

A review on graft compatibilizer for thermoplastic elastomer blend

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Abstract. A biodegradable thermoplastic elastomer (TPE) blend is developed by blending poly (lactic acid) (PLA) and natural rubber (NR) or epoxidized natural rubber (ENR) and it is a sustainable substitution in recent years for synthetic polymers. PLA is high in mechanical strength and compostable, but it is highly stiff and brittle. The incorporation of NR or ENR to PLA increases the impact strength and toughness of PLA. However, the disparity in polarity between PLA and elastomer phase like NR and ENR results in TPE blend being incompatible. Hence, compatibilization is essential to improve its polarity and develop interactions. Compatibilizer that composed of two different polymer is known as graft compatibilizer with the aid of grafting agent. The graft compatibilizers are divided into two categories. The first type is made up of one polymer and grafting agent and, the other one is composed of two polymer groups and grafting agent. These two types of graft compatibilizer can be prepared via two different method such as direct melt blending and solution. Apart from this, the TPE blend is produced via the melt blending technique with mixing machines such as internal mixer and extruder. This article has reviewed the preparation of the graft compatibilizer and blending technique of TPE. Based on the findings, the graft compatibilizers has a significant role in improving miscibility and compatibility across blend composed of different phase.

1 Introduction

The development of polymers that capable to be recycled and degrade has received the utmost attention because of rising ecological issues and limited petroleum resources. Crude oil is the source of many plastics production. Synthetic polymer causes environmental impact due to plastic longevity and slow deterioration. Therefore, the development of biodegradable polymers using monomers from renewable materials provides an alternative for synthetic polymers [1,2].

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The most popular bio-based conventional material is polylactic acid (PLA). PLA is compostable naturally and having higher mechanical characteristics. Their biodegradability is an advantage and an excellent alternative to synthetic polymers. PLA synthesized from aliphatic polyester that is readily biodegradable from crops that mostly contain starches and sugar. Sustainability, biocompatibility, ease of processing, and energy efficiency are PLA's benefits [3-5]. Usage of PLA has increased on a wide scale for various applications. However, despite composability, these polymers are unable to substitute in broad applications of commodities polymers. Given this fact, PLA has few restrictions such as extreme stiffness, less resilience to brittle, relatively slow crystallization, and gas permeability. Enhancing the toughness of PLA are via blending with rubber is a more convenient and economical method to solve those drawbacks [6,7].

Natural rubber (NR) and epoxidized natural rubber (ENR) are elastomers obtained from natural source and completely biodegradable. ENR is chemically modified from NR and it has epoxy ring. Naturally, elastomer acts as a toughening agent and stress concentrators to enhance the material's brittleness by aligning across the neighbouring rigid matrix material. NR and ENR improve the impact properties by absorbing fracture energy by rubber particles [4,5]. Hence, TPE blend is suitable for applications of high-performance. Besides, cost-effectiveness, renewability, hardness, and durability are advantages of elastomer. Elastomer also demonstrates good stretchability, elasticity high mechanical strength, heat tolerance, and the ability to be rescinded in deformation [6-8].

However, TPE blend of PLA/NR and PLA/ENR is unable to achieve optimum properties as the polarities are different; thus, it acts as a barrier in achieving a homogenous phase for proper miscibility. In need of well-distributed miscible phases, the blend system of TPE needed a compatibilizer to attain compatibility [3-6]. Compatibilizer improves the interfacial mechanism of the immiscible polymer blend via compatibilization. Compatibilization refers to the formation of bonds chemically between the different phases of the polymeric substance by providing an optimal morphological [9,10].

Maleic anhydride (MA) is used as a grafting agent and compatibilizer. It has unsaturated bond that will break and interacts with the hydroxyl groups. MA has a lower toxic rate and is chemically reactive. MA reacts with the double bond of elastomer, and MA also reacts with PLA through ring-opening polymerization. In other words, MA acts as a linker between PLA and elastomer to form the grafting [3,4,6-8]. When ENR reacted with MA it will lead to formation of succinic anhydride (SA) that react functional group of PLA. At the end of reaction, grafting network form between PLA and ENR. The grafting bridge in between PLA and ENR also can take place via reaction of epoxy ring of ENR and carboxylic group of PLA. A better adhesion force will develop and strengthens the polymer blends' mechanical properties by inducing better interactions. Grafted compatibilizers are will be more compatible for TPE blend because it contains functional group similar to parent polymer it will react and lead to higher interaction with the other phase [3-6]. Therefore, this review paper will focus on grafting technique to prepare graft compatibilizer and melt blends of the TPE blend.

2 Graft compatibilizer preparation

Synthesis of copolymerization with grafting agent produces graft compatibilizer [6]. It involves two different functional groups and monomers to build a network through grafting. The grafting mechanism requires monomers of polymers involved in a blend to form graft

copolymers that act as graft compatibilizers [3,5,6]. There are two techniques to prepare graft compatibilizer which are direct melt blend grafting and solution grafting as explained in following section. Besides, graft compatibilizers have two categories. The first category forms grafting between thermoplastic and elastomer such as PLA-g-ENR and PLA-g-NR. Meanwhile, the second category involves thermoplastic or elastomer for grafting on MA like PLA-g-MA, NR-g-MA and ENR-g-MA. Both grafting techniques can be applied for both categories of graft compatibilizers.

2.1 Direct melt blend grafting

Direct melt blending grafting techniques are performed with the internal mixer. Based on findings, this method widely applied for the first category graft compatibilizer. Internal mixer filled with a preset amount of elastomer or thermoplastic together MA and catalyst at the same time. During the melt blending grafting, MA reacts with the double bond of elastomer like NR to form (NR-g-MA) [11-15,18] as shown in Figure 1 (a) and ENR to form (ENR-g-MA) [8] as illustrated in Figure 1(b). For both NR and ENR, MA grafted by converting to succinic anhydride and hydrogen abstracted. MA also reacts with PLA through ring-opening polymerization to form (PLA-g-MA) and MA grafted onto backbone of PLA as demonstrated in Figure 1 (c) [11,12,15]. For second category of graft compatibilizer like PLA-g-NR [4], thermoplastic, elastomer, MA and catalyst added simultaneously. Direct melt blend grafting consumes less chemicals and time [4]. This grafting is prepared at a fixed duration, temperature and rotor speed.

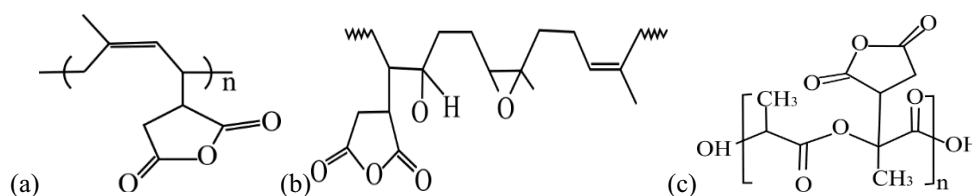


Fig 1. (a) NR-g-MA [13], (b) ENR-g-MA [8], and (c) PLA-g-MA [27]

2.2 Solution grafting

The solution grafting technique began with a standard solution preparation for hydrolysis reaction by dissolving NR into toluene at fixed temperature [3,6,16]. Subsequently, the initiation of free radicals by the inclusion of MA and benzoyl peroxide (BPO). BPO initiates a reaction between the functional unit of NR and the MA to form the grafting network NR-g-MA [3,6,16] at a constant temperature for fix duration under constant mixing in an inert atmosphere. Later, to precipitate the NR-g-MA, acetone [3,6,16] is added and dried using a hot-air oven.

Determining the grafting content is the next step to identify the amount of MA grafted onto the NR. At the boiling temperature of toluene, 1g of NR-g-MA dissolved in 100 ml of toluene and water added as a solvent for the reflux method. Hydrolysis reaction initiated by water which consecutively converted the anhydride functions to carboxylic acid functions. Then, the titration method was applied to find out the content of carboxylic acid by using

(0.025 N) potassium hydroxide that dissolves in a solution of benzyl alcohol/methanol (1/9) (v/v) together with 1% of phenolphthalein as an indicator [3,6,16]. Following that, an esterification process was performed to form PLA-g-NR graft compatibilizer as shown in Figure 2 (a). In toluene, pellets of PLA and NR-g-MA solution were added and continuously stirred. This process assisted with DMAP as a catalyst to speed up the grafting mechanism. The obtained solution evaporated over the tray. The amount of PLA-NR graft compatibilizer was evaluated through a Soxhlet reaction using sodium hydroxide in methanol [3,6].

Apart from that, for grafting of PLA together with ENR, ENR dissolved with toluene overnight and then hydrochloric acid included to initiate acid hydrolysis reaction. The hydrolysed ENR act as initiator for PLA when dissolved together in toluene to allow ring opening polymerization reaction. At the end of reaction, the solution of PLA-ENR precipitated and filtered to obtain PLA-g-ENR graft compatibilizer as demonstrated in Figure 2 (b) [17].

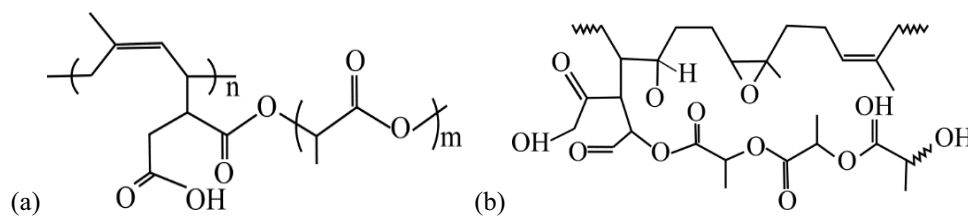


Fig 2: (a) PLA-g-NR [13] and (b) PLA-g-ENR [8]

3 Melt blending of TPE blend

Most TPE blends are processed via the melt blending method since it does not involve solvent exposure, and no solvent elimination is required. Furthermore, melting blending operates at a higher temperature to facilitate blending and promotes miscibility. Typically, PLA/elastomer blends with efficient dispersion developed by direct physical mixing. Via physical mixing, the PLA and the masticated elastomer are distributed and come in interfacial contact. Melt blending involves the force of shear to reduce the size of regions of immiscible polymers. The melt blending of TPE is usually performed using an internal mixer or extruder.

3.1 Melt blending via extrusion

The blending of TPE widely conducted with an extruder via extrusion mechanism. First, masticated elastomer, graft compatibilizer and antioxidant blended then followed PLA pellets [13]. A similar procedure was applied for the TPE blend without antioxidants [14]. Besides, prior to blending of NR and PLA, antioxidant and MA was premixed [7]. Besides, the blending of PLA/NR was performed with two different compatibilizers, such as PLA-g-MA and NR-g-MA in several studies [15,18].

In several studies, the extrusion temperature (ET) was fixed at a higher temperature to a lower temperature from the feed zone to the die zone. The barrel temperature was fixed from 190°C to 175°C [2]; 200°C to 180°C [19]. Meanwhile in certain studies, the barrel temperature set at lower temperature to higher temperature from feeding section to die section of extruder. The temperature of barrel fixed at 120°C to 160°C [7,20]; 150°C to 170°C [5,21,22]; 160°C

to 190 °C [18]. Melt blending of extrusion was performed at a different extrusion speed (ES) like 150 rpm and 190 rpm [7,20]. Melt blending with extrusion is done with varying the barrel in most of studies while maintaining constant extrusion speed as shown in Table 1. The summary of melt blending of TPE blends via extruder is tabulated below in Table 1.

Table 1. A summary of compatibilizers and processing conditions applied for TPE melt blending using extruder

No	TPE blend	Ratio	Compatibilizer	Processing conditions	References
1	PLA/ENR	90/10	-	ES:100 rpm ET:150°C - 170°C	[5]
2	PLA/NR	90/10	MA (1,2,3 wt%)	ES:150 and 190 rpm ET:120°C - 160°C	[7]
3	PLA/NR	90/10	NR-g-MA and PLA-g-MA (1,3,5,10 wt.%)	ET:150°C and 160°C	[11]
4	PLA/NR	90/10	NR-g-MA (2,4,6phr)	ES:150 rpm ET:170°C	[13]
5	PLA/NR	100/0, 95/5, 90/10, 85/15, 80/20	NR-g-MA	ES:100 rpm ET:160°C -180°C	[14]
6	PLA/NR	100/0, 95/5, 90/10, 85/15, 80/20	NR-g-MA and PLA-g-MA (3phr)	ES:100 rpm ET:160 °C -180°C	[15]
7	PLA/NR	90/10	NR-g-MA and PLA-g-MA (1,3,5,10 wt.%)	ET:160°C -190°C	[18]
8	PLA/ENR	100/0, 80/20, 70/30	-	ES:35rpm ET:200°C-180°C	[19]
9	PLA/NR	90/10	PLA-g-NR (2.5-10w pph)	ES:150 and 190 rpm ET:120°C-160 °C	[20]
10	PLA/ENR	100/0, 80/20, 70/30	-	ES:50 rpm ET:150°C- 170°C	[21]
11	PLA/ENR	90/10, 80/20, 70/30	-	ES:60 rpm ET:150°C-170 °C	[22]

3.2 Melt blending via internal mixer

Fabrication of TPE blend using internal mixer is very simple where all the thermoplastic, elastomer and graft compatibilizer added one time [1,8,23,24]. In few studies, the initial stage started with a mastication of rubber and then PLA included at last stage [6]. Melt blending of using internal mixer also carried out with different processing conditions such as mixing temperature (MT) with a range of (160-200) °C, rotor speed (RS) (30-90) rpm, and mixing duration (MD) (10-15) minutes [6]. However, few researchers prefer adding PLA at the initial stage into the internal mixer for plasticization reaction for up to 3 minutes. Then add rubber and compatibilizer which, then continue to blend for another determined duration at fixed temperature and rotor speed [25]. Based on the findings shown in Table 2, the processing temperature and rotor speed is constant throughout the internal mixer as it doesn't have different zone for blending. The summary of melt blending via internal mixer is listed in Table 2 below.

Table 2. A summary of compatibilizers and processing conditions applied for TPE melt blending using internal mixer

No	TPE blend	Ratio	Compatibilizer	Processing Conditions	References
1	PLA/ENR	100/0, 95/5, 90/10, 85/15, 80/20	-	RS:60 rpm MT:160 °C MD:6 min.	[1]
2	PLA/ENR	90/10	ENR-g MA (0.15, 0.30, 0.45, 0.60 phr)	RS:60rpm MT:170 °C MD:10 min	[8]
3	PLA/NR	80/20	PLA-g-NR (1-5% (w/w))	RS:80 rpm MT:190 °C MD:8 min	[6]
4	PLA/ENR	99/1, 97/3, 95/5, 90/10, 80/20	-	RS:60 rpm MT:170 °C MD:10 min	[23]
5	PLA/ENR	100/0, 90/10, 80/20, 70/30	-	RS:50rpm MT:170°C MD:13min.	[24]
6	PLA/NR PLA/ENR	100/0, 90/10, 80/20, 70/30	-	RS:50 rpm MT:170 °C MD:15 min	[25]

4 Compatibility of PLA/ENR blend

The use of grafted compatibilizers such as PLA-g-MA, ENR-g-MA, PLA-g-NR and PLA-g-ENR efficiently enhances compatibility between TPE blends and minimizes phase separation. MA may also interact extensively with the aliphatic chain of the PLA polymer matrix when an activator such as peroxide is added [9]. The linkage between ENR's epoxy ring and PLA's carboxylic group produces grafted compatibilizer of PLA-g-ENR [26]. The succinic anhydride (SA) ring forms from anhydride of MA after grafting into an ENR. The SA will react with the hydroxyl group of PLA. PLA-g-ENR compatibilizer as a final product will form [6,12,13]. PLA-g-ENR graft compatibilizers grafted via two different types of linkages: ester bonds and ether bonds [1,5]. The interaction between ENR and PLA will develop a new functional group belongs to the methine group (CH-O) [5]. Additionally, MA grafting agent is compatible with PLA and would form (PLA-g-MA). These reactions lead to bonding between PLA and ENR for miscible blend formation. Therefore, MA is compatible with both PLA and elastomer to allow grafting. Upon good compatibility by graft compatibilizer, the non-compatible blends turn into partial miscible structures with a hydrogen bond [26] and improve the toughening effect.

5 Conclusion

To conclude, the inclusion of grafting agent like MA generated graft compatibilizers via graft copolymerization. Direct melt blending technique is fast compared to solution grafting since multiple steps involved. Besides, second category compatibilizer will be more suitable for TPE blend as it composed of both functional groups. Compatibilizer incorporation in a blend of PLA/ENR enhanced properties and makes it possible to overcome limitations. Most importantly, as these graft compatibilizers are made up from renewable source, the entire compatibilized TPE blend is recyclable and biodegradable.

The authors would like to thank the Department of Higher Education, Ministry of Higher Education of Malaysia, for financial support for this research through the Fundamental Research Grant Scheme (FRGS) (9003-00798).

The authors also like to extend their great gratitude to Research Management Center, Universiti Malaysia Perlis (UniMAP), for all the supports given.

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