

High-Frequency Welding of Thermoplastic LLDPE/PA 6/PE-g-MAH Ternary Blends

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ABSTRACT: High frequency (HF) welding of linear low density polyethylene (LLDPE) melt blends with polyamide 6 (PA6) was done at 27.12 MHz using maleic anhydride grafted polyethylene (PE-g-MAH) as compatibilizer. HF welding was not possible for the blends at room temperature, but possible at higher temperatures (50, 80°C) although the maximum relaxation frequency was lower than the operating frequency. Greater dielectric constant, dissipation factor, and welding performance were obtained when PA 6 was premixed with PE-g-MAH rather than the one-shot pro-

cess where all the components were mixed simultaneously. This was interpreted in terms of lowered viscosity of PA 6 phase, which encapsulates the flow effectively and provides great skin effect. Also, the peeling force of resin-resin was greater than resin-nylon mesh due to the higher melting temperature and vacancy of nylon mesh. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3355–3360, 2008

Key words: high frequency welding; LLDPE; PA 6; PE-g-MAH; dielectric constant

INTRODUCTION

High-frequency (HF) welding is a clean, controllable, and quick process which needs little warm-up time.¹ In many applications, films are cut into complex shapes and assembled to make the final part such as shoes, inflatable boats, and medical packaging. In such assembly of films, a preferred method of processing is HF welding due to the speed and complexity of the shape to be welded.

However, HF welding is limited to high dielectric materials having great permanent, orientation dipoles and thus typically applied for poly(vinyl chloride) (PVC), poly(ethylene-co-vinyl acetate) (EVA), polyamide (PA), and thermoplastic polyurethane (TPU).² These resins are relatively expensive compared to polyolefin. Moreover, PVC which has been the mainstream polymer of HF welding emits volatile organic compounds. So, the development of new HF weldable polyolefin which can replace PVC is of practical importance.^{3,4} The polyolefin resins are not directly applicable for HF welding since they are not polar. To render them with polarity, a

copolymer of ethylene with a polar comonomer,⁵ or a multilayer film based on a mixture of polar polymer and polyolefin⁶ have been employed. Patents have also been issued for method,⁷ machine,⁸ and process of HF welding.⁹

In this article, linear low density polyethylene (LLDPE) has been melt blended with polyamide 6 (PA6) in the presence of maleic anhydride grafted polyethylene (PE-g-MAH) as a compatibilizing agent. Based on the rheological principle, flow encapsulation by the low viscosity component (PA 6) is expected to give great skin effect and welding performance. A two-stage blending sequence as well as one shot methods has also been made to examine the effect of mixing sequence.^{10,11} Blends were characterized in terms of rheological, dielectric, and mechanical properties in addition to HF weldability.

EXPERIMENTAL

Materials

Three grades of LLDPE (4220F, 4222F, and 4141C, Samsung Total) were rheologically characterized to create blend morphology which is suitable for HF welding. PA 6 (Ultramid B3, BASF) was used as high dielectric constant material. PE-g-MAH (Polybond 3009 series, Uniroyal Chem., MAH content: 1.2 wt %) was used as compatibilizer. LLDPE and PE-g-MAH were dried in hot-air circulating oven at

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TABLE I
Formulations of LLDPE/PA6/PE-g-MAH Ternary Blends

Run	4220F (wt %)	Ultramid B3 (wt %)	Polybond 3009 (phr) MAH 1.2 wt %
LLDPE 4220F	100	0	0
LN		30	0
Series 1	LMN1		30/0.5
	LMN2		30/1.0
	LMN3		30/2.5
	LMN4		30/5.0
	LMN5		
Series 2	LMN6	70	1.0
	LMN7		2.5
	LMN8		5.0
Ultramid B3	0	100	0

60°C and PA 6 was dried at 80°C for 24 h before use.

Compounding

Melt viscosity of the base resins were measured using RDA II (Rheometrics Scientific) using parallel plates with diameter of 2.5 cm and cell gap of 0.05 mm. Two different blending sequences were taken to study the effect of mixing on HF weldability.¹² The formulations of blending are listed in Table I. In Series 1, PA 6 and PE-g-MAH were premixed in a Haake internal mixer (Haake Rheocorder with two Banbarry type rotors) at 235°C and 150 rpm for 10 min. The premixed compound and LLDPE were subsequently mixed in Haake single screw extruder ($L/D = 25$) with a temperature profile of extrusion, 220°C (feed)—240°C (compression)—245°C, (head)—230°C (die). In Series 2, compounding was done by one shot process where three components were extruded at the same time under the same condition as Series 1.

Characterizations

Dielectric analysis

To measure the dielectric properties of blend, the golden electrode was made by chemical vapor deposition method. Samples with average thickness of 600 μm were molded using hot press at 210°C. Sam-

ples were placed in a temperature-controlled chamber. The frequency was swept from 100 Hz to 40 MHz at various temperatures (23, 50, 75, and 80°C) and the dielectric constant (ϵ') and dissipation factor ($\tan \delta$) were read-off from HP 4194A impedance/gain-phase analyzer (Hewlett-Packard).

HF welding and peeling forces

HF welding was done by a HF welding machine (Fig. 1) with the welding condition in Table II. Metallic electrode is used to seal the two pieces of film. The brass bar provides pressure and temperature required for sealing. When pressure is applied, HF energy is conducted to the electrode and melts the film. Typically, HF welding frequency is 27.12 MHz and electric field strength is above 10 kV.

To study the effect of substrate, two types of welding substrates, i.e., resin (resin–resin welding) and nylon mesh (resin–nylon mesh welding) have been used. Peeling forces of welded samples were measured with Universal Testing Machine (UTM, Tinius Olsen 1000) at a constant crosshead speed of 100 mm/min. Tests were made at room temperature and at least seven runs were made to report the average.

Active heating power

The active heating power (W) of HF welding is based on the dielectric dissipation into heat which is given by eq. (1):

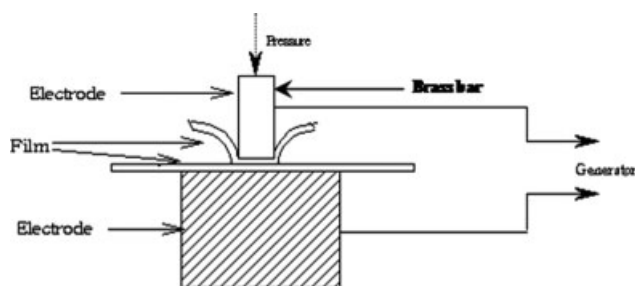


Figure 1 Schematic setup of HF welding.

TABLE II
Welding Conditions

Factors	Conditions
Frequency (MHz)	27.12
Pressure (kgf/cm^2)	3
Voltage (kV)	10
Holding time (s)	6
Welding time (s)	5
Electrode temperature ($^{\circ}\text{C}$)	23, 50, 80°C

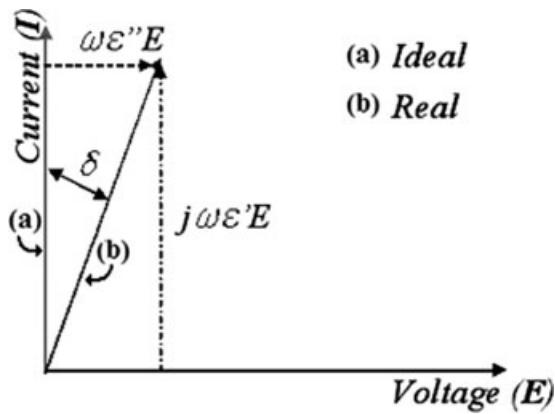


Figure 2 Real (ϵ') and imaginary (ϵ'') parts of the complex dielectric constant (ϵ^*) in an alternating electric field.

$$W = 2\pi f \epsilon' E^2 \tan \delta \quad (1)$$

where f and ω are cyclic and angular frequencies, ϵ' is dielectric constant, E is electric field, and $\tan \delta$ is dissipation factor which is defined as (Fig. 2)

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad (2)$$

The ϵ'' is the loss factor corresponding to the dielectric dissipation into heat.

RESULTS AND DISCUSSION

Choice of base resins and blend compositions

To increase the skin effect the high dielectric component (PA 6) should be exposed to the surface. In

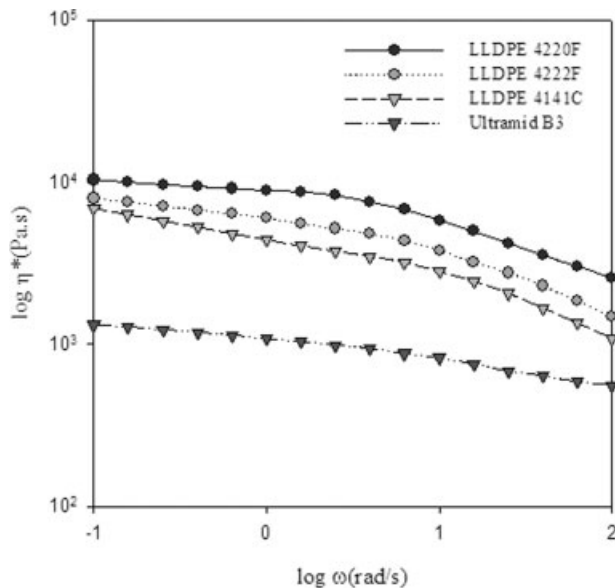


Figure 3 Complex viscosities (η^*) of three grades of LLDPE and PA 6 as a function of oscillating frequency (ω) ($T = 245^\circ\text{C}$).

principle this can be done in extrusion by the energy minimization principle where low viscosity component encapsulates the flow. For this low viscosity component should form continuous phase according to¹³

$$\frac{\eta_{\text{LLDPE}}}{\eta_{\text{PA6}}} = \frac{\phi_{\text{LLDPE}}}{\phi_{\text{PA6}}} \quad (3)$$

where η and ϕ are the viscosity and volume fraction of each component. When the above condition is satisfied, the blends are cocontinuous, and volume fraction above the condition makes the component continuous. Lower viscosity component tends to become continuous phase at lower volume fraction.

Figure 3 shows melt viscosities of components as a function of oscillating frequency. It is seen that PA 6 shows by far the lowest melt viscosity. Among three of the LLDPEs, 4220F shows the highest viscosity. So, it is most probable that the flow is easily encapsulated by PA 6 when the 4220F is being used as base olefin resin. The minimum composition for

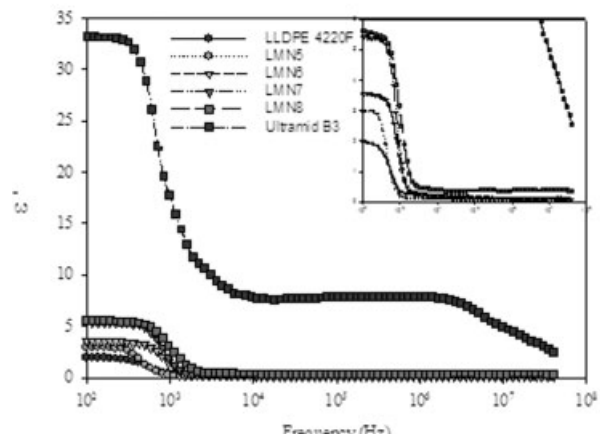
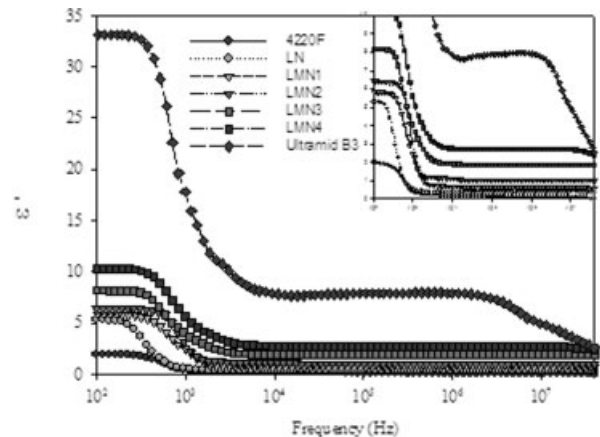


Figure 4 Dielectric constants at $T = 23^\circ\text{C}$; (a) Series 1, (b) Series 2.

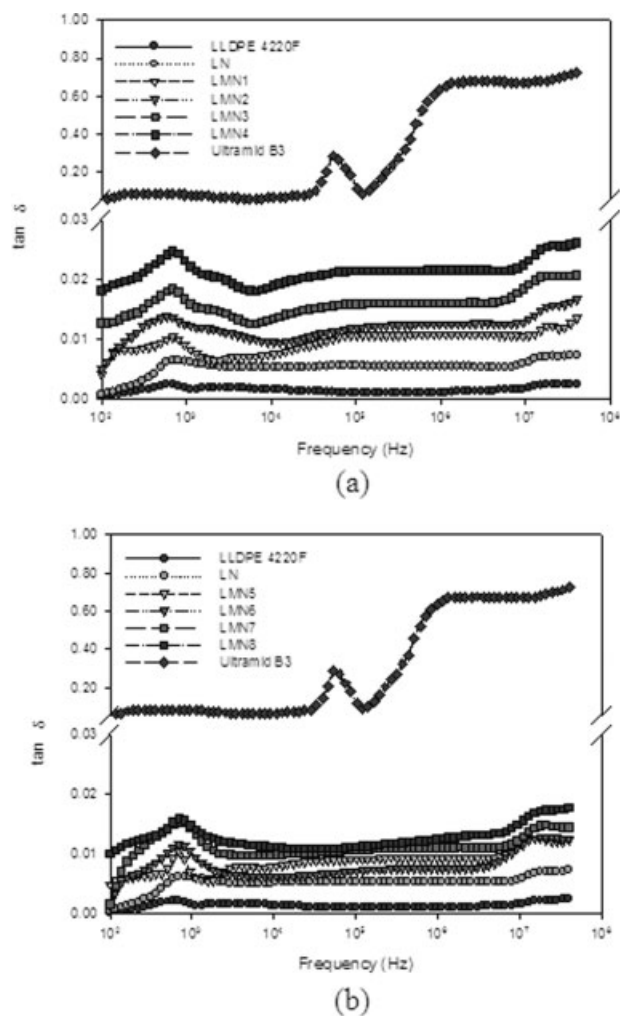


Figure 5 Dissipation factors at $T = 23^{\circ}\text{C}$; (a) Series 1, (b) Series 2.

cocontinuity is estimated by LLDPE : PA 6 = 7.5 : 2.5 (w/w) from the viscosity data read out. Therefore, when the composition of PA 6 is greater than 25%, PA6 is likely to foam the continuous phase and encapsulates the flow. So, our blend composition was fixed at 7 : 3 (LLDPE : PA6).

Dielectric analysis

Figure 4 shows the measured dielectric properties of the blends at room temperature (23°C). Dielectric relaxation of PA 6 occurs at about 50 kHz and LLDPE at about 1 kHz. The relaxation frequency increases with the addition and increasing content of PE-g-MAH due to the increased number of dipole. However, the increase is marginal and it is still below 1 kHz. Therefore, the dipoles of the blends do not follow the polarity change of the welding frequency (27.12 MHz), and satisfactory welding is not expected at room temperature.^{14–16}

Regarding the effect of blending sequence, Series 1 gives higher dielectric constant and dissipation factor than Series 2. It seems that the PE-g-MAH having the lowest viscosity further lowers the viscosity of PA 6 phase (Series 1 premixed PE-g-MAH and PA6) leading to great encapsulation of the flow by PA 6 phase and great exposure of PA 6 to skin.

The cause of high frequency welding is the dissipation factor [eq. (1)] at frequency region above 10 MHz. Figure 5 shows that the dissipation factor shows a rise above 10 MHz for LLDPE and blends and it is by far the highest for PA 6 and the lowest for LLDPE. For blends, it increases with the increase of PE-g-MAH. A small relaxation peak of LLDPE (Fig. 5) is probably due to the presence of α -olefin (1-butene) as comonomer in LLDPE since the pendant group of 1-butene induces polarization. Although PA 6 is the dominant dielectric component in the blends, relaxation frequency of the blends is close to that of LLDPE due to the insulation effect of LLDPE. Similar case was reported for LDPE/ZnO

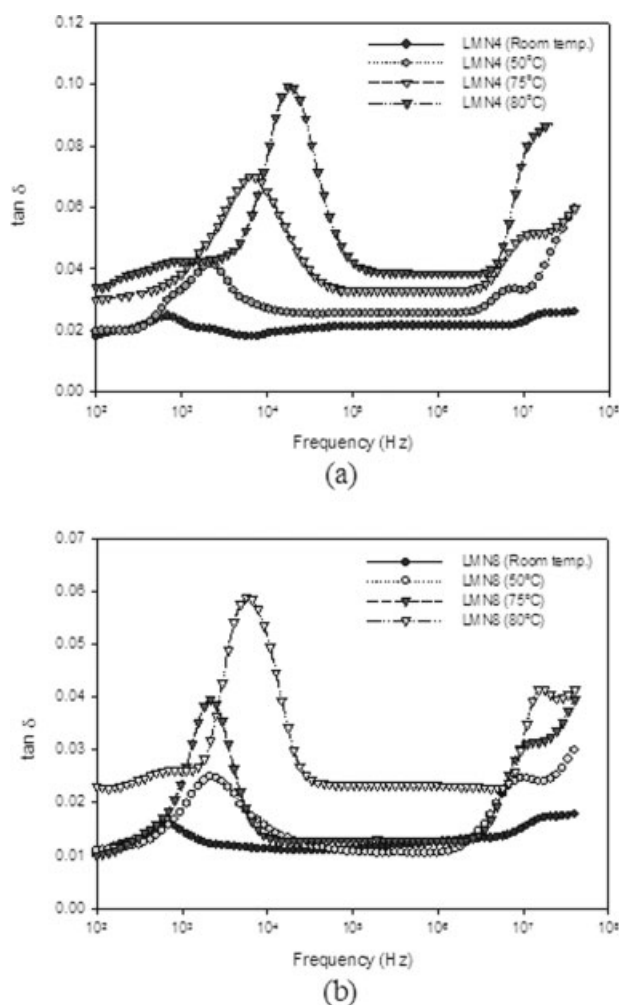


Figure 6 Dissipation factors at various temperatures; (a) LMN 4, (b) LMN 8.

TABLE III
Peeling Forces and Peeled Surfaces at 50°C

Results	Resin + Resin		Resin + Nylon mesh	
	Adhesion	Peeling force (N/m)	Adhesion	Peeling force (N/m)
LN	Δ	565	Δ	439
LMN 1	○	588	○	494
LMN 2	○	653	○	645
LMN 3	○	980	○	678
LMN 4	○	1585	○	1111
LMN 5	Δ	155	Δ	254
LMN 6	Δ	326	Δ	498
LMN 7	○	686	Δ	629
LMN 8	○	1206	Δ	931

Excellent (⊙), good (○), Partial welding (Δ), Fail (×).

composite by Hong et al.,¹⁷ where LDPE matrix was placed between ZnO particles and dielectric permittivity of ZnO particles has been interfered.

The effect of temperature on dielectric relaxation of the blends is seen in Figure 6 for LMN 4 and LMN 8. Since the polarization of internal dipole and dipole mobility increase with increasing temperature, dissipation factor increases and the peak shifts to higher frequency as temperature increases. Especially, the increase at 80°C is pronounced. It is also noted that the effect is more pronounced with Series 1 (LMN 4) than Series 2 (LMN 8), implying that the Series 1 is better for welding than Series 2.

Active heating power

Table IV shows active heating power of the blends as well as the virgin resin calculated by eq. (1). With increasing PE-g-MAH content, heating power increases due to the increased number of dipoles in carbonyl groups of PE-g-MAH. This gives increased loss factor at welding frequency. It is also seen that the heating power of Series 1 is much greater than the Series 2, indicating that more of PA 6 is exposed to the surface with Series 1.

Optimum welding temperature

Dielectric relaxation occurs when the experimentally allowed time (inverse of the imposed frequency) passes through the relaxation time of the dielectric which depends on temperature. So, the temperature at which the relaxation frequency becomes identical to the operating frequency (27.12 MHz) can be estimated based on the Arrhenius relationship:^{15,16}

$$f = f_0 \exp\left(-\frac{E_a}{k_b T}\right) \quad (4)$$

where f_0 is a preexponential factor, E_a is the loss energy due to dielectric dissipation and k_b is the Boltzmann constant (8.62×10^{-5} eV/K). When the experimental data are plotted according to the above equation, the following relationships are obtained;

$$f = 3.35 \times 10^{12} \exp(-0.587/8.62T \times 10^{-5}) \quad (\text{LMN 4})$$

$$f = 1.09 \times 10^8 \exp(-0.306/8.62T \times 10^{-5}) \quad (\text{LMN 8})$$

The optimum temperatures for maximum dielectric loss at 27.12 MHz were obtained by extrapolation to the operating frequency. They were 192.3°C

TABLE IV
Peeling Forces, Peeled Surfaces, and Heating Power at 80°C

Results	Resin + Resin			Resin + Nylon mesh	
	Adhesion	Peeling force (N/m)	Heating power (W)	Adhesion	Peeling force (N/m)
LN	○	629	0.04	○	445
LMN 1	⊙	666	0.34	○	522
LMN 2	⊙	912	0.75	○	657
LMN 3	⊙	1010	1.05	○	961
LMN 4	⊙	1676	2.48	○	1372
LMN 5	○	509	0.01	○	284
LMN 6	○	823	0.14	○	608
LMN 7	○	902	0.45	○	784
LMN 8	○	1348	0.67	○	1019

Excellent (⊙), good (○), partial welding (Δ), Fail (×).

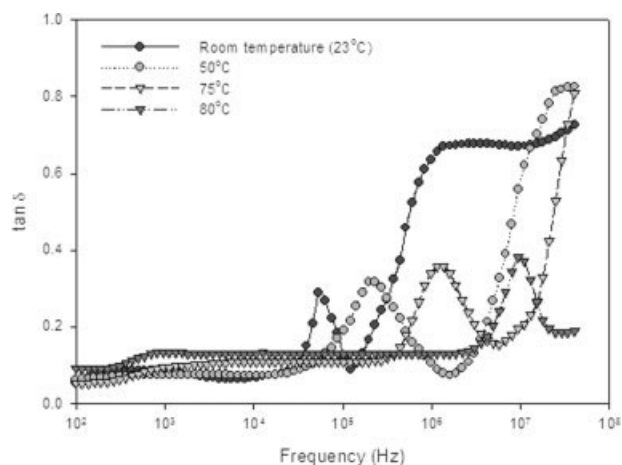


Figure 7 Dissipation factors of PA 6 at various temperatures.

for LMN 4 and 327.8°C for LMN 8, which are much higher than the melting temperature of LLDPE (about 120°C).

HF welding

HF welding has been performed at 23, 50, and 80°C, respectively, and the results were determined by the naked eyes as excellent (⊙), good (○), partial welding (△), and fail (×) (Tables III and IV). HF welding was not possible at room temperature. At 50 and 80°C, the two parts were welded as suggested from the great $\tan \delta$ values in the region above 10 MHz. Heating above the glass transition temperature of PA 6 (50°C) provides the material with great chain mobility, and the dissipation factor quickly approaches the welding frequency with increasing temperature (Fig. 7).

Peeling forces

The weld strength of the blends measured by T-peel test at 50 and 80°C are shown in Tables III and IV. Maximum peeling force (1676.9372 N/m) is obtained when LMN 4 (Series 1) is welded at 80°C. The uncompatibilized blend (LN) was not satisfactory welded at all temperatures where the peeled surface was not uniform. Peeling force of resin–resin was greater than resin–nylon mesh. It is supposed that nylon mesh has hardly been melted and electric field on the surface has not been applied uniformly due to the vacancy of the nylon mesh.

CONCLUSIONS

High frequency (HF) welding of LLDPE melt blends with polyamide 6 (PA6) was done at 27.12 MHz using maleic anhydride grafted polyethylene (PE-g-MAH) as compatibilizer.

Dielectric relaxation of PA 6 occurred at about 50 kHz and LLDPE at about 1 kHz. Though marginal, relaxation frequency increased with the addition and increasing content of PE-g-MAH due to the increased number of dipoles. Although PA 6 was the dominant dielectric component, relaxation frequency of the blends followed LLDPE due to the insulation effect of LLDPE.

The dissipation factor showed a rise above 10 MHz for LLDPE and blends and it is by far the highest for PA6 and the lowest for LLDPE. For blends, it increased with increasing PE-g-MAH content. The dissipation factor increased and the peak shifted to higher frequency as temperature increased and the effect was more pronounced with Series 1 (LMN 4) than Series 2 (LMN 8).

HF welding of the blend was not possible in the absence of PE-g-MAH. It was possible for compatibilized blends at elevated temperatures (50 and 80°C). These results were suggested by the dielectric measurements.

Greater dielectric constant, dissipation factor, and welding performance were obtained when PA 6 was pre-mixed with PE-g-MAH instead of mixing all the components simultaneously. This was interpreted in terms of lowered viscosity of PA 6 phase, which effectively encapsulates the flow and provides great skin effect.

The peeling force of resin–resin was higher than resin–nylon mesh due to the higher melting temperature and vacancy of nylon mesh.

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