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Physical characterization of some copolyamide/ethylene propylene diene rubber (EPDM) blends

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In order to understand the processing-mechanical-property relationships, the effects of adding a small amount of maleated ethylene-propylene rubber (EP-g-MA) on the rheological properties of some copolyamide/EPDM blends were evaluated. The changes of the dynamic rheological parameters and some processing characteristics show that the blends with EP-g-MA display a different behavior from that of the homopolymer blend, viscoelastic measurements being sensitive to the composition of the blends. The obtained data showed the incompatibility of the binary coPA/EPDM blends due to the structural difference of the components. Better processability resulted because of high melt flow rate of coPA and increased mobility of elastomer macromolecules. The presence of EP-MA in the blend leads to the enhancement of the interfacial viscosity and adhesion due to the intermolecular interaction between the functional groups of the blend components produced during processing, the experimental curves corresponding to the loss and storage moduli as well as dynamic viscosity for uncompatibilized and mainly compatibilized blends are higher than those calculated by the additivity rules.

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1. Introduction

Polymer blends have become fascinating materials of research. Several research papers have been published in this area and over 450 blends have been successfully commercialized [1, 2].

It is now a common practice that toughness of a thermoplastic polymer is modified by blending with an elastomer, in general. Numerous studies on different thermoplastic and elastomer systems have been conducted [3-9]. Various theories have also been proposed to explain the toughening mechanisms in polymers.

Among the different types of polymer blends, thermoplastic materials from rubber/thermoplastic blends have attracted a lot of interest as they have many valuable properties. It is well-known that blends consisting of nylon and elastomer possess excellent toughness; however, due to its highly polar amide end-groups, nylon is incompatible with elastomer. In general, it is believed that functionalization of the elastomer is a preferred approach to enhance the interfacial properties between these polymers. The elastomer component increases the toughness especially immediately after injection molding and at low temperatures.

In general, polyamides are immiscible with elastomers due to the structural differences (absence of specific interactions) and also caused by free volume effects resulting from different thermal expansion coefficients. But such polyamide/elastomer blend systems have a relevant practical application.

Blends of polyamides and unfunctionalized rubbers are not tough because the rubber particles formed during melt blending are too large and adhesion may not be adequate. A practical solution is to graft maleic anhydride (MA) to the rubber prior to blending with the polyamide [10-13] MA grafted ethylene-propylene copolymer (EPR-*g*-MA) and styrene–(ethylene-*co*-*butylene*)–styrene triblock copolymer (SEBS-*g*-MA) [11, 14] are successful examples of such rubbers that are useful for toughening polyamides. The MA units can react with the amine end groups of the polyamide to form *in situ* graft copolymers at the rubber-matrix interface that decrease the interfacial tension and retard particle coalescence during mixing, resulting in uniformly distributed rubber particles in the polyamide phase of sizes within the useful range for effective toughening. The graft copolymer also enhances interfacial adhesion. For nonfunctional rubber, addition of a third component that acts as a dispersant for the rubber in the polyamide phase is an interesting alternative [15, 16].

For incompatible blends, high mechanical energy is needed to disperse the minor phase (by mixing) and after mixing coalescence may occur if the blend morphology is not stabilized. Interfacial forces such as the interfacial tension become important and can change the rheological signature of the blend significantly. Moreover the elastic properties of incompatible blends depend on energy storage mechanisms at the interphase. The relaxation of the dispersed phase itself is often much longer than the relaxation of the polymer chains of the individual components.

Rheological properties of elastomer modified polymer blends are of prime importance as their understanding would help in optimizing the commercial production of the blends. Several papers have been published on polyamide/rubber blends, but the rheological properties of polyamide and EPDM blends based on torque rheometer data are scarce [17, 18].

It is well known that the geometry of the mixing equipment and the operating conditions have a strong

effect on the mixing intensity and quality. Consequently, the chemical structure, the morphology and the rheology of the blends will be affected. It should be realized that the processing of such reactive polyamide/elastomer blends is of high complexity, since chemistry, morphology, and rheology continuously and mutually interact, and finally, determine the physical/mechanical properties of the blends [19-21].

This paper deals with the analysis of the presence of a maleated elastomer (Exxelor VA 1803 from EXXON CHEMICALS) as compatibilizing agent in the blends of ethylene-propylene-diene terpolymer (EPDM) with a copolyamide (coPA) by evaluating the changes of the rheological properties (dynamic mechanical parameters) and some processing characteristics.

2. Experimental

2.1. Materials

The main characteristics of the polymers selected for this study are the following:

Ethylene-propylene-diene terpolymer (EPDM, Terpit C®) was provided by ARPECHIM Pitesti (Romania) and contains 44.8% propylene, 3.5% ethylidene norbornene (EBN) as added diene, number of CH_3 groups per 100C: 0.983, unsaturation C=C / 1000C: 0.184, density: 0.826g/cm^3.

The second polymer used was a random aliphatic *copolyamide* obtained by direct melt polycondensation, through a "one-pot" technology described elsewhere [22, 23]. The main copolyamide characteristics are: chemical composition – a ternary statistic copolymer of adipic acid and sebacic acid with hexamethylene diamine and ε – caprolactame 6/6.10/6.6; molecular weight, M_n=2800-3000 g/mol, polydispersity index, I (M_w/ M_n)=1.050; granulation: 0.3 - 0.5 mm; density (at 23 °C): 1.11g/cm^3; cristallinity: 58%; melting temperature interval: 125-135°C; melt flow index (MFI, 2.16 daN/190 °C) = 18-20 g/10min.

The compatibilizing agent with trade name Exxelor VA 1803, (an ethylene-proylene rubber grafted with maleic anhydride) was kindly supplied by Exxon Chemical. The EP--MA compound contained 0.7% of MA, composition by weight: 43% ethylene, 57% propylene. Other characteristics are: melt flow rate (230°C/10kg) 22, density: 0.86 g/ cm³, glass transition temperature -57°C.

2.2. Blend preparation

The blends were prepared by melt mixing in a HAAKE RHEOCORD 9000 mixer (equipped with two internal roller mixers and a capacity of mixing chamber of 50 cm^3). As the mixing head is volume sensitive, the feeding amount is calculated by considering the volume of the cavity, density of the material and 85 % of the capacity utilization. The melt mixing was performed as follows: when the mixing chamber reached the desired temperature (200°C), a dry-blend of coPA and EPDM with or without EP-MA in the ratio given in Table 1 was charged into the chamber and was mixed at a rotational speed of 50 rpm, for 10 minutes.

Prior to the melt processing step, the blend components were dried in a vacuum oven at least for 24 h at 70°C, in order to eliminate the hydrolyzing effect of the absorbed water.

2.3. Methods of investigation

Processing behavior was evaluated from the torque-time curves recorded during the blending on a HAAKE Rheocord 9000 mixer. A machine calibration at the required mixing temperature and rotation speed was performed for an empty mixing chamber.

Melt rheological tests were conducted in a HAAKE RT20 Rotovisco-Oscillatory Rheometer in parallel plates oscillatory mode. Dynamic rheological properties as that dynamic viscosity, shear modulus (G‘) and loss modulus (G") being analyzed at a temperature of 200 ^{o}C both for the pure polymers and several blend systems.

3. Results and disscusion

3.1. Processing behavior

A caracterization of the blends containing coPA, EPDM and EP-g-MA is particularly interesting in view of understanding of the interactions that are expected to take place between the polymers during mixing. The torque curve is obviously "viscosity sensitive". If the speed is constant, variation in torque among samples at the same temperature is indicative of viscosity difference.

From the torque vs. time curves shown in Fig 1, recorded during the experiments carried out in the Haake Rheocord mixer one can observe that the viscosity of the binary blends coPA/EPDM has values between those of the homopolymers coPA and EPDM. The processing characteristics like torque after 1 minute and final torque, as well as specific energy after 1 minute of mixing (Table 1) depend on the blend composition, their values being higher by the increase of the elastomer content in the blend.

Copolyamide displays a low torque value, representative of a low viscosity. For the blends where the copolyamide content is higher, one can observe a better processing in melt mixing, the values of torque and mixing energy being lower than for binary blends having 5/95 coPA/EPDM mixing ratio. This is due to the low molecular weight (high melt flow rate) of coPA. The highest values are observed for the blends with higher amount of EPDM due to the high melt viscosity of EPDM.

Analysing Fig. 1 one can observe that the introduction of the EP-g-MA in the binary blends coPA/EPDM leads to an increase of the melting viscosity probably due to the interactions that take place between the polar groups from the maleated EP and amino end groups or -NH-CO- groups from the copolyamide.

Table 1. Processing behavior for the coPA/EPDM blends.

Composition	$TQ_{1\ min}$, (Nm)	TQ_{fin} , (Nm)	Emixing, $_{1\ min}$ (KJ/g)
Neat polymers			
coPA	0.86	0.31	0.007
EPDM	25.98	19.51	0.301
coPA/ EPDM Blends			
5coPA/95EPDM	18.33	15.36	0.209
10 coPA/90 EPDM	11.25	11.83	0.126
15 coPA/85 EPDM	7.08	7.29	0.078
coPA/ EPDM Blends with 5% EP-g-MA			
5coPA/95EPDM	19.07	18.02	0.217
10 coPA/90 EPDM	13.62	11.25	0.152
15 coPA/85 EPDM	9.81	8.23	0.108

$TQ_{1\ min}$ – torque after 1 min
TQ_{fin} – final torque
Emixing, $_{1\ min}$ – specific energy of mixing after 1 min

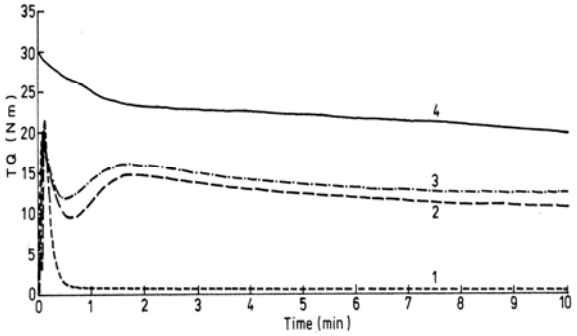


Fig. 1. Torque-time curves for coPA/IPP blends with or without compatibilizing agent: (1) – copolyamide; (2) – 10 coPA/40EPDM; (3) - 10coPA/70EPDM + 5 EP-g-MA; (4) – EPDM.

3.2. Rheology

Rheology provides the key to the relationships between viscoelasticity, molecular structure and processing performance. The molecular structure of the polymer system and the rheology determine the behavior during processing.

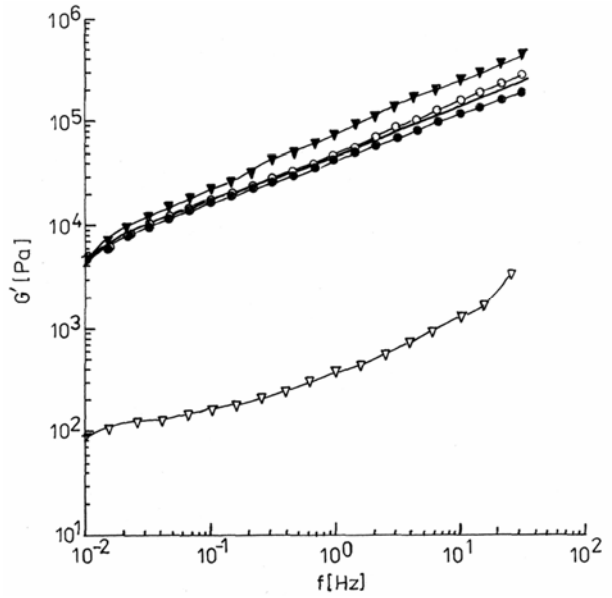
Rheological measurements are extensively used to study polymer melts. In addition to the viscosity, an oscillation measurement provides also a measurement of the materials elasticity, represented by the storage modulus G'. G" correlates with the flow behaviour in the mold and strongly influences the relaxation behavior and consequently orientation and frozen-in strains. Relative warpage effects and melt strength depend also on the elastic nature of the polymer melt and the resultant flow behaviour in the mold [24].

As observed from the obtained data (Fig. 2), the dynamic rheological properties have an apparent similar evolution for all studied binary coPA/EPDM blends. Dynamic viscosity, shear modulus (G') and loss modulus (G") have values situated between those of the main components of the blends. Because of the high content of the elastomer, the rheological curves are closer to that corresponding to EPDM component, at lower frequencies, the values being almost similar. The G' and η* values of coPA/EPDM blends has no apparent change due to the coPA content varying slightly from 5 to 15 wt%.

The differences appear for higher oscillating frequencies; this is associated with an increase of the free volume of the rubber component and therefore with an increase of the motion ability of the rubber molecules.

Fig. 2 a) shows the shear modulus G' vs. frequency for binary coPA/EPDM blends mixed at 50 rpm and 200 ^{o}C with different copolyamide loadings. The graph points out that the addition of coPA into EPDM matrix results in an increase of copolyamide stiffness. The greater the amount of coPA in the blend, the more significant is the effect. The increase in G' values is particularly relevant at higher frequencies.

In the presence of a compatiblizer at the interface, the rubber phase is more dispersed. The direct result of the interfacial coupling is an increase of the interfacial thickness [25]. The anhydride group of the maleated EP can react with the $–NH_2$ end groups or the –CO-NH- groups of the coPA, the intermolecular interaction leads to the formation of a copolymer between the elastomer and copolyamide, thus decreasing the mobility of the PA molecules. These interactions can stabilize the interface by reducing the coalescence and interfacial tension, resulting in enhancement of the interfacial viscosity and adhesion. This is the reason why coPA/EPDM blends containing EP-MA exhibits higher shear, loss modulus and dynamic viscosity than the binary blends.



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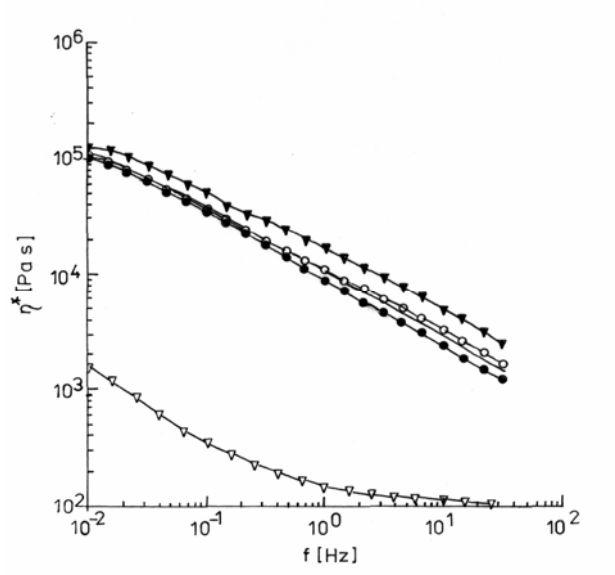

b

Fig. 2. *Variation of dynamic rheological properties: (a) shear modulus (G'); (b) dynamic viscosity (η*) function of frequency for coPA/EPDM blends EPDM; ─▽─ coPA; ─●─ 15co PA/85EPDM; ─○─ 10co PA/90EPDM ── 5coPA/95EPDM.*

As one can observe from Fig. 3 – 5, the experimental curves corresponding to the loss and storage moduli as well as dynamic viscosity of the uncompatibilized and compatibilized blends are higher from those calculated by the additivity rules. In case of the blends containing EP-MA, the differences between the calculated and experimental curves are more obvious than in the case of binary blends due to the interactions in the system.

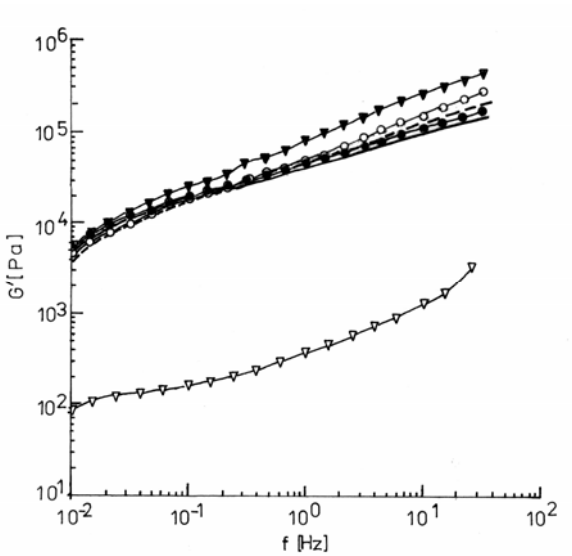

Fig. 3. Relationship between dynamic storage modulus G' and frequency for: ──▽── coPA; ──▼── EPDM; ──○── 5coPA/95EPDM exp ──── 5coPA/95EPDM calc ──●── 5co PA/95EPDM + EP - MA exp ─ ─ ─ 5coPA/95EPDM+ EP-MA calc.

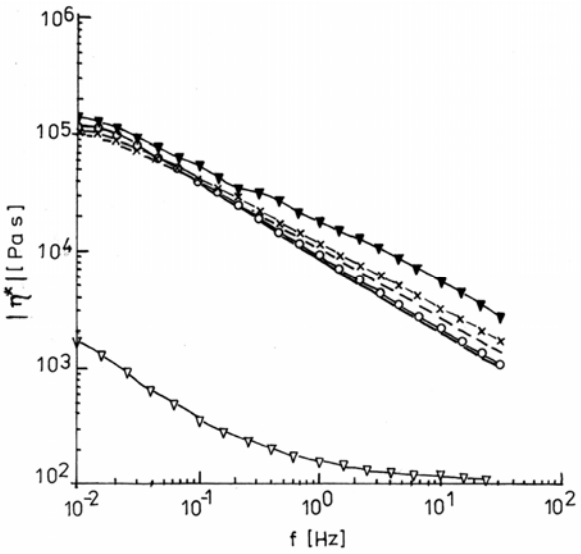

Fig. 4. Relationship between dynamic viscosity (η) and frequency for: ──▽── coPA; ──▼── EPDM; ──○── 5coPA/95EPDM exp ──── 5coPA/95EPDM calc ──x── 5co PA/95 EPDM + EP - MA exp ─ ─ ─ 5coPA/95EPDM+ EP-MA calc.*

As for the 15coPA/85EPDM blends, the values of loss modulus *G*" increases significantly with the increasing of frequency (Fig. 4a). On the other hand, compared with the pure copolyamide, the slopes of blends in the whole range of frequencies appear to be slightly increased. The reason

for these is due to the fact that the dynamic rheological behavior of blends is mainly dependent on EPDM matrix because is the continuous phase in the blends. The changes in the rheological behaviour of the blends in presence of the maleated EP, can be observed even for a very small content of coPA (5 wt%) mainly at higher frequencies of oscillation. The deviation in the viscosity curves is more evident, the reactions between the components and the EP-MA in the blends leading to decreasing of the molecular mobility, so the increasing of the dynamic viscosity.

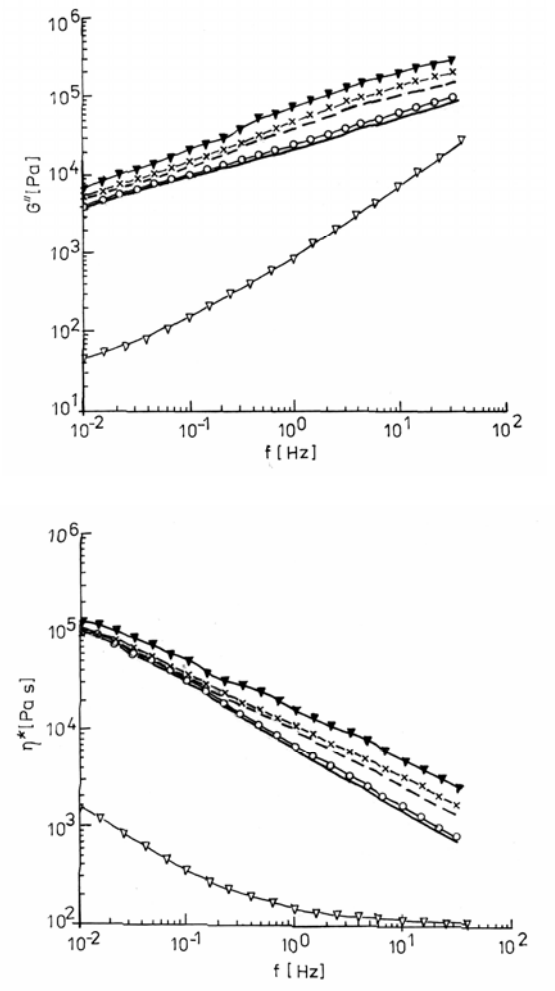

Fig. 5. (a) Loss modulus G'' and (b) dynamic viscosity as a function of frequency for --▽-- coPA; --▼-- EPDM; --○--15coPA/85EPDM exp ----15coPA/85EPDM calc --x-- 15coPA/85EPDM + EP-MA exp - - -15coPA/85EPDM + EP-MA calc.

4. Conclusions

Processing and rheological behaviour of some coPA/EPDM blends having various compositions and containing or not EP-MA as compatibilizing agent were studied by evaluating torque-time and dynamic rheological curves.

The obtained data showed the incompatibility of the binary coPA/EPDM blends due to the structural difference of the components. Better processability resulted because of high melt flow rate of coPA and increased mobility of elastomer macromolecules.

The rheological curves for coPA/EPDM blends showed essentially the same profile as the pure EPDM due to the low amount of copolyamide used in the blends. The differences appear for higher oscillating frequencies where an increase of the motion ability of the rubber molecules exists.

The presence of EP-MA in the blend leads to the enhancement of the interfacial viscosity and adhesion due to the intermolecular interaction between the functional groups of the blend components produced during processing, the experimental curves corresponding to the loss and storage moduli as well as dynamic viscosity for uncompatibilized and mainly compatibilized blends are higher from those calculated by the additivity rules.

Oscillatory measurements are quite useful in the studies of the processes that involve a structural change in the sample.

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