J Mater Sci (2008) 43:6167–6176
DOI 10.1007/s10853-008-2930-5

Effect of liquid additives on morphology and properties of thermoplastic elastomers prepared from phase-modified EPDM elastomer and isotactic polypropylene blends

**Pinka Chakraborty · Anirban Ganguly ·
Suman Mitra · Anil K. Bhowmick**

Received: 24 March 2008 / Accepted: 5 August 2008 / Published online: 26 August 2008

Abstract Thermoplastic elastomers (TPEs) were prepared from ternary blends of ethylene propylene diene poly methylene rubber (EPDM), isotactic polypropylene (PP), and low loadings (5–10 phr) of different types of interfacial phase modifiers (like maleated EPDM, styrene-ethylene-co-butylene-styrene block copolymer, and maleated PP). These showed much improved physico-mechanical properties compared to the binary blend of EPDM-PP. The effects of non-polar paraffin oil and polar di-octyl phthalate liquid additives (5–20 phr) were investigated in these phase-modified ternary and binary EPDM-PP blends. Only 5 phr of liquid additives provided synergistic improvement in physical properties (maximum stress, modulus, and elongation at break) and generated improved finer morphology of the ternary blends as revealed from scanning electron and atomic force microscopy studies. Enhanced physical properties and dynamic mechanical properties of these blends were explained with the help of better phase morphology and enhanced crystallinity of the blends.

Introduction

Polymer blends are one of the most interesting and useful classes of materials [1–5], which offer a convenient and less expensive alternative to develop new type of materials that can be tailor-made to meet specific requirements. Polymer blends are generally categorized into two main classes: miscible blends that exist in a single homogeneous phase and may exhibit synergistic properties and immiscible blends that have two or more different phases, showing at least two glass transition temperatures (T_gs). Apart from these two, there is a third category of blends, called technologically compatible blend, which exists in two or more different phases on a microscale, yet displays excellent combination of properties [1, 2]. Most of the polymer blends are thermodynamically immiscible, which results in poor interfacial adhesion and macroscale phase-separated morphology, and generally leads to poor mechanical properties.

Blending an elastomer with a thermoplastic polymer can result in thermoplastic elastomers (TPE) where the elastic property of an elastomer is combined with the processability of the thermoplastic polymers [4–7]. The combination of these properties makes these blends a good alternative to crosslinked rubbers. The hard thermoplastic segments that act as physical crosslinks are thermally labile and allow TPEs to soften and flow under shear force at elevated temperature as in the case of true thermoplastics. TPEs bridge the gap between conventional rubbers and thermoplastics. Different TPE systems have been discussed extensively in books by Legge et al. [8], Bhowmick and Stephens [9], Walker and Rader [10], De and Bhowmick [11], Baranwal and Stephens [12], Bhowmick [13], etc.

Studies on Polypropylene (PP)/Ethylene Propylene Diene poly Methylene (EPDM) thermoplastic elastomeric olefins (TEOs) have been carried out by several authors as a range of properties can be obtained just by changing the blend compositions [7–19]. PP and EPDM are considered incompatible, although their molecular structures have some similarity. Many attempts have been made to enhance the miscibility and/or the plastic/rubber interfacial interaction to improve the mechanical properties of the blend. The problems can be mitigated by the incorporation of a compatibilizer.

P. Chakraborty · A. Ganguly · S. Mitra · A. K. Bhowmick (✉)
Rubber Technology Centre, Indian Institute of Technology,
Kharagpur, West Bengal 721302, India
e-mail: anilkb@rtc.iitkgp.ernet.in

The judicious choice of a compatibilizer can often result in improved mechanical properties of the blend and reduces interfacial tension between the blend components. Both these effects promote a stable, fine distribution of the dispersed phase within the matrix phase. In addition, these improve interfacial adhesion between the blend components, which facilitates stress transfer across the interfaces, reducing possibility of an interfacial failure [16–19].

Our recent studies indicate that by using compatibilizing agents in the blends, there is 50% improvement in tensile strength, 25% increase in modulus, and 200% enhancement in elongation at break properties [20, 21]. These results are in line with the work by Roy Chowdhury and Bhowmick [22], Jha and Bhowmick [23], Kader and Bhowmick [24], Jacob et al. [25], and Patel et al. [26] on different types of rubber and plastic blends from the same laboratory. It has been observed that many commercial EPDM/PP TPEs contain oil and additives. However, the literature on this subject is very classified and not accessible readily [27–34].

Hence, in the present work, we have focused on the effect of low molecular weight liquid processing additives like non-polar paraffinic oil and polar di-octyl phthalate (DOP) on the morphology and physico-mechanical properties of EPDM-PP and the phase-modified EPDM-PP TPEs.

Experimental

Materials

The basic characteristics of the materials used in this study are listed in Table 1. Ethylene Propylene Diene poly Methylene rubber (EPDM, Buna EPG 2470) was obtained from Lanxess, Germany. Maleated EPDM rubber (Royaltuf 465), low ethylene content, supplied by Crompton—Uniroyal Chemical Co., Naugatauk, CT (USA), was used. Isotactic polypropylene (homopolymer, Koylene ADL) was supplied by IPCL, Vadodara, India. Maleic anhydride grafted PP (Polybond 3200) was supplied by Crompton–Uniroyal Chemical Co., Naugatauk, CT (USA). Poly [styrene-b-(ethylene-co-butylene)-b-styrene] (Kraton G1652) was supplied by Shell Chemical Co. Washington Blvd., OH (presently Kraton Polymers, Houston, TX). Paraffinic mineral processing oil (Sunpar® 150, supplied by Sun Oil Co., Philadelphia) and Di-octyl Phthalate (Palatinol® DOP; $C_{24}H_{35}O_4$, supplied by BASF, Germany) were used as low molecular weight liquid additives. Laboratory reagent grade heptane was purchased from Nice Chemical Co. Cochin, India, for selective etching purpose.

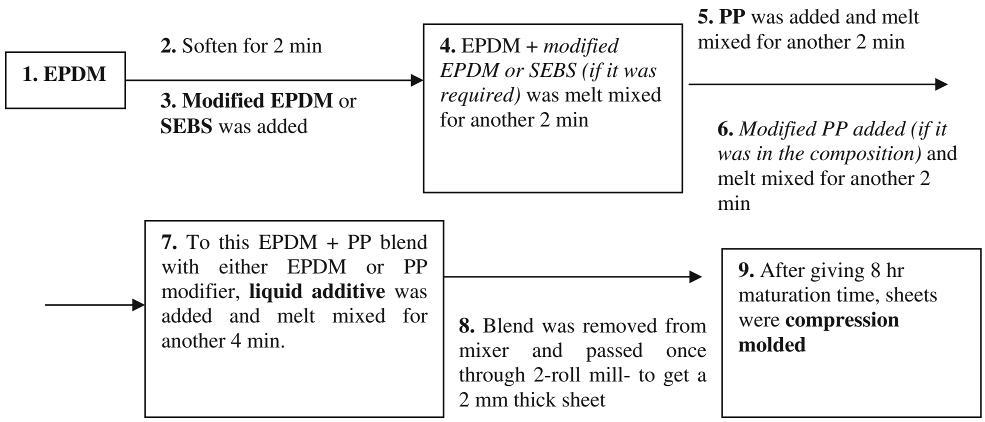
Preparation of the blends

All blends were prepared in an internal batch mixer (Sigma blender by S.C. Dey & Co, Kolkata, India), having mixing chamber volume of 100 cc at a temperature of 190 °C and 40 rpm using sigma type rotor. The blending sequence in the internal mixer used was as follows:

Table 1 Characteristics of the materials taken

Materials	Characteristics details
EPDM (*Buna EPG ®2470*)	Mooney viscosity $ML_{(1+4)}$ at 125 °C = 24, ethylene content = 69%, Termonomer (ENB) content = 4%, specific gravity = 0.86
PP (*Koylene ADL*)	Isotactactic PP, MFI 230 °C/2.16 kg = 5.6 g/10 min, specific gravity = 0.905
MAEPDM (*Royaltuf® 465*)	Maleic acid/maleic anhydride monomer = 1 wt.%, $ML_{(1+4)}$ at 125 °C = 60, ethylene content = 55%, specific gravity = 0.89
SEBS (*Kraton® G1652*)	Styrene content = 30%, MFI @230 °C, 2.16 kg = 5 g/10 min, specific gravity = 0.91
MAPP (*Polybond ®3200*)	Maleic anhydride = 1 wt.%, MFI @190 °C, 2.16 kg = 110 g/10 min, specific gravity = 0.91
Paraffin oil (*Sunpar® 150*)	Low volatility, open cup flash point (ASTM D92) = 245 °C and boiling point = 384 °C, specific gravity = 0.85 at 200 °C
Di-octyl Phthalate (DOP): (*Palatinol® DOP)*	MW = 391, ester content, minimum = 99.6 wt.%, maximum acid no. = 0.07 mg KOH/g, specific gravity = 0.98–0.985
Heptane	Boiling range (90%) = 90–100 °C, specific gravity = 0.70

At first, EPDM was allowed to soften for 2 min. Modified EPDM (or SEBS) was added to molten EPDM and melt-mixed for the next 2 min. Then PP was added gradually and melt-mixed with the resultant blend for another 2 min. In the case of the blends with modified PP, after 2 min of EPDM addition, PP was incorporated and melt-mixed for 2 min. At the last stage, modified PP was added and the mixing was carried out for another 2 min. In both the cases, liquid additives were slowly added at this stage and the mixing was continued for another 4 min. The blend was removed immediately after mixing from the mixer and passed once through a two-roll mill (Schwabenthan, Berlin, Germany) to get a sheet of about 2 mm thickness in molten condition. After giving 8 h of maturation time, the sheets were compression-molded (Moore Press, Birmingham, UK) at 180 °C for 4 min at 5 MPa pressure in between Teflon foils. Flow diagram of blend preparation and the time schedule followed is provided in Scheme 1. The sheets were then cooled down to room temperature under the same pressure. In order to focus the study on the effect of liquid additives (added in 5, 10 or 20 phr) alone, a



Scheme 1 Flow diagram of blend preparation and the time schedule followed

constant rubber–plastic ratio of 74:26 was chosen for the binary and ternary EPDM-PP-phase-modified blends to have maximum possible rubbery properties.

Morphological characteristics

Scanning electron microscopy (SEM)

Morphology studies by scanning electron microscopy of different blend compositions were performed using JSM5800, by JEOL, Japan, operated at 20 kV of acceleration voltage at room temperature. The elastomeric component of the blends was etched out by using heptane solvent for 3 h. The extraction of the elastomer was nearly quantitative and left a polypropylene matrix that was somewhat swollen but recovered after proper drying. The samples were sputter coated by gold prior to scanning.

Atomic force microscopy (AFM)

For detecting surface phase morphology, scanning and analysis of the samples were carried out using a multimode AFM with a nanoscope IIIa controller by Digital Instruments Inc., Santa Barbara, CA, USA. Phase images were acquired for surface morphologies of different blends in air at ambient conditions (25 °C temperature, 60% humidity) with a tapping mode Si probe (TESP) having nominal spring constant of 40 Nm^{-1}.

Wide angle X-ray diffraction (WAXD)

WAXD of the blends and the neat polymers was performed using PW 1820 X-ray diffractometer (PHILIPS, the Netherlands) at acceleration voltage of 20 kV and 20 mA with Cu k_α ($\lambda = 0.1542$ nm) radiation source. The scans were carried out in the range of goniometer angle (2θ=) 10–60° at a scanning rate of $3°\mathrm{min}^{-1}$. The area under the crystalline and amorphous portions was determined in arbitrary units and the percent crystallinity [20] was calculated using the following equation:

$$\%\,\text{crystallinity} = \frac{I_c}{I_c + I_a} \times 100 \qquad (1)$$

where I_c and I_a are the integrated intensity of peaks corresponding to crystalline and amorphous phases of the polymer respectively. The area under the curve was calculated using ORIGIN 7.0 software by the Gaussian method and graphical plotting.

Tensile stress–strain properties

Mechanical properties were measured as per ASTM D 412-98 in a universal tensile testing machine (UTM) Zwick/Roell Z010 (Zwick GmbH and Co., Ulm, Germany) at a crosshead speed of 500 mm/min at room temperature. The specimens were die-punched into dumbbells for tensile measurements from 2 mm thick sheets with ASTM Die-C. The TestXpert®II software was used for data acquisition and analysis. Tension set was measured at 25 °C after stretching the samples for 10 min at 100% elongation, according to ASTM D412-98. The average of three results was reported in each case.

Dynamic mechanical thermal analysis (DMTA)

Viscoelastic properties of the blends along with the control polymers were carried out with a dynamic mechanical thermal analyzer (DMTA IV) (Rheometric Scientific, Inc., Piscataway, NJ, USA) operated in tension-compression mode in the temperature range of −100 to 130 °C (at a heating rate of 2°C/min, constant input sinusoidal frequency of 1 Hz, and 0.01% strain amplitude). Storage modulus (E'), loss modulus (E''), and damping coefficient (loss factor, tan δ) were measured as a function of temperature for all the representative samples under identical testing conditions.

Results and discussion

Effect of phase modifiers on EPDM-PP blends

The physico-mechanical properties and phase-separated morphology of immiscible EPDM-PP blends have been greatly influenced by the use of appropriate phase modifiers—modified EPDMs, modified PPs, and block copolymer as reported in our earlier publication [20]. These phase modifiers have acted as interfacial agents to enhance interfacial adhesion, generate finer dispersion, and improve morphological stability to compatibilize the immiscible blends. In the following sections, the effects of low molecular liquid additives on the properties and morphology have been discussed with reference to the phase-modified and the control EPDM/PP blends.

Effect of liquid additives on the mechanical properties of the unmodified and the phase-modified EPDM/PP blends

Variation of mechanical properties of the unmodified and the modified EPDM/PP blends with varying oil and DOP concentrations is registered in Table 2. With the addition of liquid additives up to a certain level, maximum stress, elongation at break, and modulus of the blends are improved with respect to the control samples in most of the cases. The values of percentage improvement are recorded in the parentheses.

In the case of both the unmodified and the modified blend systems, it is observed that with the addition of oil, σ_{max} (maximum stress) and elongation at break values increase sharply up to 5 phr concentration followed by a decrease at further loading of 10 and 20 phr of oil (Fig. 1 and Table 2). It is also tangible from the moduli values (Table 2) that the unmodified and the modified blends give maximum value at 5 phr oil concentration, beyond which it decreases with increasing oil concentration. It is observed that the tension set values tend to increase for all the blends compared to the control blends (A, C_8, E_8, and F_8), after the addition of oil. As the elongation at break for sample A (EPDM + iPP) was only 84% and tension set was measured at 100% elongation, the said test could not be performed for A. This was one of the criteria (elongation at break must be more than 100%) that A was not meeting initially for TPE. On phase modification and oil addition, the elongation at break increases considerably. But this increase in tension set is the least for 5 phr oil-modified blends compared to 10 and 20 phr oil-modified blends (Table 2). The figures for tension set values of 26, 28, and 36% for A-Oil_5, C_8-Oil_5, and F_8-Oil_5 are lower compared to the values of 40% or more for higher loadings of additives in the respective samples, as depicted in Table 2. The trend with different phase modifiers is almost the same.

Table 2 Effect of liquid additives on mechanical properties of the unmodified and modified EPDM-PP blends

Sample[a]	Modifiers (phr)[c]	Maximum stress, σ_{max} (MPa)	Elongation at break (%) (with% change)	Modulus (MPa) at elongation of		Tension set (%)
				50%	100%	
A	Nil	4.64	84	4.54	–	–
A-Oil_5[b]		7.59 (64%)	409 (387%)[d]	5.81 (28%)	5.96	26
A-Oil_{10}		6.30 (36%)	475 (465%)	4.40 (−3%)	4.55	40
A-Oil_{20}		4.58 (−1%)	376 (348%)	3.44 (−24%)	3.54	56
C_8	MAEPDM (8)	3.68	130	3.42	3.64	14
C_8-Oil_5		7.94 (116%)	551 (324%)[e]	4.65 (36%)	4.85	28
C_8-Oil_{10}		5.98 (63%)	360 (177%)	4.47 (31%)	4.72	24
C_8-Oil_{20}		4.24 (15%)	233 (44%)	3.41 (−0.3%)	3.76	44
E_8	SEBS (8)	6.90	252	5.64	6.03	18
E_8-Oil_5		8.84 (28%)	516 (105%)[f]	5.16 (−8.5%)	5.49	36
E_8-Oil_{10}		6.01 (−13%)	366 (45%)	4.00 (−29%)	4.45	32
E_8-Oil_{20}		2.37 (−66%)	175 (−30%)	2.03 (−64%)	2.27	20
F_8	MAPP (8)	5.39	178	5.64	6.03	18
F_8-Oil_5		8.37 (55%)	520 (192%)[g]	5.00 (−11%)	5.22	36
F_8-Oil_{10}		5.88 (9%)	381 (114%)	4.04 (−28%)	4.36	36
F_8-Oil_{20}		5.45 (1%)	334 (88%)	4.09 (−27%)	4.29	40
A	Nil	4.64	84	4.54	–	–
A-DOP_5		6.55 (42%)	394 (369%)[d]	4.87 (7%)	5.00	32
A-DOP_{10}		6.49 (41%)	468 (457%)	4.46 (−2%)	4.58	44
A-DOP_{20}		2.75 (−41%)	205 (144%)	2.33 (−49%)	2.52	36

[a] Effective rubber–plastic blend ratio (=74:26) was kept in all the blends

[b] Subscript values after the liquid indicate added amount of liquid additives (5, 10 and 20 phr)

[c] The number in the subscript after C, E and F indicates polymeric phase modifier concentration, e.g., 8 parts per 100 parts of respective polymer

[d,e,f,g] The values in the parenthesis indicate percent change of the properties (e.g., Maximum stress, elongation at break, and modulus at 50% elongation) for liquid additive modified blends with respect to those of the blends A, C_8, E_8, and F_8, respectively

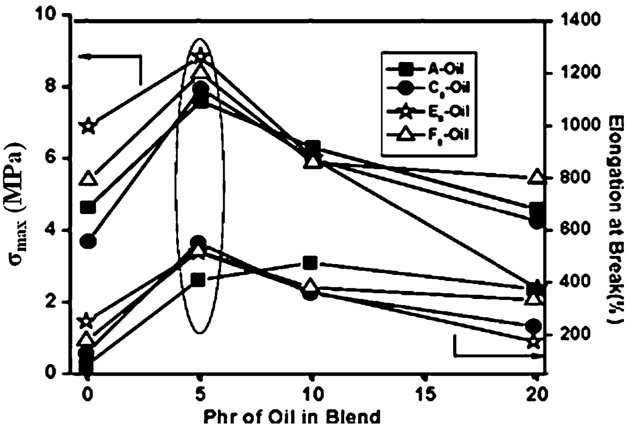


Fig. 1 Effect of oil on σ_{max} and elongation at break for different EPDM-PP blends (A, C_8, E_8, and F_8)

Only one exception is found in E_8-Oil samples where 20 phr oil shows minimum tension set (20%) as SEBS can take even more oil for its structure. But the maximum stress, modulus, and elongation at break values have dropped considerably for this 20 phr oil loaded blend compared to 5 phr oil loaded E_8-Oil$_5$ sample. It is concluded that the unmodified and the modified EPDM-PP blends with 5 phr oil loading give the optimum σ_{max}, modulus, and elongation at break (%) values (Fig. 1).

The effect of DOP on the mechanical properties of EPDM/PP blends is also shown in Table 2. It is clearly visible that with the addition of DOP into the unmodified EPDM-PP blend, σ_{max}, modulus, and elongation at break increase up to 5 phr concentration. With further addition of DOP, σ_{max} and modulus (Table 2) decrease gradually. The elongation at break value increases up to 10 phr DOP loading (Table 2) which decreases on further loading of 20 phr mostly due to extensive internal lubrication in the blend. The tension set value is 32% for A-DOP$_5$ blend.

These enhanced mechanical properties in both oil and DOP loaded systems may be due to the higher crystallinity and physical interaction between the components and finer morphology of modified blends compared to the unmodified EPDM/PP blend, as discussed later. Hence, with the optimized dose of 5 phr liquid additives, modified blends have been taken up for dynamic mechanical thermal analysis and microscopic studies.

Results of DMTA

In order to study the viscoelastic behavior of thermodynamically immiscible but technologically compatible EPDM/PP blends, DMTA has been carried out in tension-compression mode. Figure 2a depicts almost no drop in storage modulus (log E') on paraffinic oil modification (5 phr) in the binary EPDM/PP blend. The tan δ versus temperature plots for different EPDM-PP blends indicate the presence of two transitions from glassy to rubbery state with increase in temperature. The T_g of the rubbery and the plastic phase is shifted by 5 and 3 °C, respectively (as shown from the tan δ plots), due to a plasticization effect by oil in this binary blend. Similar plots of log E' and tan δ versus temperature for the ternary blends with and without additives have been made and the results are shown in Table 3 with representative plots in Fig. 2b. There is a

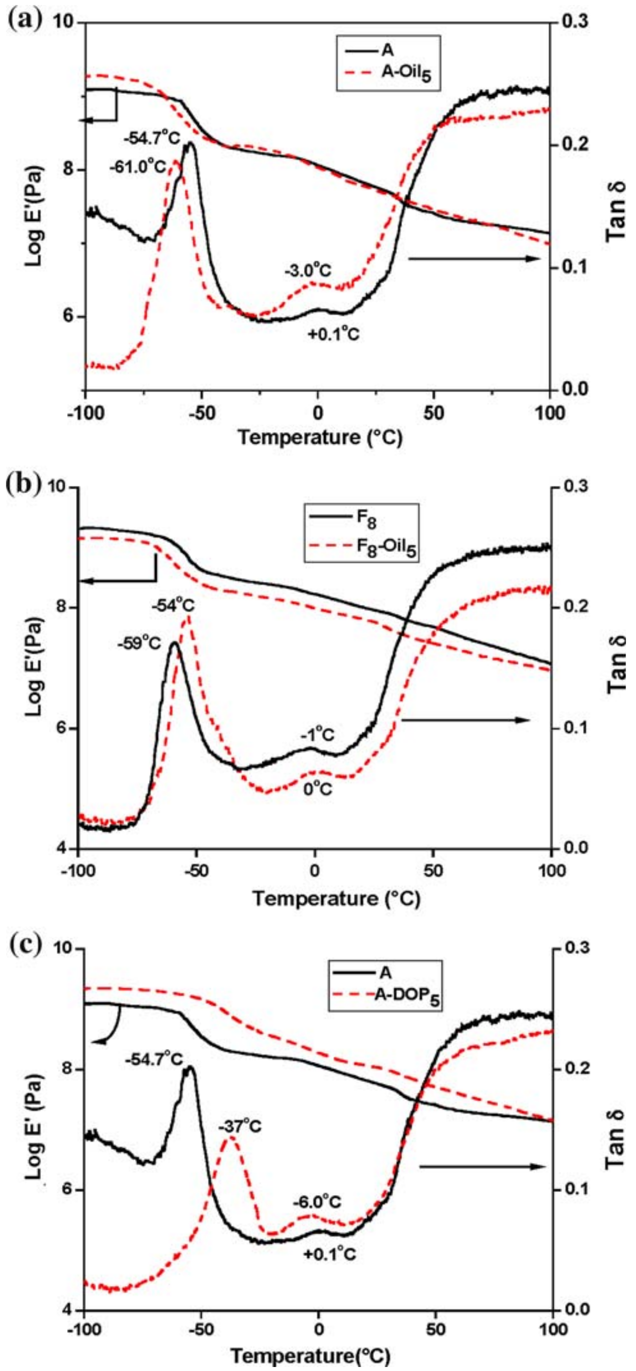


Fig. 2 Tan δ and log E' versus temperature plots of (**a**) A & A-Oil$_5$, (**b**) F_8 & F_8-Oil$_5$, and (**c**) A & A-DOP5 blends

Table 3 Dynamic mechanical properties of EPDM, PP, modified, and unmodified EPDM-PP blends

Sample	log E' (Pa)			T_g (°C)		Tan δ maxima at	
	At temperature (°C)			T_{g1}	T_{g2}	T_{g1}	T_{g2}
	0	25	75				
EPDM	6.72	6.21	5.73	−50.1	–	0.485	–
PP	9.38	9.20	8.72	–	−4.3	–	0.052
A	8.06	7.76	7.25	−54.7	0.1	0.203	0.067
A-Oil$_5$	8.03	7.72	7.24	−61.0	−3.0	0.188	0.089
C$_8$	7.67	7.23	6.97	−37.4	10.9	0.160	0.079
C$_8$-Oil$_5$	7.15	7.03	6.79	−58.0	−23.0	0.181	0.093
E$_8$	7.64	7.57	6.99	−52.6	−18.5	0.145	0.061
E$_8$-Oil$_5$	7.27	7.02	6.40	−58.0	−8.0	0.181	0.086
F$_8$	8.22	7.96	7.36	−53.7	0.5	0.193	0.065
F$_8$-Oil$_5$	7.99	7.76	7.16	−59.0	−1.0	0.169	0.084
A-DOP$_5$	8.28	8.04	7.71	−37.0	−6.0	0.144	0.078

T_{g1} and T_{g2} = glass transition temperatures corresponding to EPDM and PP phases, respectively

decrease in E' values for the phase-modified systems upon addition of oil over the temperature range studied.

In all the cases, it is observed that the tan δ peaks originated due to the rubbery (at around −54.7 °C) and the plastic phases (at around 0.1 °C) have shifted to a lower temperature after addition of oil into the control blend systems. Only exception to this is the peak for plastic phase of EPDM-PP-SEBS-Oil quaternary blend (Table 3). It is well known that SEBS can take up a lot of oil. Also, as SEBS acts as a compatibilizer for PP and EP blends, and SEBS-PP combination makes a good blend, the oil is mostly in the SEBS phase [35, 36]. As a result, T_g of PP phase increases. In the case of C$_8$ blend, MA-EP reacts with the PP during blending, thus increasing the polarity of PP and restricting the segmental mobility of PP chains due to interaction. This results in higher T_{g2} for C$_8$. However, the shift in T_g toward lower temperature is mainly due to the plasticization effect of the oil on the control blend systems. With the addition of oil, mobility of the polymer chain increases due to increase of free volume of the polymer, which lowers down the glass transition temperature, and thereby improves the low temperature flexibility of the blend. It is also observed that the T_g peak for the rubbery (EPDM) region is shifted more as compared to PP (see representative Fig. 2b), due to more structural similarity between paraffin oil and EPDM (having 69% ethylene content).

The tan δ versus temperature plots for EPDM-PP-DOP system are given in Fig. 2c. A very interesting feature is observed from the plots. With the addition of 5 phr of DOP, the tan δ peak for the rubbery region is shifted to a higher temperature, whereas tan δ peak for PP is shifted to a lower temperature. So, DOP plasticizes the PP phase rather than the EPDM phase here. The storage modulus is much higher in the rubbery region compared to the storage modulus of the unmodified EPDM-PP blend, due to an increase in the crystallinity of the continuous PP phase, as discussed later.

Analysis of blend morphology

Analysis of SEM photomicrographs

Scanning electron photomicrographs of the binary, ternary and the quaternary blends with oil are shown in Fig. 3a–e. Morphology of the blends varies with the concentration of the components and also with the viscosity of the two phases. Multiphase morphology becomes visible after etching with the solvent, heptane. Heptane (good solvent for EPDM, but not for PP) etches out the rubber phases which can be viewed as dark holes or patches in the dark-bright contrast of SEM morphologies for the blends.

In the present work, a dispersed morphology of the EPDM phase is observed. Although the high-concentration component normally becomes the matrix phase, viscosity plays a dominant role in determining the morphology of the blends. Due to a higher viscosity, the EPDM phase has become the dispersed phase even with a high rubber to plastic ratio (74:26) in the blends [20]. In the case of the unmodified EPDM-PP binary blend, no clear morphology is observed even after solvent etching of the rubber phase (Fig. 3a) (and hence no measurement of domain size has been attempted). This corroborates the lower values of maximum stress and % elongation at break and reduced storage modulus of the EPDM-PP binary blend (Table 2). On incorporation of oil as an additive, definite morphology is generated. After oil modification of the unmodified and the phase-modified EPDM-PP blends, well-distributed cavitated stretched phases are formed with few circular domains (Fig. 3b–d). Domain sizes of the modified blends are given in Table 4. The formation of well-distributed morphology is due to the shear action of oil-filled EPDM phase.

It can be noted that with the addition of phase modifiers, MAEPDM, SEBS, and MAPP to the EPDM-PP blend, the domain sizes of the dispersed rubber phase vary from 0.9 to 3.6 μm, from 0.5 to 4.8 μm, and from 7 to 30 μm, respectively, for C$_8$, E$_8$, and F$_8$, as reported in our earlier publication [20]. With the addition of only 5 phr of oil or DOP, these domain sizes have further reduced to finer dispersed domains of rubbery phase in the resulting TPEs.

Figure 3e shows the SEM phase micrographs for DOP-modified EPDM-PP blend. This morphology has relatively larger, almost circular domains with few cavitated stretched domains (Table 4). For the 5 phr DOP-modified

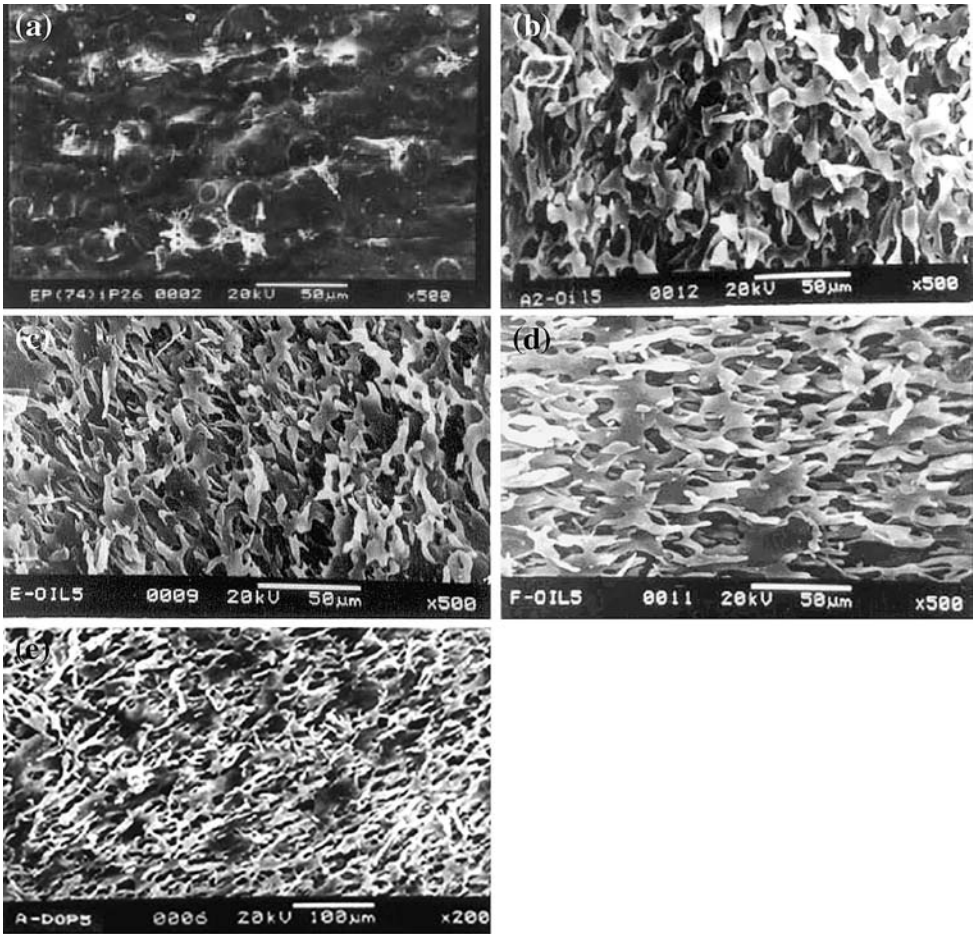


Fig. 3 SEM micrographs of (**a**) binary A, and oil blended ternary blends, (**b**) A-Oil$_5$, (**c**) E$_8$-Oil$_5$, (**d**) F$_8$-Oil$_5$, and (**e**) A- DOP$_5$

Table 4 Analysis of SEM images: domain size of the rubber phases of liquid modified blends

Samples	Circular domain size (μm)	Stretched domain size (μm)	
		Transverse direction	Longitudinal direction
A-Oil$_5$	2.6–14.0	5.0–18.0	9.0–45.0
C$_8$-Oil$_5$	0.5–2.0	10.0–18.0	4.5–11.0
E$_8$-Oil$_5$	1.0–9.0	9.0–34.0	1.0–9.0
F$_8$-Oil$_5$	1.0–12.0	12.0–59.0	1.0–11.0
A-DOP$_5$	2.2–16.0	16.0–35.0	1.5–13.0

blend, the average dispersed phase domain size ranges from 1.5 to 35 μm. Again, this well-distributed phase morphology explains the better mechanical properties of DOP-modified EPDM-PP blend compared to the control blend (neat EPDM-PP).

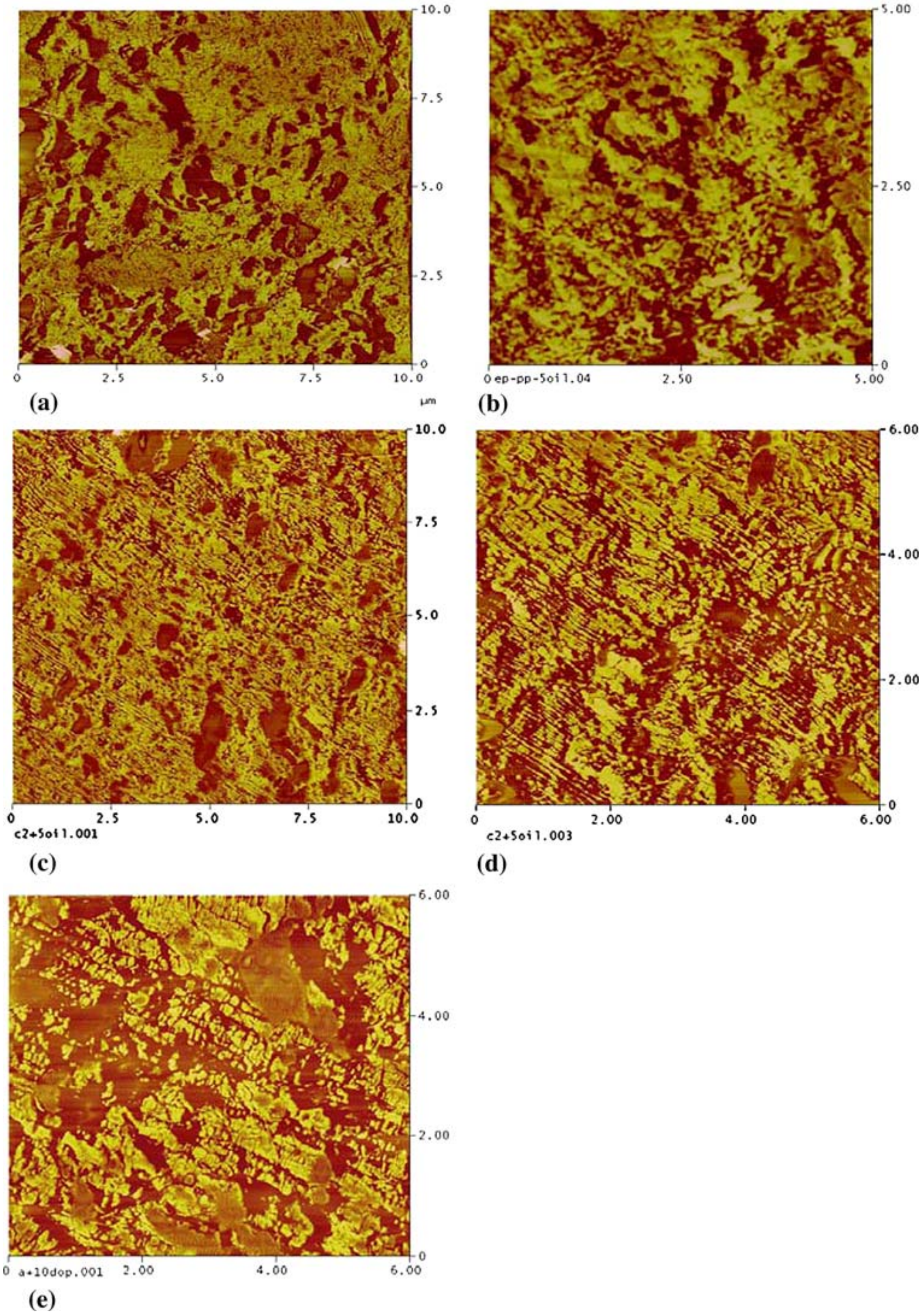
Nanomorphology by AFM

The surface morphology of the respective blends is obtained using AFM in tapping mode by magnifying a small region of the surface. These are shown in Fig. 4. In this mode, the brightest sites on the phase image correspond to a more rigid component and the darkest sites correspond to a less rigid component [37]. Though SEM studies for characterizing the morphologies generated by EPDM-PP blends are available [4–7, 16–19, 22–26, 38–41], proper analysis of these blends by AFM is still obscure.

For the oil-modified EPDM-PP blend, circular to cylindrical rubber domains are observed on the PP matrix (Fig. 4a–c). These circular domains are in the range 140–300 nm for small domains and 700–900 nm for large domains. The length of the cylindrical domains lies in the range 1.10–1.60 μm with width 230–360 nm. On harder tapping with higher force, onto the rubbery region, a distributed morphology of soft segments in the dispersing PP matrix can easily be observed in a small scan area of 5 μm (Fig. 4b). This in-depth investigation in morphology is beyond the scope of SEM characterization technique.

AFM phase images demonstrate improvement of the surface morphology with the addition of 5 phr of paraffinic oil or DOP in the unmodified and the modified EPDM-PP. This binary EPDM-PP does not show any distinct

Fig. 4 AFM phase images of EPDM-PP-Oil$_5$ (**a**, **b**), MAEPDM phase modified EPDM-PP-oil$_5$ blended TPE (**c**, **d**), and EPDM-PP-DOP$_5$ ternary blend (**e**) showing rubber domains dispersed on PP matrix in different magnifications



morphology initially, as a result of which poor physical properties have resulted [20]. On incorporation of only 5 phr of oil, a finer morphology is developed. From 100 µm^2 image in Fig. 4a and 25 µm^2 image in Fig. 4b, a distinct morphology is evident in the case of 5 phr oil-modified EPDM-PP TPE. Circular and semi-circular rubbery patches (300–600 nm) are observed as dispersed phase in the continuous PP matrix of the same blend (Fig. 4a, b). For the MAEPDM phase-modified EPDM-PP blend (MAEPDM$_8$–EPDM-PP), even finer morphology is observed (Fig. 4c–d). Distinct PP lamellae having a length from 0.5 to 2.0 µm and width from 50 to 100 nm is evident from Fig. 4c–d with finer dispersion of the rubbery domains. Proper dispersion of the finer rubbery phases in a continuous PP matrix as elucidated from morphological studies by SEM and AFM microscopic studies is responsible for the better physical (mechanical and dynamic mechanical) properties of these TPEs.

Incorporation of DOP into an unmodified EPDM-PP blend shows similar improved morphology with distributed rubber phase into the PP matrix (Fig. 4e). It gives mainly cylindrical rubbery domains in the continuous matrix of PP. The rubbery domain size ranges from 1.0 to 1.5 µm in length and is 500 nm in diameter. This well-distributed morphology corroborates improved mechanical and dynamic mechanical properties of DOP-modified EPDM-PP blend.

It seems that PP becomes compatible with oil at the temperature of blending (190 °C), reducing the viscosity of the plastic phase and increasing the difference between the plastic and the rubber [42]. The morphologies obtained in this case become finer as a result of compatibility. However, the polar DOP drives both the phases to generate finer morphology. The reason is not clear to us at this stage.

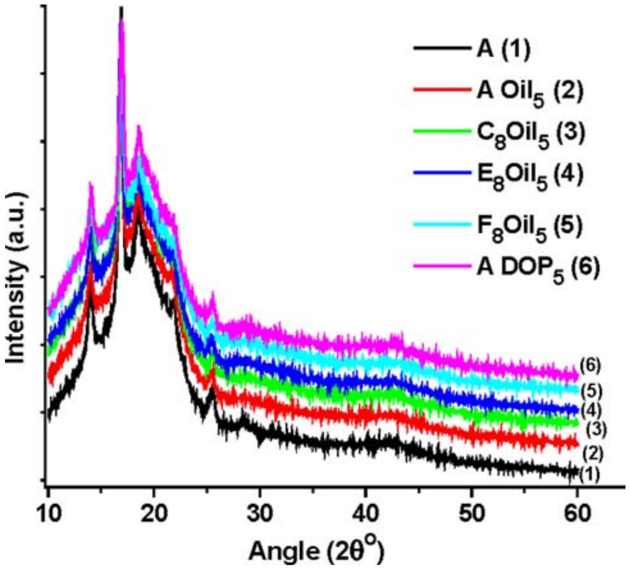


Fig. 5 Changes in WAXD pattern of blends of PP-EPDM with and without modifiers in the presence of 5 phr oil and DOP

Crystallinity from WAXD

Crystallinity (X_c) of various EPDM-PP blends with and without oil modification has been calculated (using Eq. 1) from the WAXD plots (Fig. 5). These values are reported in Table 5.

Crystallinity of PP is calculated to be 39% (Table 5). From XRD data, it is clearly observed that initial crystallinity of PP decreases to about 66% of its original value when it is blended with EPDM rubber, as given in Table 5. When EPDM-PP blend is further modified by different concentrations of oil, crystallinity increases by 43.6% compared to the control system of EPDM-PP blend. When modified EPDM-PP ternary blends (with either of the phase modifiers—MAEPDM, SEBS, or MAPP) are used and oil is incorporated as an additive, these blends show the same trend. In all these cases, crystallinity of the oil-modified systems is higher than that of the control blend systems.

This can easily explain the improvement of the mechanical properties (Table 2) of the oil modified EPDM-PP blends. The non-polar oil has compatibility with non-polar EPDM and PP. The oil is absorbed by the PP melt in large proportions. The result is in line with the observation by Ellul [7, 32]. Oil partitions between the EPDM and the PP phases in the melt state and competes with EPDM for distribution in the PP matrix. Due to the lower molecular weight of oil, it penetrates more into the PP matrix than into the higher molecular weight EPDM phase. When these blends are cooled down, oil comes out off the PP phase easily. It helps in crystallization of PP. Then the oil is mainly redistributed into the EPDM phase later.

Similarly, the percent crystallinity of the DOP-modified blend is much higher than that of the unmodified EPDM-PP blend. The higher mechanical properties of the DOP-

Table 5 Percent crystallinity change on blending liquid additives to different EPDM-PP blends

Sample	% Crystallinity (X_C)	Change in crystallinity after adding liq. additives (%)	Δ % Crystallinity with respect to PP	Δ % Crystallinity with respect to EPDM-PP
PP	39.0	–	–	–
A	13.3	–	−66.0	–
A-Oil_5	19.1	+43.6	−51.1	+43.6
C_8	12.4	–	−68.3	−6.7
C_8-Oil_5	17.6	+41.9	−54.9	+32.3
E_8	12.3	–	−68.5	−7.2
E_8-Oil_5	20.1	+63.4	−48.5	+51.1
F_8	14.0	–	−64.0	+5.7
F_8-Oil_5	14.5	+3.6	−62.8	+9.0
A-DOP_5	22.4	+68.1	−42.7	+68.1

The designations for A, C_8, E_8, F_8, Oil_5, and DOP_5 are provided in Table 2 modified system can be explained by the higher percent crystallinity of the blend.

Conclusions

Thermoplastic elastomers (TPE) based on EPDM-PP blend were prepared by using different modifier systems. These unmodified and modified blends were further blended with both non-polar and polar liquid additives such as paraffinic oil and DOP, respectively, with varying concentrations. The liquid additives showed synergistic effects on the properties and the morphology of the modified and the unmodified EPDM-PP blends. With only 5 phr of the liquid additives, 50% improvement in $\sigma_{\max}$ and 400% in elongation at break were registered for some blends. In the case of the maleic-modified EPDM-PP blend, more than 100% improvement in $\sigma_{\max}$ was observed. Enhancement of mechanical properties depends upon the modifier concentration and its nature.

Dynamic mechanical thermal analysis showed that the paraffin oil plasticized EPDM phase more compared to PP phase. Thus, it improves the low temperature flexibility of the blend systems. On the other hand, DOP exhibited more affinity toward the PP phase. A complex interaction is present between blends and polar/non polar liquid additives.

Generation of a better phase morphology with well-distributed dispersed rubbery phases was observed in the case of the polar DOP and non-polar paraffinic oil-modified blends, as revealed from scanning electron and atomic force microscopic studies. The morphology was correlated with the improved mechanical and dynamic mechanical properties.

Wide angle X-ray diffraction showed an increasing trend of crystallinity of the resulting blends after addition of the liquid additives, which is another important reason for the improvement of physical properties of TPEs.

References

1. Paul DR, Newman S (1978) Polymer blends, vols 1 and 2. Academic Press, New York
2. Utracki LA (1990) Polymer alloys and blends: thermodynamics and rheology. Hanser, Munich
3. Coran AY, Patel R (1980) Rubber Chem Technol 53:141
4. Coran AY (1995) Rubber Chem Technol 68:351
5. Sabet SA, Pudyak RC, Rader CP (1996) Rubber Chem Technol 69:476
6. Winters R, Lugtenburg J, Litvinov VM, Duin MV, de Groot HJM (2001) Polymer 42:9745. doi:10.1016/S0032-3861(01)00504-3
7. Ellul MD (1998) Rubber Chem Technol 71:244
8. Legge NR, Holden G, Quirk RP, Schroeder HE (eds) (1996) Thermoplastic elastomers: a comprehensive review, 2nd edn. Hanser, Munich
9. Bhowmick AK, Stephens HL (eds) (2001) Handbook of elastomers, 2nd edn. New York, Marcel Dekker Inc.
10. Walker BM, Rader CP (eds) (1988) Handbook of thermoplastic elastomers, Ch. 4, 2nd edn. Van Nostrand Reinhold, New York
11. De SK, Bhowmick AK (1990) Thermoplastic elastomers from rubber–plastic blends. Ellis Horwood, West Sussex, UK
12. Baranwal KC, Stephens HL (eds) (2001) Basic elastomer technology, Ch. 13, ACS Rubber Div. 1st edn. Akron, OH
13. Bhowmick AK (ed) (2007) Current topics in elastomers research, Ch. 5, 1st edn. Taylor & Francis, CRC press, Florida
14. Sengupta P, Noordermeer JWM (2005) Polymer 46:12298. doi:10.1016/j.polymer.2005.10.075
15. Sengupta P, Noordermeer JWM, Sengers WGF, Gotsis AD (2003) Elastomer 38:27
16. Duin MV (2006) Macromol Symp 11:233
17. Jayaraman K, Kolli VG, Kang SY, Kumar S, Ellul MD (2004) J Appl Polym Sci 93:113. doi:10.1002/app.20414
18. Ponsard-Fillette M, Barre's C, Cassagnau P (2005) Polymer 46:10256. doi:10.1016/j.polymer.2005.08.015
19. Sengupta P, Noordermeer JWM (2004) J Elast Plast 36:307. doi:10.1177/0095244304042668
20. Chakraborty P, Ganguly A, Mitra S, Bhowmick AK (2008) Polym Eng Sci 48:477. doi:10.1002/pen.20984
21. Chakraborty P, Ganguly A, Mitra S, Bhowmick AK (Jan 8–10, 2008) Proceeding of the Int. Conf. Rub. Rub-Like Mat, ICRRM, IIT Kharagpur, India, p 113
22. Choudhury NR, Bhowmick AK (1998) J Appl Polym Sci 38:1091. doi:10.1002/app.1989.070380609
23. Jha A, Bhowmick AK (1997) Rubber Chem Technol 70:798
24. Kader A, Bhowmick AK (2001) Rubber Chem Technol 74:662
25. Jacob C, De PP, Bhowmick AK, De SK (2001) J Appl Polym Sci 82:3304. doi:10.1002/app.2189
26. Maiti M, Patel J, Naskar K, Bhowmick AK (2007) J Appl Polym Sci 102:5463. doi:10.1002/app.25106
27. Gessler AM, Haslett WH (1962) US Patent 3037954
28. Fischer WK (1973) US Patent 3758643
29. Coran AY, Patel R (1978) US Patent 4104210
30. Eisele U, Jache D, Mott L, Schabel KH (1988) US Patent 4745149
31. Gessler AM, Kresge EN (1979) US Patent 4132698
32. Ellul MD, Hazelton DR (2006) US Patent 7094837
33. Ito Y, Nakahama H, Ichino K (2007) Wipo Patent WO/2007/060843
34. Medintseva TI, Kuptsov SA, Erina NA, Prut EV, Soedineniya V, Ai Seriya, Seriya B (2007) Semenov Inst Chem Phys 49:54
35. Veenstra H, Verkooijen PCJ, van Lent BJJ, van Dam J, de Boer AP, Nijhof Abe PHJ (2000) Polymer 41:1817
36. Ohlsson B, Tornell B (1996) Polym Eng Sci 36:1457
37. Yerina N, Magonov SN (2003) Rubber Chem Technol 76:846
38. Karger-Kocsis J, Kalló A, Kuleznev VN (1981) Acta Polym 32:578. doi:10.1002/actp.1981.010320912
39. Litvinov VM (2006) Macromolecules 39:8727. doi:10.1021/ma061911h
40. Feng W, Isayev AI (2004) Polymer 45:1207. doi:10.1016/j.polymer.2003.12.033
41. Dai YQ, Wang B, Wang SJ, Jiang T, Cheng SY (2003) Radiat Phys Chem 68:493. doi:10.1016/S0969-806X(03)00216-0
42. Abraham T, Barber N, Mallamaci M (2007) Rubber Chem Technol 80:324