

## Proposed reaction routes of Ethylene-vinyl acetate (EVA)/Thermoplastic Polyurethane (TPU) Blends

*Dr. Jagannath Biswas<sup>1</sup>*

*Md. Serajuddin Bhuiyan<sup>2</sup>*

<sup>1</sup> Associate Professor, Dept. of Textile Engineering, Green University of Bangladesh

<sup>2</sup> Professor, Dept. of Textile Engineering, Green University of Bangladesh

**Abstract:** Blends of ethylene-vinyl acetate (EVA) and thermoplastic polyurethane (TPU) were prepared and their interfacial compatibility was improved with maleic anhydride (MA) by melt blending method. A coarse EVA/TPU blended morphology was turned into finer morphology by MA addition, which was confirmed by scanning electron microscopy (SEM), melt rheology and mechanical behavior. The processing torque of the blends increased with the addition TPU in EVA. Further, this value increased sharply when MA is added in the presence of DCP. The sharp increment of torque indicates a chemical reaction occurs with maleic anhydride with the help of free radical generator species. A possible reaction mechanism is proposed from all experimental results. So a thermodynamically stable and compatible blend of EVA/TPU could be possible by introducing MA and DCP and all these findings are strongly supportive and in favor of the proposed reaction route.

**Keywords:** Thermoplastic Polyurethane; Morphology; Rheology; Free Radical.

### 1 Introduction

Homopolymers are polymers or polymer materials with a single homogeneous system, whereas copolymers and polymer blends are considered hetero-polymer systems. Copolymers consist of two or more polymer systems that chemically reacted during the polymerization process. Copolymer based resins may have unique properties compared to the simple homo-polymer systems. Polymer blends, alloys or interpenetrating polymer networks (IPN) consist of two or more polymer systems mechanically or physically intermixed, but retaining the two distinct polymer phases [1-3]. Polymer alloys or blends may have unique properties compared to the resin systems based on homopolymers.

Melt blending is a direct and economic way of producing multiphase new materials from different polymers compared to the solution blending or latex mixing. In general, Banbury mixers, mixing extruder, and twin-screw mixers are suitable for melt-mixing elastomer with plastics [4]. Melt-mixing avoids problems of contamination, solvent or water removal, etc. But making thermodynamically miscible and stable blends is a major concern for polymer scientists [5]. In most cases, addition of a third component in the blends brought more homogeneity in the admixture. These additives are technically termed as 'compatibilizers'. Block copolymers [6] and ionomers [7] are such type of compatibilizers for immiscible blends.

Ethylene-vinyl acetate (EVA) is a copolymer of ethylene and vinyl acetate (VAc), and possesses elastomeric property, which varies with comonomer compositions. These EVA thermoplastics are easy to process and could be blended with other thermoplastic or thermosetting resins by conventional melt-mixing procedure [8-12]. EVA plays a vital role in enhancing impact property of a brittle polymer [13]. Blends of EVA with polyethylene (PE) have found several applications as packaging films, sheets for automobile parts, electric

cable application, extruded foam etc. In footwear industry, EVA has a unique place due to its low cost, good transparency and low density, but it is poor in shrinking behavior upon compression [14, 15].

Thermoplastic polyurethanes (TPUs) are another class of polymers with properties covering from a high performance elastomer to tough thermoplastic. They have high tensile strength, abrasion and tear resistance, oil and solvent resistance, low temperature flexibility and wide versatility in chemical structures. TPU is a linear segmented block copolymer consists of alternating hard and soft segments [16, 17].

In this present work, blends of EVA and TPU were prepared by melt blending, using maleic anhydride (MA) as a reactive compatibilizer and dicumyl peroxide (DCP) as a thermo-sensitive initiator. In many reports on MA incorporated blends, several researchers argued that MA functions well with polymers which are polar in nature [21]. Recently, Park et al.[9] and Zhang et al.[18] are also reported that MA can effectively make compatibilized blends with non-polar polyolefins. But they cannot explain the reaction mechanism of good compatibility of their research. We believe that without establishing a suitable reaction route, this research will lead more time consuming and uncertainty. In our previous paper we mention all properties of this blends ignoring possible chemical reaction [17]. The possible interim reactions that evolved during blending the constituents with or without MA were postulated. In addition, this article describes the properties of the blends by incorporating TPU and MA with EVA. Thus, we extend the study and find a way of suitable reaction path of the blends in terms of morphology, rheology and mechanical properties (Shamim, 2022).

## **2 Experimental**

### **2.1 Materials**

The EVA copolymer with 28 % of vinyl acetate (VA) was purchased from Dupont, Welmingto DE, USA. Maleic anhydride (MA) was purchased from Shinyo Pure Chemical (Gunma, Japan) and used without further purification. Ester type thermoplastic polyurethane (TPU) was provided by Hosung Chemex Co., Korea. Dicumyl peroxide (DCP: 99 % purity) used as an initiator, was purchased from Aldrich (St. Louis, MO).

### **2.2 Blending and Sample Preparation**

EVA and TPU were dried prior to blend in a vacuum oven for 5 hours at 50 °C. Blends of EVA/TPU were mixed in the weight ratio of 100/0, 95/05, 90/10, 80/20, 70/30, 0/100 wt.%, using a counter rotor type of Brabender plasticoder (PL-2000) internal mixer, Germany. The mixing temperature and rotating velocity (rpm) are same for all specimens and the mixing condition is determined upon empirical results, at 190 °C, 30 rpm of rotor speed, and for 6 min of reaction time. Similarly, EVA/TPU blends containing 0.5 and 1 phr of MA with 0.3 phr of DCP are also prepared by one-shot process.

The pure polymers and blended materials were compression molded into a dumbbell bar according to ASTM D412 using a Carver laboratory hot press at  $2 \times 10^4$  Pa and 190°C.

### **2.3 Measurements**

Morphology of the cryogenically fractured surfaces was examined by scanning electron microscopy (SEM: Hitachi S-4300) in a magnification of 3000. The fractured surface of the specimens was coated with gold prior to the SEM examination.

The tensile property was measured with a universal testing machine UTM (Instron 4465) at room temperature at 30 % humidity according to ASTM D412 and the tensile strength, modulus, and elongation at break were calculated.

Processing melt viscosity torque of the blends was obtained during sample blend preparation and the raw data was plotted with time.

The proposed reaction mechanism was ascertained from fundamental chemical theory and literature survey [20].

## 3 Results and Discussion

### 3.1 Morphology

The morphology of the EVA/TPU blends with and without maleic anhydride was represented in Figure 1 and the inset number in each Figure indicates TPU content in the blends. The SEM photographs in Fig. 1(I) are the blends without MA, which show a distinct two-phase morphology. Comparatively hard TPU phase was embedded in EVA matrix and is the indication of incompatible coarse morphology for all proportions of TPU.

The effect of the addition of maleic anhydride (MA) into the EVA/TPU system is also studied in the presence of dicumyl peroxide (DCP). Figures 1(II) and 1(III) represent the SEM photographs of EVA/TPU blend in the presence of 0.5, 1 phr of MA, respectively. As seen in these figures, the incorporation of MA significantly improves the phase morphology of the blend compared to the blends without MA. The existence of two-phase discrete morphology is difficult to distinguish by the addition of MA. By increasing the amount of MA from 0.5 to 1 phr, the morphology improvement is not very discernible.

### 3.2 Proposed Reaction Path

Figure 2 indicates the possible reactions between blend components during the melt-mixing. For convenience we categorize these reactions in three different steps: (1) free radical generation step, (2) hydrogen abstraction from  $\text{-CH}_2\text{-}$  linkage of EVA and TPU and (3) combinations of the reactive species.

In step one, DCP is dissociated and generate free radicals by heat and mechanical shearing in the mixer. The peroxide radical is subsequently creating the grafting site on EVA for maleic anhydride. We overlooked some probable intermediate stages like mutual termination of EVA macroradicals ( $\text{EVA}\cdot$ ) and TPU macroradicals ( $\text{TPU}\cdot$ ) that may form during grafting reaction between MA and EVA or TPU. A typical polyurethane structure has been shown with one hard and soft segment in order to describe hydrogen abstraction mechanism in step two. Hydrogen of TPU in soft segment is more vulnerable to attack than that in hard segment. So, by abstracting one hydrogen radical ( $\text{H}\cdot$ ) by peroxide free radical, one of the carbon atom in soft segment become a very reactive ( $\text{C}\cdot$ ) species. Finally, in step three, maleanated EVA and TPU are chemically bonded at their respective reactive site. As we can see in the later section, due to this chemical bonding, unusual torque increment is observed in all maleanated blends of EVA/TPU. Cassu et al.[19] proposed a mechanism, where compatibility study of polystyrene and polyurethane blends was verified using poly(styrene-co-maleic anhydride) as reactive stabilizer. They reported torque versus time curve, which showed high value for all reactive blends, and proposed the occurrence of a chemical reaction while mixing. The same behavior is occurred for our system; the rheological behavior in term of torque is too high and it may happen due to the interchain cross-linking reaction by MA in the presence of DCP. Thus, the reaction step we stated here presumably be true for our research. These routes are also satisfying some fundamental chemical reactions.

### 3.3 Mechanical Properties

Figure 3 represents the stress-strain (S-S) curve of neat EVA, TPU, and EVA/TPU (80/20) blends with and without MA. From the S-S curve it could easily visualize the highest and lowest elongation of neat EVA and TPU respectively, than their blends. In addition, TPU is a very tough material with higher stress on tensile loading characteristics than neat EVA or their blends. The tensile stress of blend increased significantly by the

incorporation of MA. But higher MA content decreases tensile stress, which indicates the plasticizing effect of MA.

### 3.4 Torque Behavior

Figure 4 represents the torque values for the neat EVA, TPU and EVA/TPU(80/20) blend with 0, 0.5, and 1 phr of MA during processing at 190 °C as a function of time in minutes. Sometimes, melt rheology and reactive nature of the polymeric blends could be ascertained from the processing torque [22]. As seen in this figure, the torque of neat EVA is very low and that is very high for TPU. The processing torque of the blends increased with the addition TPU in EVA. Further, this value increased sharply when MA is added in the presence of DCP. The sharp increment of torque indicates a chemical reaction occurs with maleic anhydride with the help of free radical generator species. So, MA is acting as a reactive compatibilizer and it result in this high torque. The proposed reaction mechanism, described in earlier section, between EVA and TPU via maleic anhydride is also attributable for this high torque.

## 4 Conclusion

SEM photographs show that non-maleated blends of EVA/TPU are incompatible but they are compatible in the presence of MA and show a good dispersion of TPU in EVA matrix. We also proposed here a inter-chain EVA and TPU reaction path for describing some unexpected properties of the blends. The processing torque of the blends increased with the addition TPU in EVA. Further, this value increased sharply when MA is added in the presence of DCP. The sharp increment of torque indicates a chemical reaction occurs with maleic anhydride with the help of free radical generator species. So, a thermodynamically stable and compatible blend of EVA/TPU could be possible by introducing MA and DCP. Our assumed reaction routes are also obeyed most of the fundamental chemical reactions. So, all these findings are strongly supportive and in favor of the proposed reaction route and we may conclude that our reaction sequence is true.

*Figure Caption:*

Figure 1. Comparison of SEM photographs on EVA/TPU blends. (I) without MA, (II) with 0.5 Phr MA, and (III) with 1 Phr MA ( inset number indicates TPU content in each Figure).

Figure 2. Possible reactions of MA with EVA and TPU in presence of a free radical.

Figure 3. S-S curve of the neat EVA, TPU, and EVA/TPU (80/20) blend.

Figure 4. The torque of the neat EVA, TPU, and EVA/TPU (80/20) blend as a function of MA.

EVA/TPU blends I

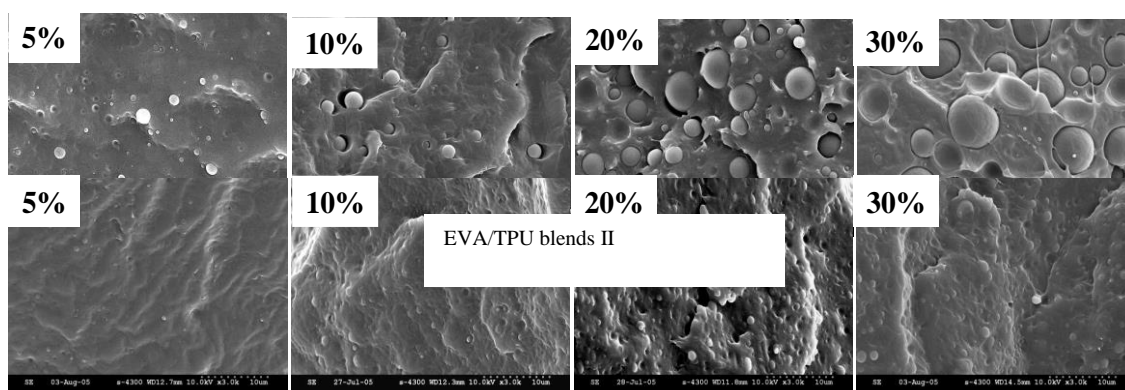
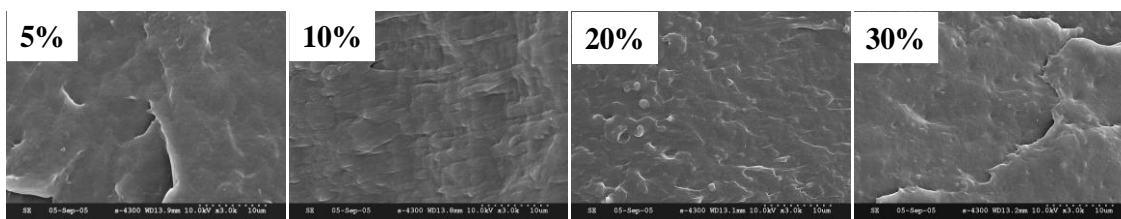
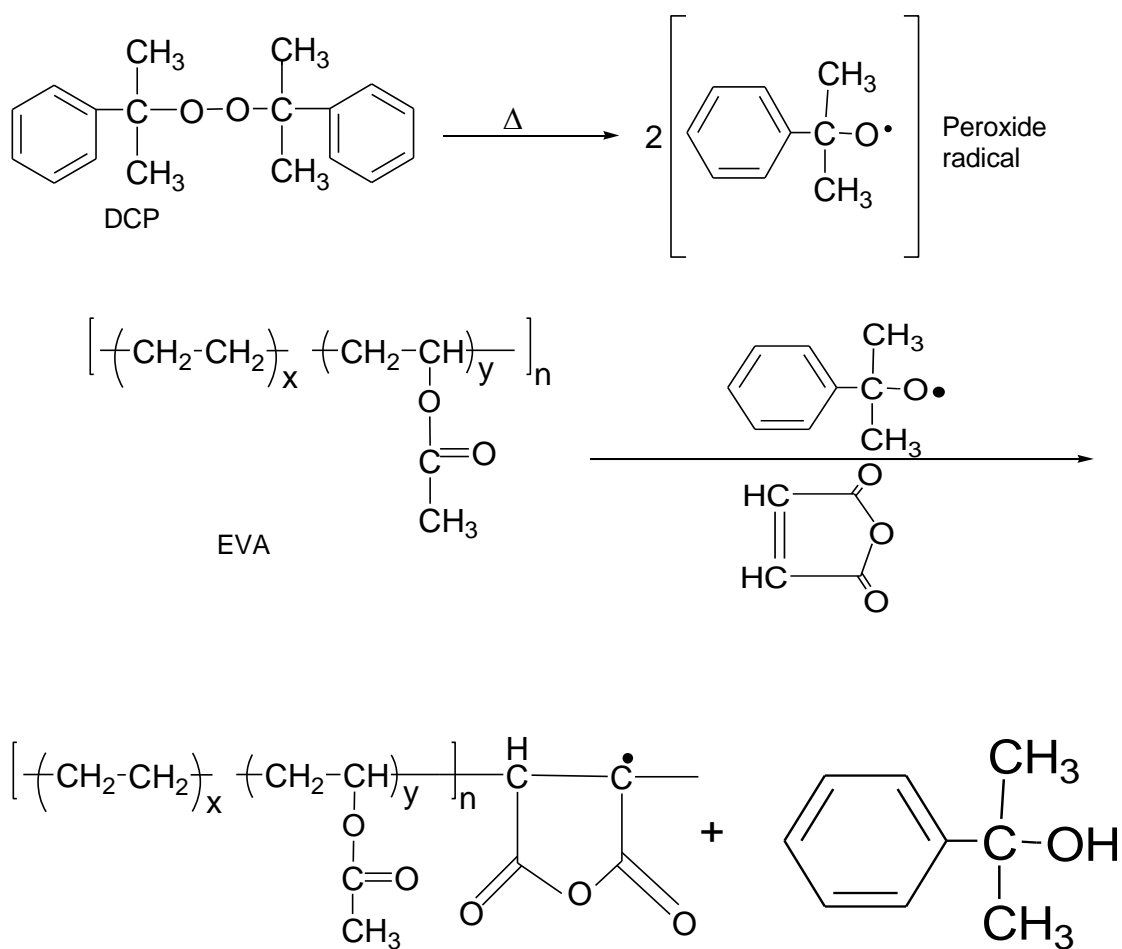


Figure 1



EVA/TPU blends III

Step I.



**Step II.**

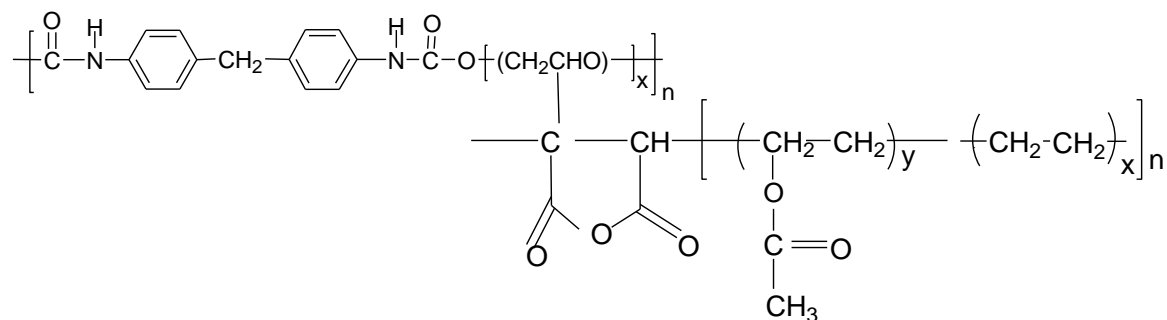
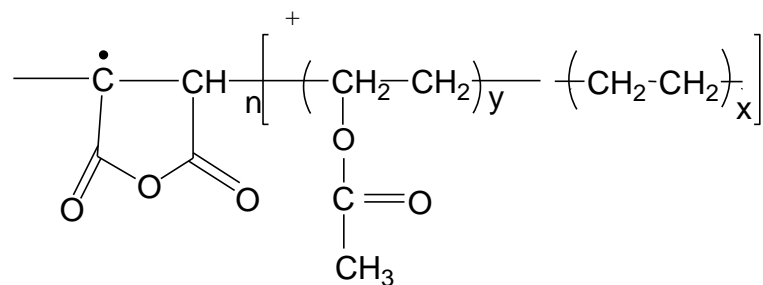
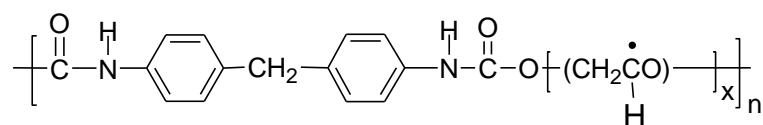
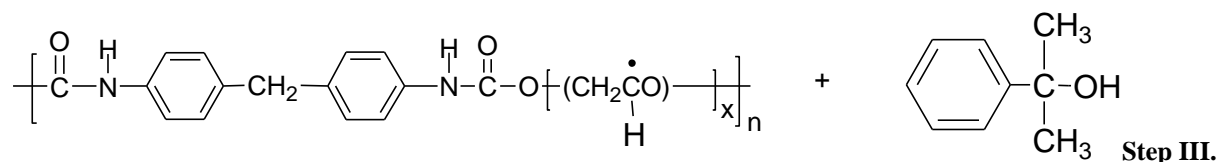
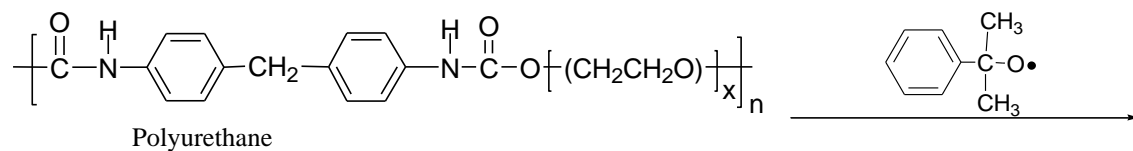


Figure 2

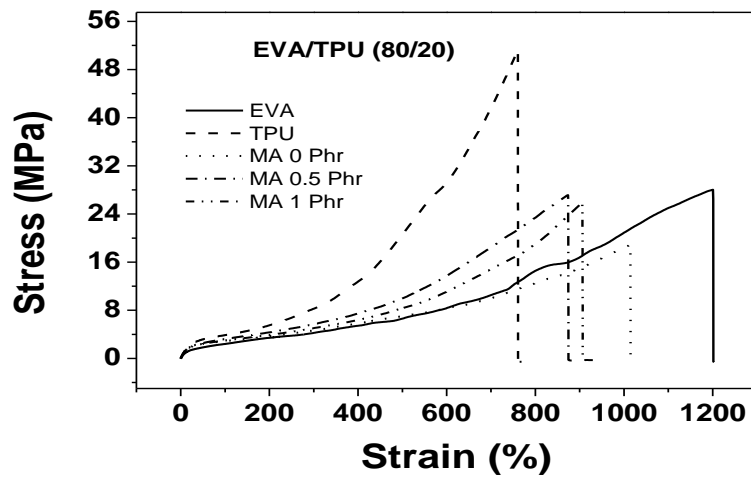
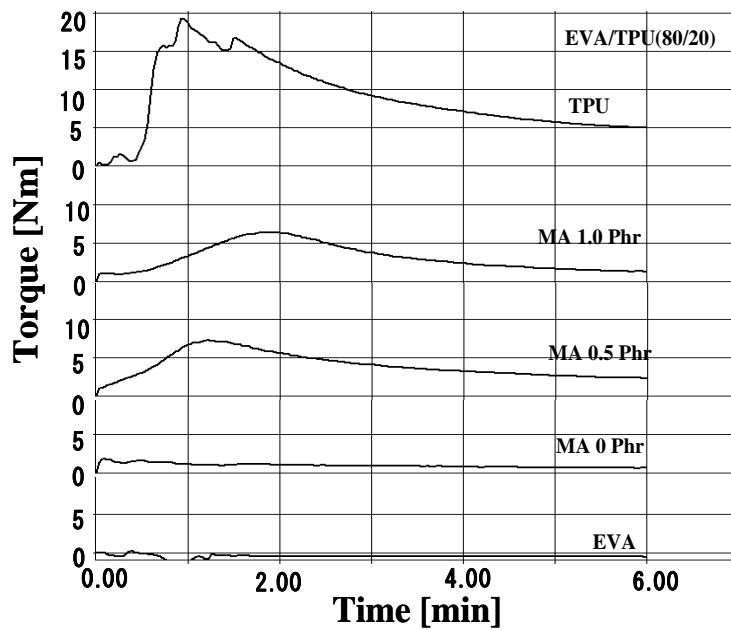


Figure 3

Figure 4

Table 1. Characteristics of the materials used in this study.



5 Material	Characteristics	Source
EVA 28	MI 3.0 g/10min VA content 28.0 wt% Density 0.951 g/cm <sup>3</sup>	Dupont. U.S.A
TPU	Polyester type	Hosung Chemex Co., Korea
MA (maleic anhydride)	98% purity, T <sub>m</sub> . 54°C	Shinyo Pure Chemical, Japan
DCP (dicumyl peroxide)	99% purity, T <sub>m</sub> . 39°C	Aldrich, U.S.A

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