus plane. The occurrence of two intense absorption bands in the 680 – 900 cm^{-1} range, accompanied by other weaker bands (for more complex molecules), determines different ways of CH deformation outside the plane, by molecular symmetry modification.

The absorptions corresponding to the presence of mono or poly-sulphur mercaptans or metathiazoles bonds, which are responsible for semi-efficient crosslinking of studied composites, have occurred in the domain of 2700 – 2250 cm^{-1}. Also, the absorptions assigned to the presence of sulphur from the traditional crosslinking systems were

Table 4
THE SWELLING DATA (G_M, %) FOR POLYMER SAMPLES IMMERSED OVER TIME IN CARBON TETRACHLORIDE

No.	Sample code	Immersion time (h)					
		1	2	3	24	48	72
CONTROL POLYMERS							
1	**PEID**	1.23	2.06	2.06	6.61	11.57	14.05
2	**EP**	32.10	46.09	55.97	107.82	101.65	66.26
CHEMICAL MICROSTRUCTURING							
3	**S 6**	26.19	41.67	44.44	72.22	73.81	45.63
4	**S16**	18.72	28.31	35.61	111.41	87.44	80.13
5	**S18**	16.77	26.75	36.30	76.85	65.81	62.48
6	**S20**	16.30	25.65	28.05	78.41	81.77	79.85
7	**S24**	17.29	25.81	36.59	90.22	85.96	81.20
TECHNOLOGICAL MICROSTRUCTURING							
8	**SM 18 T1**	19.87	36.34	44.72	95.65	98.45	66.46
9	SM 18 T2	26.04	41.67	51.56	102.08	101.56	69.27
10	SM 18 R2	23.14	37.65	46.67	99.61	96.86	65.10
11	SM 18 R3	23.23	43.87	56.13	89.68	93.55	63.22
12	**SM 20 T1**	19.25	35.71	44.72	93.79	96.58	63.35
13	SM 20 T2	19.57	36.60	43.83	93.19	94.04	63.83
14	SM 20 R2	29.19	44.86	56.76	88.65	91.35	58.38
15	SM 20 R3	27.68	44.64	58.93	85.71	85.71	54.46
16	**SM 24 T1**	20.73	33.45	38.91	92.73	97.45	66.18
17	SM 24 T2	19.85	33.59	38.17	88.55	90.08	60.31
18	SM 24 R2	20.54	87.50	42.86	86.61	87.50	57.59
19	SM 24 R3	22.64	36.80	42.45	75.47	81.13	51.87

Table 5
THE ABSORPTIONS FOR **S 6** AND **SM 2** SAMPLES AS REPRESENTATIVES OF ELASTIC-PLASTIC COMPONENTS

Wave number [cm^{-1}]	S6 sample			S24 sample			Vibration type	Vibrations allocation
	benzene	p-xylene	CCl$_4$	benzene	p-xylene	CCl$_4$		
3700-3600	3630			3630			ν(OH) symm.	OH non-associated groups HO…H
3600-3500	3580			3580			ν(OH) asymm.	OH associated groups HO…H
3100-3000		3080			3080		νCH asymm	
3100-2700	3050-2945	high concen-tration		3050 2945	high concentra-tion		νCH; νNH	vibrational combinations – aromatic cycle and many methyl, methylene groups
2900-2700	gradual			gradual			νCH; νN-CH$_3$	vibrational associations
2700-2500	2602 2550	2685		2602 2550	2685		ν(-S-S-, -S-H)	sulphur bonds from sulphur compounds (mercaptans metathiazole)
2300-2200	2290			2290			ν(OH), ν(CO)	vibrational combinations associated to the absorption in 1420 – 1300 cm^{-1} range
2100-1700	2020			2020			ν(CO)	vibrational associations – carbonyl combinations, aromatic nucleus (harmonics)
	1925			1925				
	1840	1855		1840	1855			
	1790	1800		1790	1800			
1800-1700	1720	1760		1720	1760		ν(CO)	carbonyl combinations
1700-1600	1640	1670		1640	1670		ν(CO); possible sinusoidal	carbonyl combinations + combination band
1600-1500	1595 1565	1590 1575	1520	1595 1565	1590 1575	1520	ν(CC)$_{inel}$	aromatic cycle
1500-1400	1500 1460	overlap-ping		1500 1460	over-lapping		δ CC)$_{inel}$ δ (CH$_3$)$_{as}$	ring vibrations within coupling network with assymm. deforming vibrations of CH$_3$ group

continuare

Range							Assignment	Description
								...ions of CH₃ group
1400-1300	1380	1345		1380	1345		δ(CH₂) δ(CH₃)ₛ	shearing CH₂ adjacent groups, CH₃ within propylene
1300-1200	1280 1220	1210	1230 1200	1280	1210	1230 1200	γ(CH); ν(CN)	vibrational associations - detached propylene units, tertiary amines
		1190 1180		1220 1190	1190 1180			
	1145	1140 1135		1145	1145 1135			
1100-1000	1010	1080 1065			1080 1065		-N-C=S/-N=C-S	group isomerism
1000-900		1000 980	980 955		1000 980	980 955	-N-C=S/-N=C-S	group isomerism
1000-900		925			930		S-S	disulphides
900-800	825			825			γ(CH)	ethylene units, methylene segments
900-800			820-680			820-680	C – C	network + substitution1,2,4, (and bands appearance from 1900-1750 cm⁻¹)
800-700	730	800 755		720	805 755		ring + network	cristalinity, prevails amorphous form, including ordered segments
700-600	630	665 615	605	635	665 615	605	aromatic ring	vibrational associations
700-600							S – S	
500-400		450	470 435		465	470	S – S	polysulphide bonds

detected in the spectral ranges of 650 – 400 cm⁻¹ and 1100 – 900 cm⁻¹, respectively. In the last range, the group isomerism -N-C=S↔-N=C-S, that is representative to the semiefficient crosslinking systems has been evidenced.

The appearance of some bands within the domain of 700 – 750 cm⁻¹ does not signify a certainty for the presence of some extended chains, having adjacent methylene groups. The dual absorption as spectral twins or the appearance of a large band in this range, could indicate the presence of a permanent change in the geometric configuration, showing the existence of irregular amorphous formation, that includes regular crystalline segments within its macromolecule.

Conclusions

The technology used to obtain polymeric microstructures of polymer composites with variable content of structured elastomer and polyolefine plastics has the advantage of simultaneously curing and processing together the elastomer and plastics melt., respectively. The composites resulted from mixtures (1 : 1) of EPDM rubber and PEID high density polyethylene having a plastics structure, in which small crosslinked EPDM particles are dispersed.

The pure PEID polyethylene shows a low swelling by immersing in all three solvents: benzene, *p*-xylene and carbon tetrachloride, while the pure EPDM rubber (at the beginning period) increases twice its volume in benzene, after which it dissolves itself; EPDM rubber dissolves fast in carbon tetrachloride. Also, our investigation shows that the composite control mixture is swellings in the first hour of contact with any of solvents.

For conventional cured composites with the increase of the accelerator/suphur ratio from 0.4 to 0.74, the samples immersed in benzene and p-xylene have shown low and close values of swelling. In carbon tetrachloride, the samples with accelerator /sulphur ratio of 0.4 have shown high swelling values, even over 100% at 24 h of contact with solvent. So, the following order of swelling action of solvents was established:
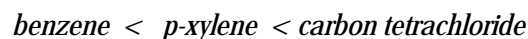
benzene ≈ p-xylene < carbon tetrachloride
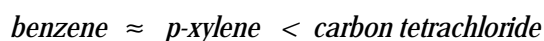
For the EV cured systems, from the increasing the accelerator/sulphur ratio comes out the increasing of swelling value; the swelling is lower for the curing ratio of 1.85, comparable with value of 0.75 for the same ratio for the conventional systems and remains constant for the 1.85 and 6.34 ratios. For these composites, the order of solvents is:

benzene < p-xylene < carbon tetrachloride
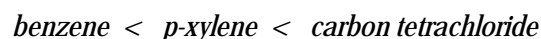
For the semi-EV cured composites, the swelling was increased with increasing of curing ratio from 1.85 to 6.34. The swelling values were keeping in the same order of the three solvents:

benzene < p-xylene < carbon tetrachloride

The increasing of accelerator/suphur ratio has not produced important variations by immersion in benzene and *p*-xylene, excepting some decreasing of swelling in carbon tetrachloride. The enhance of stirring during mixing, produces a better crosslinking, leading to a lower swelling. The increasing of stirring time has generally led to the decrease of swelling, indicating also a better crosslinking.

Using the IR spectroscopy it is proven that the crosslinking to prepare the polymer composites by classical curing systems induces changes within polymeric structures, due to large contribution of disulphide and polysulphide intermolecular bonds; the reactive attack of accelerator-sulphur couple on α-methylene hydrogen from the polymer molecules is thus evidenced.

The results are useful for selecting the operating conditions in composite manufacturing and for judicious choosing of how to use the composites based of EPDM rubber and polyethylene.

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