

Effect of Cross-linking Systems on the Thermal Behaviour of Nylon copolymer (PA6,66) and Ethylene-Propylene-Diene (EPDM) Rubber Blends and their Kinetic Analysis

Cibi Komalan*, K E George**, S Thomas***, K T Varughese****

The thermal stability of nylon 6,66 and ethylene-propylene-diene rubber of dynamically vulcanised blends were studied by thermogravimetric analysis. The composition of nylon copolymer and EPDM was fixed at 70/30 ratio by weight. The blends were prepared by melt mixing in a Brabender Plasticorder. Thermogravimetric analysis showed that the decomposition proceeds through a single step even though the blends are immiscible and the cross-linked blends were more thermally stable than uncross-linked blends. The kinetic parameter of the degradation process is also studied.

1.0 INTRODUCTION

The thermal behaviour of polymers is of much importance as a tool in material characterisation. Fabrication of a variety of articles and their end uses needs a detailed understanding of thermal degradation of polymers. Thermal properties are relevant to the potential use of polymeric materials in many consumer-oriented applications. Polymer blending is a useful technique for designing materials with a wide variety of properties. An important commercial advantage is that polymer blends offer a way to produce new materials by using already existing polymers, which thus reduces development costs. Dynamic vulcanisation is the process of vulcanising an elastomer during its melt mixing with a molten plastic. As a result of this, new thermoplastic elastomers (TPEs) which have many properties as good as or even better than those of elastomeric polymers are obtained. Several articles [1-10] are available to prove the great impact of the thermal stability of polymers on blending.

2.0 EXPERIMENTAL INVESTIGATION

2.1 Materials used

Nylon copolymer (PA6,66) of melting point 148°C and density of 1.12 g/cc was supplied by SRF Ltd., Chennai, India. EPDM with E/P ratio 58/37.5% and DCPD content 4.5 % was obtained from DSM, the Netherlands. Sulphur (S) and dicumyl peroxide were used as cross-linking agents. Triallyl cyanurate (TAC) is used as a co-agent for the DCP vulcanisation. Tetramethyl thiuram disulphide (TMTD) and 2-mercaptobenzothiazole (MBT) were used as accelerators. These were supplied by RT Vanderbilt Company, Norwalk, USA. Zinc oxide (ZnO) and stearic acid were used as activators. These were obtained from BDH Chemicals Ltd., Mumbai. All these materials were rubber grade chemicals.

Prior to all the melt processing steps, polyamide copolymer was dried in a vacuum oven at 80°C for 24 hours.

*S N M College, Maliankara, Kerala 683 513, INDIA

**Department of PS&RT, Cochin University of Science and Technology, Cochin 682 022, Kerala, INDIA

***School of Chemical Science, M.G University, Kottayam 686 560, Kerala, INDIA

****Central Power Research Institute, Bengaluru-560 080, Karnataka, INDIA.

2.2 Sample preparation

Cross-linking was carried out with sulphur (S), dicumyl peroxide (DCP), and a mixture of S and DCP (SD). The mixing temperature and rotor speed used were 180°C and 80 rpm respectively. Nylon was melted for 2 minutes and then masticated EPDM was added. After five minutes of mixing, curatives were added followed by the addition of sulphur at the 8th minute. Mixing was continued for 7 minutes after the last ingredient was added. The batch was dumped, cut into small pieces, and remixed for an additional 3 minutes to ensure homogeneity.

In the case of peroxide curing, nylon and EPDM was melt mixed for 4 minutes. After 4 minutes of mixing, the co-agent TAC was added followed by peroxide. The mixing was continued for another 5 minutes to complete the dynamic vulcanisation process. The formulations used are shown in Table 1.

TABLE 1 COMPOSITIONS AND CODES OF THE SAMPLES USED				
Ingredients	Designation of blends			
	N ₇₀	N ₇₀ S	N ₇₀ D	N ₇₀ SD
Nylon	70	70	70	70
EPDM	30	30	30	30
ZnO	—	1.5	—	1.5
Stearic acid	—	0.3	0.3	0.3
TMTD	—	0.15	—	0.15
MBT	—	0.07	—	0.07
Sulphur	—	0.3	—	0.3
DCP	—	—	0.3	0.6
TAC	—	—	0.6	1.2

2.3 Thermogravimetric analysis

The thermal degradation studies of the blends were carried out in TGA analyser (Perkin-Elmer). The samples (2.0±0.2mg) were degraded under a nitrogen flow (30cm³min⁻¹) in a thermobalance under dynamic conditions at a heating rate of 20°C min⁻¹. The samples were scanned from 28°C room temperature to 600°C.

3.0 RESULTS AND DISCUSSIONS

Polymers are useful in certain ranges of temperature—a low temperature limit below which they are brittle and a high temperature limit above which they soften, degrade and ultimately decompose. The main objective of the present investigation is to determine the thermal degradation behaviour of dynamically vulcanised polymer blends.

The dynamic vulcanisation of rubber generally provides a significant improvement in the degradation temperature since more energy is required to break the bonds formed during vulcanisation. Figs. 1 and 2 show the thermograms and derivative thermograms of dynamically cross-linked systems using various cross-linking agents. Both the initial decomposition temperature (T_{onset}) and the degradation temperature corresponding to the two weight losses (T_{max}) show increase upon vulcanisation. The data obtained from the thermograms and derivative thermograms are presented in Table 2.

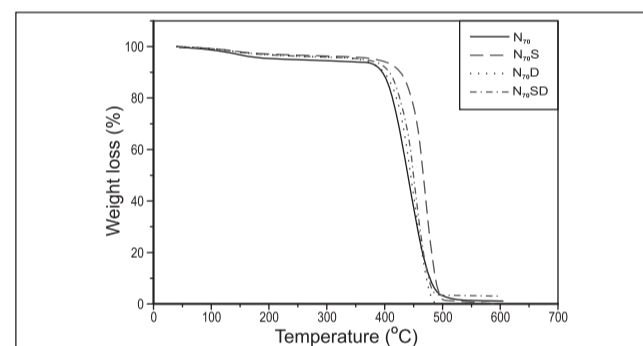


FIG. 1 THERMOGRAMS OF DYNAMICALLY VULCANISED N₇₀ PA/EPDM BLENDS WITH DIFFERENT CROSS-LINKING SYSTEMS

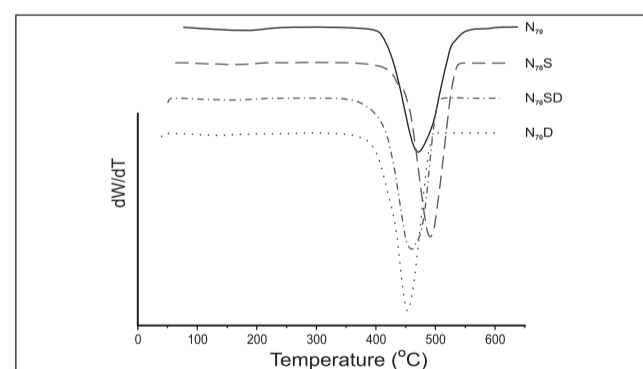


FIG. 2 DERIVATIVE THERMOGRAMS OF DYNAMICALLY VULCANISED N₇₀ PA/EPDM BLENDS WITH DIFFERENT CROSS-LINKING SYSTEMS

Sample	T _{onset}	T ₅₀	Weight loss at 400°C (%)	Weight loss at 450°C (%)	DTG Peak values (°C)
N ₇₀	372	439	12.2	62.9	440
N ₇₀ S	382	466	5.9	23.3	471
N ₇₀ D	370	444	10.5	58	448
N ₇₀ DS	375	449	8	49.9	453

Among the vulcanised blends, the initial decomposition temperature is highest for the sulphur cross-linked system. DCP cross-linked system has got lowest values. This is because using peroxide as a curative might cause the degradation of nylon and result in the poor thermal stability of blend system. This type of results has been reported by Huang et al. [11]. Mixed vulcanising system has got intermediate thermal stability as expected. The degradation temperature follows the order, N₇₀S > N₇₀DS > N₇₀D. The improvement in the thermal stability as a result of dynamic vulcanisation can be explained on the basis of the type of cross-links formed and the cross-link density. The sulphur vulcanised system produces mono and polysulphide linkages, the peroxide system gives rise to C-C linkages, the mixed system produces both polysulphide linkage and C-C linkages. The second factor to be considered is the cross-link density. The sulphur cross-linked system shows the highest cross-link density (4.2x10⁴mol/g). The increased cross-link density, in turn, increases the number of bonds that has to be broken during the degradation process. This naturally increases the thermal stability of the blends. The temperature corresponding to 50% weight loss (T₅₀) also increases as a result of dynamic vulcanisation.

3.1 Kinetic analysis of thermal decomposition

In the present study, kinetic parameters for the thermal decomposition of the nylon 6,66 and

EPDM cross-linked blends have been determined from the TG curves by applying an analytical method proposed by Coats- Redfern [12].

In the Coats-Redfern method, activation energy is obtained from the equation:

$$\ln \left[\frac{g(\alpha)}{T^2} \right] = \ln \left\{ \frac{AR}{\phi E} \right\} (1 - 2RT/E) - \frac{E}{RT} \quad (1)$$

Where, α is the decomposed fraction at any temperature

ϕ is the heating rate

E is the activation energy for decomposition.

Activation energy (E) can be calculated from the slope of the curve and from the intercept value, pre-exponential factor (A) can be calculated. The order of decomposition reaction was determined from the best linear fit of the kinetic curve that gives the maximum correlation coefficient.

Numerous mathematical equations are suggested by various authors based on the integral method to determine the kinetic parameter of thermal decomposition. All the thermogravimetric data were analysed using nine mathematical equations proposed by Satara [13] and the effects of cross-linking on kinetic parameters were studied. The form of $g(\alpha)$ which best represents the experimental data gives the proper mechanism. The nine possible equations and the rate controlling process in each case are given in Table 3.

From the calculations, we found that the Mampel equation fits well in the case of various unmodified and modified nylon copolymer/EPDM cross-linked blends. This shows random nucleation as the mechanism of degradation in the rate controlling process. The kinetic parameters for the main stage thermal decomposition of various nylon copolymer/EPDM blends are given in Table 3.

TABLE 3			
EFFECT OF CROSS-LINKING SYSTEMS ON KINETIC PARAMETERS FOR THE THERMAL DECOMPOSITION OF VARIOUS 70/30 NYLON COPOLYMER/EPDM BLENDS			
Sample	Activation energy (J/mol) (E)	Arrhenius parameter (s ⁻¹) (A)	Entropy of activation, ΔS (J/deg/mol)
N ₇₀	135.3	5.12 x 10 ²	-205.3
N ₇₀ S	234.8	4.13 x 10 ⁵	-144.9
N ₇₀ D	164.2	2.8 x 10 ³	-186.1
N ₇₀ SD	164.2	2.83 x 10 ³	-186.1

In the case of cross-linked systems (Table 3), the activation energy increases as a result of cross-linking. Among the different cross-linking systems used, sulphur cross-linked system showed higher activation energy values. This can be attributed to the stable bonds formed during vulcanisation. This increase in degradation temperature of vulcanised blends is due to the improved interfacial adhesion between the two components as a result of cross-linking, which has a direct influence on the thermal properties. The entropy of activation is found to be negative and the values do not follow any regular trend in the blend systems studied.

4.0 CONCLUSIONS

Thermal degradation of dynamically vulcanised nylon copolymer/EPDM blends was studied using thermogravimetry. A single degradation peak was obtained for all the blends. Dynamic vulcanisation using sulphur and DCP are found to provide improvement in the decomposition temperature. Sulphur cured system showed higher decomposition temperature. Attempts have also been made to correlate the thermal behaviour of the dynamically cross-linked

systems with the type of the cross-links and the cross-link density. The kinetic study of degradation shows random nucleation as the mechanism of degradation in the rate controlling process.

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