Dynamic Vulcanization and Thermoplastic Elastomers

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Summary: Ageing and electrical conductivity of thermoplastic elastomers (TPE) have been studied. It is shown that incorporation of LDPE leads to more stable structure of TPE during ageing. Electrical conductivity of TPE depends on blending condition.

Introduction

Much attention has been paid to the process of polymer materials production at which chemical reactions take place together with mechanical mixing of components[1]. This technology not only opens up new possibilities for well known products but also allows preparation of blends, which could not be economically made before. Among these processes the dynamic vulcanization is the best way of production of new type of polymer blends, namely thermoplastic elastomers (TPE) [2]. The dynamic vulcanization is the process of curing of the elastomers during its melt-mixing with molten plastic. The first stage of the dynamic vulcanization is the preparation of homogeneous mixture of components. The second stage is the crosslinking reaction of elastomer phase[3]. The conditions of mixing and chemical reaction determine the morphology of TPE and its properties. TPE is material consisting of continuous thermoplastic matrix where the micron scale particles of cured rubber are distributed uniformly. These materials have the classical elastomeric properties such as low tensile set and high ultimate elongation and the processing characteristics of thermoplastic resins. The thermoplastic processability of TPE requires the knowledge of the effect of filler's content and time of storage on physical properties of TPE in particular the electrical properties. Thus, the goal of this work is the investigation of ageing and electrical conductivity of TPE.

Experimental

Materials

Commercial isotactic PP: M_w=3.5x10^5, M_n=7.7x10^4, density 0.907 g/cm^3, melting point

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165 °C, degree of crystallinity 55 %.

Commercial LDPE: M_w=8.5x10^4, M_n=3.7x10^4, melting point 107 °C, degree of crystallinity 23 %. Ethylelene-propylene-diene copolymer (EPDM) manufactured by Enichem Elastomer: density 0.880 g/cm^3, propylene contents 32 %; Mooney viscosity 32 (125 °C), oil contents 50 %.

Carbon black "Ketjenblack" with diameter of particles around 300 nm was used as conductive filler.

Blend preparation

The blend of PP and EPDM has been dynamically vulcanized by using sulphur-accelerating system in co-rotating twin-screw extruder "Berstorff". The incorporation of carbon black has been carried out by a different method.

Test techniques

The TPE granules were processed to slabs by compression moulding at 190 °C, at pressure of 13 MPa and an exposure of 10 min. The slabs were cooled under pressure then the dumb-bell samples with dimensions 12 x 1.4 x 0.35 mm were cut.

The stress-strain behavior of specimens was determined at room temperature by means of "Instron-1122" at the constant crosshead speed 50 mm/min. A Du Pont DSC (Model 990) has bee used for calorimetric studies.

For the ageing experiments, TPE samples were prepared without addition of antioxidants or stabilizing agent.

Electrical measurements were performed using the four-probe technique.

Results and Discussion

a. Ageing

TPE is a blend consisting of a semicrystalline polymer PP. It undergoes a strong enhancement of mechanical properties and an increase of density during ageing at room temperature[4]. The effect of the temperature 100 °C and 130 °C and the time of TPE ageing has been published[5]. In this work TPE ageing has been studied at room temperature (Table 1).

It is seen that PP and LDPE crystallinity and Young modulus increase but ultimate elongation decreases. The properties of amorphous polymer EPDM do not change. The

decrease of amorphous phase content leads to enhancement of crystallinity and Young modulus of PP and LDPE. The change of quantity of intercrystalline voids reduces ultimate elongation. The same results are observed for blends: semicrystalline polymer/ semicrystalline polymer (PP/LDPE) and semicrystalline polymer/amorphous polymer (PP/EPDM). This effect has not been observed for ternary blend PP/LDPE/EPDM. Probably the structure of amorphous phase and the interface are changed resulting in a more stable structure of matrix during ageing.

Table 1. Change of crystallinity χ_a/χ_o, Young modulus E_a/E_o and ultimate elongation $\varepsilon_a/\varepsilon_o$ of PP, LDPE, EPDM and their blends, expressed as a ratio respective values after ageing for 6 months at room temperature (index a) and before ageing (index o).

System	χ_a/χ_o		E_a/E_o	$\varepsilon_a/\varepsilon_o$
	PP	LDPE		
PP	1.22	-	1.32	0.77
LDPE	-	1.18	1.42	1.02
EPDM	-	-	0.91	0.97
PP/LDPE=80/20	1.03	1.38	1.23	0.14
PP/EPDM=70/30	1.25	-	1.38	0.47
PP/LDPE/EPDM=28/2/70	1.05	1.02	1.07	0.98

b. Electrical conductivity of TPE

At present there is a great need in TPE materials with high electrical conductivity for different applications such as sensors, electromagnetic radiation shielding, switches etc. In this work TPE has been obtained with wide range of specific resistivity from insulators to conductors (Table 2).

The conductive network formation is explained in terms of percolation theory[6], when at certain critical content of conductive filler dramatic resistivity change occurs and so called percolation threshold is achieved (Fig. 1). In multiphase polymer blends, such as TPEs, conductive filler can be selectively localized in one of the phases or at the interface. If the filler is deposited just at the interface a dramatic reduction of resistivity occurs at a quite low amount of the filler. In addition to volume content and specific conductivity of the filler particles, the other important factors contributing to a formation of conductive network are as follows:

- polymer polarity and crystallinity, and
- the interfacial interaction between the individual filler particles and between filler and polymer.

Table 2. Effect of components mixing sequence on specific resistivity (carbon black volume fraction is 5 %).

Mixing sequence	Specific resistivity
	Ohm x cm
I	3.7×10^{13}
II	6.1×10^{15}
III	2.5

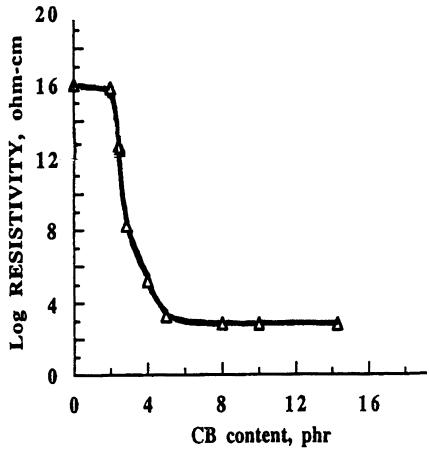

Figure 1: Resistivity vs. carbon black content.

In other words, the higher polarity of the polymer requires bigger filler content. We have shown that in semicrystalline polymers as PP and PE the percolation threshold is significantly lower as compared with the amorphous rubber (Table 3).

If the filler self-interaction dominates, the filler particles tend to form aggregates rather than conductive chains of particles. On the other hand, a good adhesion of a polymer to the filler results in an insulating layer around the particles and prevent the formation of current-conducting chains.

As seen in Table 3 the specific resistivity for TPE is significantly lower compared to that for the individual polymers (PP, PE and EPDM) at the same content of carbon black. This may be explained so that carbon black content being 10 volume % is below the percolation threshold for homopolymers and above it for TPE. Elongation at break of homopolymers is found to decrease with the increase of volume fraction of carbon

black because of reinforcing effect.

It should be stressed that production of TPEs with high conductivity and mechanical properties is possible under special conditions of blending. The filler should be distributed in both phases, preventing formation of conductive chains at the interface.

Table. 3. Percolation threshold and specific resistivity of different polymer system (carbon black volume fraction is 10 %).

N	Polymer system	Degree of crystallinity	Content filler at percolation threshold	Specific resistivity
		%	vol %	Ohm x cm
1.	EPDM	0	50	3.8×10^7
2.	PP	60	20	5.8×10^4
3.	LDPE	20	32	9.0×10^5
4.	HDPE	70	15	6.2×10^4
5.	TPE	-	2	2.5

Conclusions

It has been shown that incorporation of LDPE prevents recrystallization PP and leads to stable structure of TPE during ageing.

The electrical conductivity of carbon black filled TPE is determined by the components mixing sequence. There are two types of heterogeneous distributions of carbon black particles in filled polymer blends. One is almost predominantly distributed in one phase of a blend and the other is distributed mainly at the interface of two polymers.

References

[1] E. V. Prut, A. N. Zelenetskii, *Russian Chem. Rev.* **2001** *70,* (in press).

[2] A. J. Coran, R. P. Patel, *in "Polypropylene: Structure, Blends and Composites"V.2, Ch.6 (ed. J. Karger-Kocsic), Chapman and Hall, London.* p. 162, (1995).

[3] E. V. Prut, N. A. Erina, *SPE ANTEC, Tech. Papers.* p. 3310 (2000).

[4] L. C. E. Struik, *Plast. Rubber Process* **1982,** *2,* 41.

[5] E. V. Prut, N. A. Erina, L. V. Kompaniets, *Proceeding of ACS. Polymeicr Materials: Science and Engineering, Fall Meeting, August 23-27, Boston, Massachusetts,* **1998,** *79,* 106.

[6] F. Lux, *J. Mater. Sci.,* **1993,** *28,* 285.