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Dynamic vulcanization of novel nanostructured polyamide 6/ fluoroelastomer thermoplastic elastomeric blends with special reference to morphology, physical properties and degree of vulcanization

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ABSTRACT

Dynamic vulcanization characteristics of fluoroelastomer during simultaneous mixing with a plastic, polyamide 6, for thermoplastic elastomeric compositions were analyzed in terms of induction time, scorch time, optimum cure and dynamic cure rate for the first time to understand their processing behavior. Also, a new derivative torque vs. time plot was proposed to gain insight into dynamic curing behavior of the rubber. Evolution of morphology and properties during different stages of mixing and dynamic vulcanization was captured. Size of the dispersed rubber phase decreased from ~450 to ~130 nm with increasing degree of cure and mixing time. Interestingly, it was revealed for the first time the role of injection molding in transforming the morphology and hence properties of such vulcanizates drastically. Nanometer-sized rubber particles (60–80 nm) were generated in thermoplastic vulcanizates (TPVs) after injection molding, which were clearly reflected from field emission scanning electron microscopy and atomic force microscopy and also theoretically predicted from the critical breakup law of viscoelastic droplets in a matrix. Significant improvement of tensile properties was recorded during dynamic vulcanization and also after injection molding of the samples. Tensile strength and Young's modulus of a TPV were 34.5 MPa and 200 MPa respectively as compared to 26.5 MPa and 92 MPa for the specimen before injection molding.

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1. Introduction

Thermoplastic vulcanizates (TPVs) from rubber–plastic blends have drawn immense attention and growing market in recent years because they contribute towards substantial economic advantages by replacing conventional plastic and rubber materials for various applications [1–4]. These materials exhibit hybrid behavior of thermoplastics and thermoset rubbers [5]. Two-phase structure generation is a prerequisite for TPVs, where the plastic component is the matrix to provide melt processability and crosslinked rubber particles are dispersed in the matrix. The major advantages that result from dynamic vulcanization are superior mechanical properties, minimized permanent set, more resistance to attack by

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fluids, enhanced high temperature utility, greater stability of the microstructure in the melt, higher melt strength, and more reliable thermoplastic productivity [6]. Over the last few years, numerous researchers have reported different TPVs from various rubbers and plastics [7–13]. However, it is well known that a limited number of rubber-plastic combinations produce technologically and commercially useful blends even after dynamic vulcanization. Also, all the earlier reports deal with TPVs, where the dimension of the dispersed rubber phase is in the micrometer range. Oderkerk and Groeninckx [14] have investigated the morphology development by dynamic vulcanization and reactive compatibilization of polyamide 6 (PA6)/ethylene-propylene-diene terpolymer (EPDM) blends. They found that PA6/EPDM TPVs containing high amount of the dispersed rubber phase showed good strain recovery and mechanical properties. Maiti et al. have reported the physicomechanical properties of gas phase EPDM (GEPDM)/Polypropylene (PP) TPVs with various crosslinking systems [15]. They







showed that GEPDM/PP system exhibits better behavior in terms of heat aging, processibility, crosslink density, morphology, and physical properties when compared to conventional EPDM/PP system [15]. Ellul et al. scrutinized the crosslink densities and phase morphologies of PP/EPDM TPVs [16]. The enhancement of crosslink density of EPDM with curative content was demonstrated by means of rise in viscosity, the increased swelling resistance, and dynamic modulus of TPVs. In addition, a narrow EPDM domain size distribution and increased number average ligament thickness of PP were obtained with increase in crosslink density [16]. Chung and Coran explored phase morphologies of various rubber-plastic blends during molten-state mixing, cold pressing, and compression molding [17]. They found that the viscosity and polarity match between rubber and plastic in the blends generate finer states of dispersion, especially during the early stages of mixing. In addition, they noticed that at intermediate weight percent of rubber, cocontinuous and laminar structures are frequently generated [17]. However, the current article describes nanostructured thermoplastic elastomeric blends and their dynamic vulcanization.

Static vulcanization characteristics (uncrosslinked rubber is converted into crosslinked rubber by the process of vulcanization with addition of suitable curatives in a compression process) of various rubbers have been widely reported in the literature [18–21]. It is worth mentioning that there is no report in the literature on dynamic rheocurve analysis which represents the dynamic vulcanization behavior of the rubber during simultaneous mixing with plastic in TPVs. Also, evolution of an in-depth morphology and properties during different stages of dynamic vulcanization in nanostructured TPVs is still lacking.

In our recent publication, we have reported an effective strategy for the preparation of novel nanostructured thermoplastic elastomer blends from polyamide 6 (PA6) and fluoroelastomer (FKM) by optimizing the processing conditions [22]. Importance of injection molding in producing the nanostructured thermoplastic elastomeric blends has been highlighted. We report here development of the morphology and properties of these novel nanostructured PA6/FKM TPEs during dynamic vulcanization using various crosslinking systems. For the first time in literature, dynamic vulcanization of rubber (FKM) during mixing with plastic (PA6) was studied in terms of induction time, scorch time, optimum cure, delta torque, dynamic cure rate and derivative torque (with respect to time). Structure-property relationship at different stages of dynamic vulcanization has been described. The role of injection molding in transforming the morphology and hence properties of these vulcanizates drastically has been highlighted for the first time. The results have been analyzed by using a theoretical model.

2. Experimental

2.1. Materials

Polyamide 6 (tradename Akulon, f136) having viscosity number 245 cm³/g, density 1.13 g/cc, melting point 220 °C was supplied by DSM, Netherland. Fluoroelastomer A (a copolymer of vinylidene fluoride (VF2) and hexafluoropropylene (HFP) having density 1.82 g/cc at 25 °C, 66% F, Mooney Viscosity, ML ₁₊₁₀ at 121 °C = 20) abbreviated as FKM was procured from DuPont Dow Elastomers, Geneva, Switzerland. Hexamethylene diamine carbamate (HMDC), DIAK #1 was supplied by DuPont, India. Magnesium oxide and calcium hydroxide were obtained from standard sources.

2.2. Preparation of TPVs

PA6 granules were dried in a vacuum oven at 100 $^{\circ}$ C for 24 h before blending. The blends were compounded in batches of 50 g

polymer in a Haake Rheocord internal mixer with roller type rotor. For the preparation of the nanostructured blends, blending was allowed to proceed for 7 min at a temperature of 240 °C and 100 rpm rotor speed. After complete mixing in the internal mixer, the resulting blends were quickly removed and passed through a two-roll mill having close nip-gap at room temperature to make sheets and were cut into small pieces.

It was shown in our recent communication that the 40 PA6/60 FKM blend composition showed best thermoplastic elastomeric properties among the various compositions [22]. Therefore, this particular composition (P_4) was subjected to dynamic vulcanization using the following curing systems: such as, (1) HMDC and (2) mixed cured system (magnesium oxide, calcium hydroxide and HMDC). Formulations are given in Table 1.

The best dynamically vulcanized system at optimum level of curative concentration with respect to processability and physical properties was selected. Furthermore, using the above optimized curative concentration, other unvulcanized blend compositions were also subjected to dynamic vulcanization (see Table 1).

In addition, 40 PA6/60 FKM (P₄) blend composition was mixed in a Haake Rheocord at four different mixing times with vulcanizing agents (at optimized curative concentration, P₄MD2) and without vulcanizing agent in order to understand the morphology and properties developed during different stages of mixing and dynamic vulcanization (discussed in detail in the forthcoming section).

2.3. Molding of thermoplastic elastomers and vulcanizates

Test specimens (1–1.5 mm thick) were prepared by means of micro-injection molding machine (Haake MiniJet II) at 260 °C cylinder temperature and 60 °C mold temperature. Injection pressure and holding pressure were 800 bar and 400 bar respectively. The injection and holding times were 5 s each.

2.4. Characterization

2.4.1. Analysis of dynamic rheocurve

Dynamic vulcanization behavior of FKM was analyzed from torque—time plots which were extracted from Haake rheocurve at 240 °C and 100 rpm rotor speed. Haake Rheocord internal mixer is a useful tool in monitoring the mixing characteristic of polymer compounds by recording the torque value. Here, the rheographs were corrected based on the mixing time after the addition of rubber in the internal mixer. The important parameters extracted from Haake rheocurve are induction time ($t_{0.1}$), scorch time ($t_{0.2}$), minimum torque (M_L), maximum torque (M_H), delta torque between maximum and minimum values (ΔM), torque at optimum dynamic cure, time for optimum dynamic cure (t_{90}) and dynamic cure rate (DCR). It is well known that dynamic cure of rubber is very fast when compared to static curing. Based on this concept, $t_{0.1}$ was

| Table 1 | | | | |
|-------------|----------|-----|---------------|--------|
| Formulation | of mixes | and | vulcanization | recipe |

| System | Var par | Variation of curative concentration at a particular rubber—plastic blend ratio | | | | Optimized curative concentration at different blend ratios. | |
|------------|----------------|--|--------------------|--------------------|--------------------|---|--------------------|
| | P ₄ | P ₄ D | P ₄ MD1 | P ₄ MD2 | P ₄ MD3 | P ₅ MD2 | P ₆ MD2 |
| PA 6 | 40 | 40 (0.51) ^a | 40 | 40 | 40 | 50 (0.61) | 60 (0.71) |
| FKM | 60 | 60 (0.49) | 60 | 60 | 60 | 50 (0.39) | 40 (0.29) |
| MgO | _ | _ | 0.75 | 0.75 | 0.75 | 0.75 | 0.75 |
| $Ca(OH)_2$ | _ | _ | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| HMDC | - | 1 | 0.5 | 1 | 1.5 | 1 | 1 |

^a Volume fraction of the component in the blend.

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