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Co-Continuous Structures in Melt-Mixed PA(6,66) / EPDM Blends

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Abstract

Co-continuous structures can be found as intermediate stages during the initial stage of morphology development and during phase inversion process in blends in which the components finally forming the dispersed phasecand the matrix in the early mixing stages. Stable co-continuous morphologies can be created using suitable processing conditions. The interfacial tension and melt yield stress of one or both components of the blends plays an important role for the stability of the co-continuous structures. A lower interfacial tension leads to broader composition ranges of co-continuous structures.

Key words: Polymer blends, Co-continuous structure, Morphology

I.INTRODUCTION

For the achievement of advantageous material performance, blending of two immiscible polymers is an important technique. By blending a variety of properties can be significantly improved. Blending may also be used to lower the cost of an expensive material by mixing it with a less expensive one by maintaining the properties critical to the application. Thermoplastic elasomers (TPEs) obtained from plastic-rubber blends combine the excellent processability characteristic of thermoplastics and the physical properties of elastomers. Most of the commercial polymer blends are immiscible.The physical, mechanical and rheological properties of immiscible blends depend not only on the constituent polymers but also on the morphologies of the blends [1]. The morphology development depends on the rheological properties of the blend components, interfacial tension, blend compositions and processing conditions [2]. The structure obtained after mixing of immiscible polymers can be categorized into four basic morphology types.

- Matrix-dispersed particle structures
- Matrix – fiber structures
- Lamellar structures
- Co-continuous structures

Most commercial polymer blends have matrix-dispersed particle structure. Here is an increasing interest in co-continuous blends because this morphology type can offer better combination of the component properties than from dispersed type structures [3, 4]. Co-continuous structure gives the maximum contribution to the mechanical modulus from each component simultaneously [4, 5]. Synergistic effects on impact properties have also been shown in the literature [6,7, 8]. Examples of commercial co-continuous blends are PP/PE/EPR blends [9,10], PA6/PPE blends[11,12] and PA6/ABS [13,14] .

Regarding the formation of the co-continuous structures it is still not clear under what conditions and by which mechanism a co-continuous structure may be formed and whether a co-continuous structure can be stable or if it is simply an unstable intermediate that eventually transforms into a dispersed morphology.The final state of dispersion is important to the end use properties of a polymer blend. The component that forms the matrix generally dominated the properties of the blend. Thus, in co-continuous blends, both components contribute more equally to the properties.

II. EXPERIMENTAL

Materials

PA6,66 (nylon 6,66) of melting point 148^{0}C and density of 1.12 g/cc,was supplied by SRF Ltd. (Madras, India). EPDM (KELTAN 720) with E/P ratio 58% to 37.5% and DCPD content 4.5 % was obtained from DSM (Netherlands).

Preparation of the blends

PA6,66 was preheated in vacuum oven at 80^{0}C for 24 hrs to remove water. After keeping in vacuum dedicator for 2 hrs, the blending was performed in a Haake Rheocord 90 mixer. PA6,66 was charged into the melting chamber and melted for 2 minutes at 180^{0}C at a rotor speed of 80 rpm. Then EPDM was added. The blending was continued for 6 more minutes. Total mixing time was fixed at 8 minutes to ensure homogeneity.

The blend was taken out and compression molded in a hydraulic press at 180^{0}C, and cold pressed to give samples for testing. The blend ratios are denoted by N_{90}, N_{80}, N_{70}, N_{60}, N_{50}, N_{40},N_{30}, N_{20}. The subscripts denote the weight percentage of PA6,66 in the blend.

Preparation of samples for morphology studies

For determination of sample morphology, small bars (approx.25.3mm by 9.7mm by 3.3 mm) of the samples were placed in liquid nitrogen for 5 minutes.The bars were then fractured by bending. In order to determine the state of dispersion

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and phase continuity, a selective dissolution of the dispersed phase is attempted. For this, from the cryogenically fractured blends, EPDM was preferentially extracted from PA6,66 rich blends using Xylene vapours (Soxhlet extraction) at 150^0C for 13 hrs and PA6,66 from EPDM rich blends using Formic acid by immersing the fractured edge in formic acid for 9 hrs at room temperature. The samples were dried in an air oven at 80^0C for 24 hrs. Each etched surface was sputter coated with Au/Pd alloy. At least five photographs were taken for each sample with Scanning electron microscope (SEM, 5400,JEOL, Tokyo, Japan).

Calculation of Co-continuity by Extraction method

Extraction method is an easy and viable way to check for co-continuity when the components are soluble in specific solvents. Solvents were carefully chosen for the complete dissolution of one of the components without affecting the other component.

Uniform length of the samples were dried in vacuum oven at 80^0C for 24 hrs and then kept in vacuum dedicator for 2 hrs before weighing. The weighted out (2 to 5 g) samples were fully immersed in etchant at room temperature for 5 days. This is sufficient for the complete removal of the soluble fraction. Each polymer sample must immersed in different bottles. PA6,66 phase has been extracted from the blends with formic acid and EPDM phase with boiling Xylene. Then the remains were taken out of the solvents after 5 days, dried at 80^0C in vacuum oven and weighed carefully. A blend is considered fully co-continuous if 100% of one component can be extracted and the remaining piece is still self-supporting and its mass is approximately that in the original blend. Examples for quantification of the co-continuity degree by extraction experiments are given by Lyngaae-Jorgensen et al.[15,16,17] and Favis et al.[18,19,20].

$$\text{Continuity index} = \frac{\text{weight of initial component} - \text{weight after extraction}}{\text{initial weight of the component}}$$

It is also possible to estimate the continuity of the phases from these tests. The continuity of one phase can be defined as the fraction of the polymer that belongs to a continuous phase. For a polymer A, this parameter is evaluated from the following expression:

$$\%\ \text{Continuity of A} = \frac{m_{initil} - m_{finial}}{W(A)\ x\ m_{initial}}$$

Where W(A) is the weight fraction of A in the initial blend. When the percentage continuity of both components equals to 100%, the morphology of the blend is considered to be continuous.

Mechanical property testing

The dynamic mechanical properties of the blends were determined by using DMA-Model TAQ800.

III. RESULTS AND DISCUSSION

Co-continuous structures are complicated three-dimensional interpenetrating and intertwining structures. It is much more difficult to identify a co-continuous structure in a melt mixed blend.Solvent extraction results showed that the results are in good agreement with the morphology obtained from SEM observation (Figure: 1).

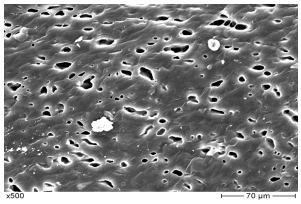

Figure 1(a) SEM photograph of solvent (Formic acid) extracted N20 blend

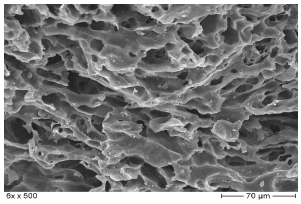

Figure 1(b) SEM photograph of solvent (Formic acid) extracted N30 blend

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Figure 1(c) SEM photograph of solvent (Boiling Xylene & Boiling Benzene) extracted N50 blend

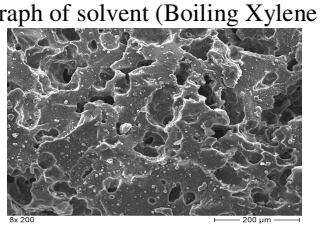

Figure 1(d) SEM photograph of solvent (Boiling Xylene) extracted N70 blend

Fig : 1 Scanning Electron Micrograph of PA6,66 /EPDM blends at a magnification of 500 times (a) N_{20},(b) N_{30}, (c) N_{50}, (d) N_{70}

The test gives results in the shorter time for macroscopic characterization so that it can be carried out in all blend samples. For the blends consisting of matrix with dispersed particles, etching of the matrix causes a complete dissolution of the blend material and a milky suspension is obtained. In the case of co-continuous structures neither of the solvents could cause complete dissolution of the blend. So a colloidal solution is obtained. From the PA6,66 rich blends ie N_{50}, N_{60}, N_{70}, N_{80}, N_{90} EPDM was extracted with boiling Xylene and from EPDM rich blends ie N_{20}, N_{30}, N_{40}, N_{50} PA6,66 phase is extracted using formic acid. In both cases a precipitate is obtained indicating the dissolution of the minor phase. N_{40}, N_{50}, N_{60} do not disintegrate completely showing onset percolation and co-continuity. Results of the dissolution test for the different blend series show the effectiveness of dissolution.

It is also possible to estimate the continuity of the phases from these tests. Results of disintegration tests of the different blend series shows the effectiveness of dissolution (Table1).

TABLE:1 Volume fraction of the different blend series after disintegration tests

Sample code	Co-continuity index of Nylon	Co-continuity index of EPDM	% Continuity
N_{20}	0.08	0.97	35.9
N_{30}	0.17	0.92	57.0
N_{40}	0.45	0.81	95.2
N_{50}	0.72	0.80	97.3
N_{60}	0.92	0.70	97.8
N_{70}	0.95	0.27	98.2
N_{80}	0.97	0.10	98.3
N_{90}	0.98	0.06	98.6

At 20% of PA6,66, the co-continuity index is nearly zero, which is confirmed from the scanning electron microscope. In N_{30} continuity increase considerably to a volume fraction of 0.17. Between N_{40} & N_{50} and N_{50} & N_{60} a semi-continuous morphology is observed (Figure:1). At N_{60} phase inversion take place and beyond which EPDM is seen to be dispersed in PA6,66 phase. From N_{60} the continuity of the phase increases gradually and reaches a volume fraction of 0.98 at N_{90}. Similar trend is observed when xylene is used as a solvent for EPDM phase. The samples containing PA6,66 & EPDM content greater than 60%, when etched with formic acid, a jelly like mass was obtained. The percentage continuity of the blends at different blend ratios are given in Figure: 2.

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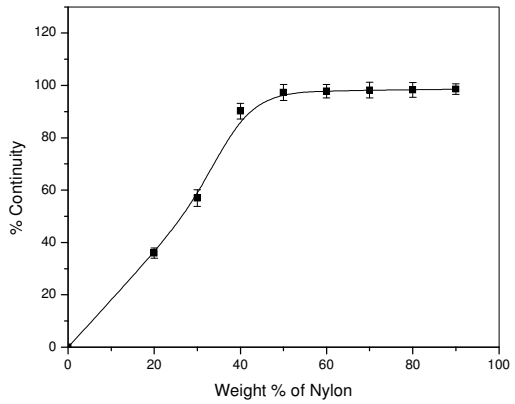

Figure :2 Effect of blend ratio on the continuity of blends

From the figure it is clear that above 40 weight % of PA6,66, the PA6,66 phase is continuous. So during extraction with formic acid dissolution of the PA6,66 will take place only up to 40 wt % and for rest of the compositions (50-90 wt%) colloidal and milky suspensions were obtained indicating the continuous nature of the PA6,66 matrix.

Mechanical properties

Dynamical mechanical analysis

Dynamical mechanical analysis (DMA) can be a useful method to distinguish between dispersed and co-continues structures. Figure: 3 represents the storage moduli (E') of PA6,66 /EPDM blends as a function of the temperature.

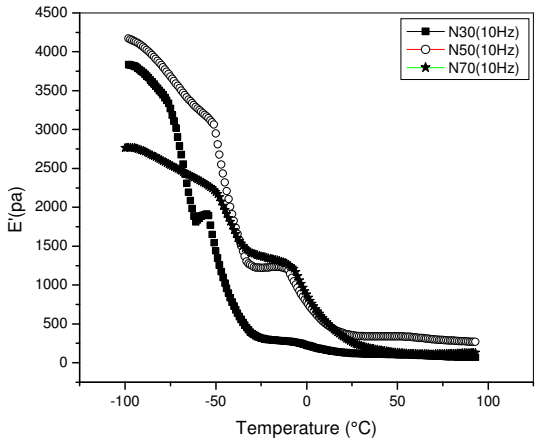

Figure: 3 Storage modulus of blends at different blend ratio

In co-continuous structures the storage modulus–temperature dependence reflects a greater contribution of both components, whereas in dispersed structures, the blend modulus is reflected by the matrix component. This is well revealed in the case of N_{50} blend ratio. The work of Groeninckx et al.[21] also explained this type of behavior. Significant changes in storage modulus and tan δ peak height (Figure: 4) were observed in the co-Continuous region.

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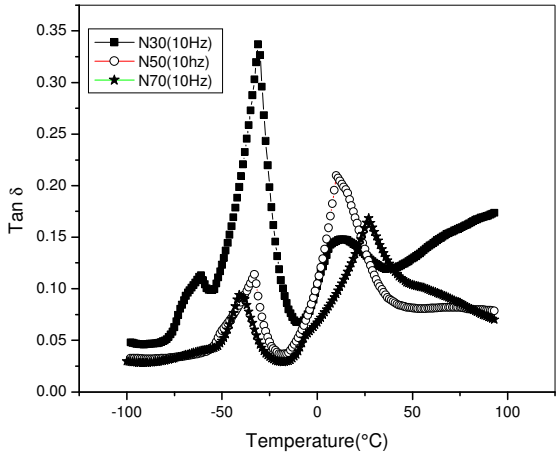

Figure :4 Tan δ Peak of the PA6,66 /EPDM blends at different blend ratio

DMA is also a sensitive tool to differentiate the co-continuous structure, which gives the level of coarseness. This effect was shown by N50 blends annealed under different annealing conditions.

IV. CONCLUSION

Co-continuous polymer blends is an interesting and challenging research topic. The structure offer promising opportunities for improving properties and creating tailor-made materials. Blends with co-continuous structures may combine the properties of both components in a favorable way. A co-continuous structure leads to the maximum contribution of the mechanical modulus from each component simultaneously. By using the extraction method one can find out the blend ratio where the co-continuity is formed. The concept of co-continuous structure generation via sheet formation shows growing evidence. However co-continuous structures seem to be inherently unstable during further processing, which is a limiting factor for their use.

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