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# Reactive Blending of Polyethylene

**Rathanawan MAGARAPHAN[1], Pornpirom MOTEPLAY[1],**
**Chaiwat TOWICHAYATHAMRONG[1], Baramee MOJDARA[1], Alexander M. JAMIESON[2],**
**and David C. MARTIN[3]**
**[1]The Petroleum and Petrochemical College, Chulalongkorn University**
**[2]Department of Molecular Science and Engineering, Case Western Reserve University, Cleveland, USA**
**[3]Department of Materials Science and Engineering, University of Michigan, Michigan, USA**

## Abstract

Reactive blendings of polyethylenes (LLDPE and HDPE) and other polymers were performed by their reactions with small reactive molecules, e.g. maleic anhydride and methyl methacrylate with dicumyl peroxide. Different processing procedures, e.g. one pot and multiple stages of mixing showed different qualities of polymer blend mechanical properties. The addition of natural rubber (NR) and maleic anhydride into LLDPE significantly improved processibility of LLDPE resins as evidenced by the increase of ultimate draw ratio and blow up ratio which directly related to the ultimate melt strength of LLDPE. Maleic anhydride was added by 1-5 wt% to *in-situ* compatibilize the blend. By using this technique the melt viscosity and morphology of LLDPE/NR blends were affected. Moreover, the molecular orientation, due to biaxial orientation in blown film, strongly affected the mechanical properties of the film; such as tensile strength and impact strength. Impact strength increased as NR loading increased; whereas, the tensile strength of films decreased. Addition of methyl methacrylate (MMA) to HDPE in a one-pot blending of HDPE and poly (vinyl chloride) obviously enhanced the modulus of the blend as a result of improved compatibility by MMA-g-HDPE. A HDPE-silk fiber composite was also prepared by the reactive blending with methyl methacrylate. The one pot process showed better properties of the composite than two-stage process due to longer residence time that was accessible to deteriorate silk fibers.

## Introduction

Reactive extrusion of polyolefins has been done since 1960s with the aim to ease the processibility of polyolefins by reducing molecular weight and to functionalize polyolefins such that they can be readily compatible with other polymers and metals. There are two methods to make functionalized polyolefins; using high temperature and low temperature with catalysts. (Gaylord, *et al.* 1982 ; Gaylord, *et al.* 1992; Heinen, *et al.* 1996; Samay, *et al.* 1995; Simmons, *et al.* 1989; and Ganzeveld, *et al.* 1992) Radical catalyzed grafting reaction of maleic anhydride (MA) and polyethylene (PE) in the bulk or solution has been studied intensively by Gaylord and Mehta. They found that MA-containing low density polyethylene (LDPE) prepared by mixing 2 %wt dicumyl peroxide (DCP) to molten LDPE at 140°C was xylene soluble (no gel formation) but when processing at 180°C, the products of LDPE/DCP mixture and LDPE/DCP/MA contained 51% and 59% xylene-insoluble part. (Gaylord and Mehta, 1982) The gel part was absent by adding electron donor materials. (Gaylord, *et al.* 1982; Gaylord, *et al.* 1992; and Samay, *et al.* 1995) However, gel effect on reducing mechanical properties is undesirable. Employing high temperature technique or avoiding the use of catalyst can minimize gel formation but requires high energy consumption. Functionalized polymers have been adapted to enhance miscibility of polymer blends; for example reactive blending of anhydride grafted ethylene-propylene rubber and polyamide to form covalent bonding (Simmons and Baker, 1989) and that of PE and polypropylene.(Kim and Yoon, 1997) The reactive blending in the melt state has some advantage over the solution mixing; i.e. short process time and no solvent recovery.

In our studies, we are going to show the reactive blending of PE and other polymers (e.g. rubber, plastic, and fiber) with and without peroxide catalyst and by different processing methods; i.e. using one-step (one pot) or multi-step mixing. For the non-catalyzed system, maleic anhydride (MA) was grafted to LLDPE and NR in the melt state and further shaping by tubular film blowing. By this technique, the melt strength of LLDPE was improved. The effects of processing conditions on molecular orientation and mechanical properties of LLDPE and its blends were also investigated.

Moreover, the catalyzed reactive blending was found to improve the blend properties of HDPE and other polymers such as poly(vinyl chloride) (PVC) and silk fibers (SF). The reactive blending was achieved by functionalized methyl methacrylate (MMA) to HDPE and then mixing the reacted HDPE with PVC or SF.

## Experimental

### Materials

LLDPE (Thai Polyethylene Co., Ltd.) shows MFI=1, density = 0.918 g/cm$^3$, $M_n$ = 3,481, $M_w$ = 84,460 and MWD = 24.26. Natural rubber (grade STR 5L, Rayong Bangkok Rubber) shows density = 0.90 g/cm$^3$, $M_n$ = 22,241, $M_w$ = 125,000 and MWD = 5.62. Maleic anhydride was purchased from Fluka Co., Ltd. SF, HDPE, and PVC were obtained from the "SUPPORT Foundation of Her Majesty Queen Sirikit of Thailand, Thai Polyethylene Co., Ltd., and Thai Plastic and Chemical Co., Ltd. MMA and DCP were purchased from Fluka.

## Procedures

### Twin screw extruder

LLDPE and NR were separately mixed with 75% and 25 % MA, respectively on a two-roll mill in order to proportionately incorporate MA in both polymers and primitively make some extent of maleic anhydride grafted LLDPE and maleic anhydride grafted NR (MA-g-LLDPE and MA-g-NR). The mixing condition was the same for each polymer; i.e. at 170°C for 8 min, then the mixtures of MA-g-LLDPE and MA-g-NR were mixed on a two-roll mill at 170°C for 5 min. The premix was then processed in a Collin twin screw extruder. Temperature settings from zone 1 to the die were 150, 155, 160, 175, 185, and 195°C, respectively, and the screw speed was at 130 rpm. The extrudate was then cooled in water at 25°C and pelletized by a granulator.

The blends were characterized for melt viscosity by an Instron capillary rheometer model 3213 at 180°C using shear rate ranging from 30 to 1200 s$^{-1}$ (the L/D ratio of capillary die was 40). Thermal properties of the blends were analyzed by a differential scanning calorimeter (DSC) with $N_2$ cooling unit. Heating and cooiing rates used were 10°C /min. The valve of the fusion heat for 100% crystalline PE ($\Delta H_{f100}$) is 299.1 J/g.

### Blown film extrusion

The LLDPE and LLDPE/NR blends were processed in a Betol blown film extruder of 15 mm diameter and a L/D ratio of 60. The molten materials were extruded through a 25 mm annular die with a die gap of 0.5 mm. The freeze line was set at 100 mm. Blow up ratio was 5. Three draw ratios were used:1, 3 and 5, respectively. Temperature settings along the barrel of the extruder and the die were 150, 155, 160, 175, 185, and 195°C, respectively. Screw speeds was set at 75 rpm.

### Mechanical testing

Tensile strength at break of LLDPE/NR blown films (30-100 μm thick) in both the MD and TD were measured using a Lloyd universal-testing machine. The test was conducted according to ASTM D882. Impact strength was determined by ASTM D256 using Instron impact tester, model ITR-2000. The films were cut to the size of 15X15 cm, speed of puncture was 4 m/sec.

Tensile (for HDPE/PVC blends) and flexural (for HDPE/SF blends) modulus determinations were performed by Instron 4206 universal testing machine following ASTM D256 and D790-96a, respectively.

### Determination of molecular orientation

The molecular orientation averaged over all chain segments is usually characterized by the orientation function defined as,

$$f = \frac{3\cos^2\theta - 1}{2}, \qquad .........(1)$$

where $\theta$ is the angle between the stretching direction and the chain axis. The orientation measurement is made possible through the use of the infrared dichoism. This method allows for the determination of the orientation function through,

$$f = \frac{(D-1)(D_0+2)}{(D+2)(D_0-1)}, \qquad ......(2)$$

where D is the measurable infrared dichroic ratio defined as $D = \frac{A\parallel}{A\perp}$, $A\parallel$ and $A\perp$ being the absorbance with the polarized infrared beam parallel and perpendicular directions to the stretching direction, respectively, $D_0 = 2\cot^2\psi$ with $\psi$ being the angle between the chain axis and the transition moment, taking $\psi$ = 0 degree. For polyethylene, the 1464 $cm^{-1}$ band, displaying a strong parallel dichroism, is related to the C-C vibration of the crystalline phase and the 1368 $cm^{-1}$ band is for amorphous phase.

## Results and Discussion

### Chemistry and structure

The glass transition temperatures of the blends used to indicate compatibility of the blends are presented in Table 1. The results showed one $T_g$ for blends when enough amount of MA was present; e.g. 3 %wt for 90/10, 5 %wt for 80/20 and 70/30 %wt LLDPE/NR (see Table 1). Moreover, incorporation of MA reduced the averaged NR dispersed phase size, e. g. from ca.1.5 to 1.0 μm, for composition 70/30 %wt as evidenced from Figure 1. Here, uniform dispersion as well as distribution of the dispersed phase is apparent.

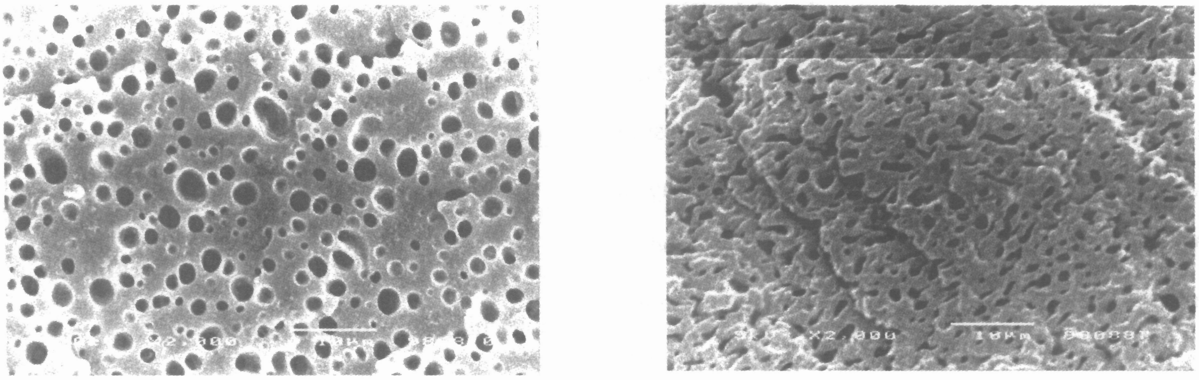


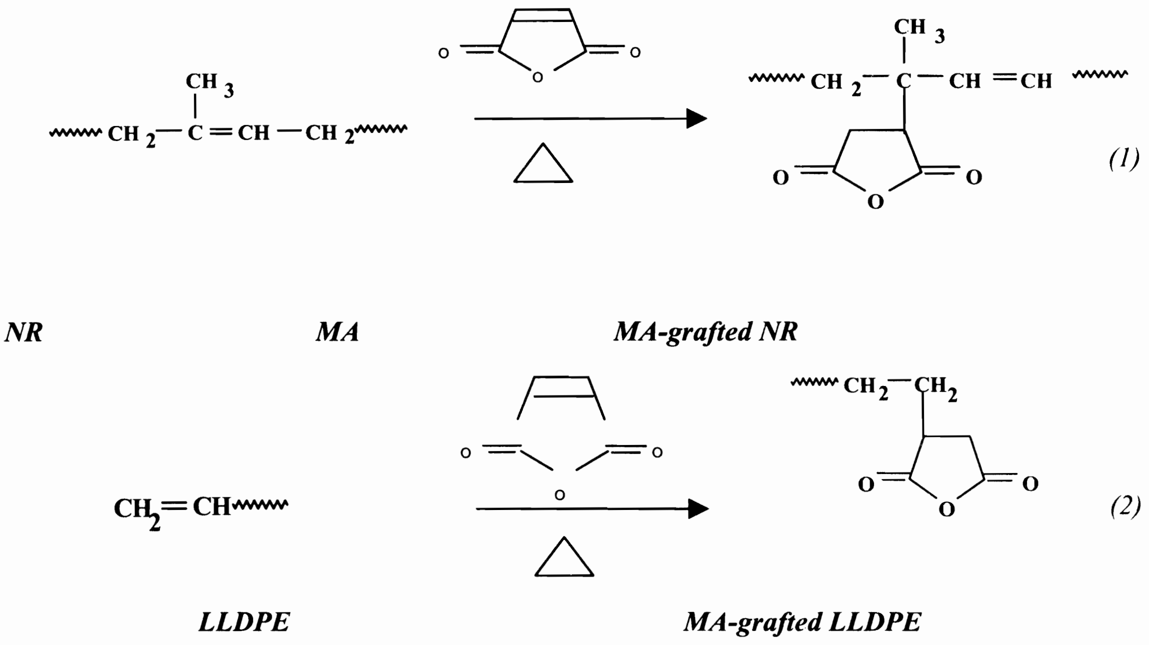
**Figure 1** Morphology of LLDPE/NR/MA at composition 70/30 (left) and with 5% MA (right) (magnification 2000X).

The reduction in particle size implies the reduction in the interfacial tension or better adhesion between LLDPE matrix and NR dispersed phase. The improvement in the compatibility of the LLDPE and NR due to the compatibilizing effects of MA-g-LLDPE and MA-g-NR formed during the reactive blending. Thermal reactions for grafting MA onto LLDPE and NR chains may be the diel-elders mechanism; i.e. the grafting reaction occurring at the double bond site on the polymer chains.(Burlett, *et al.* 1993; and Smedberg, *et al.* 1997)

Double bond sites on the NR chains are undoubted but those of LLDPE chain are often found at the end group.(Smedberg, *et al.* 1997) The reaction is also possible by the free radical mechanism due to mechanochemical shearing of NR chains. The purposed reactive products are shown in scheme 1.

**Table 1** Glass transition temperatures ($T_g$) of LLDPE, NR and LLDPE/NR blends

| **Compositions** | $T_{g1}$ | $T_{g2}$ | **% Crystallinity** |
|---|---|---|---|
| LLDPE | -21 | - | 33.81±1 |
| NR | -62 | - | - |
| 90/10/0 | -25.1 | -38 | 31.16±2 |
| 90/10/1 | -26 | -40 | |
| 90/10/3 | -60 | - | - |
| 80/20/0 | -21 | -48 | 28.74±1 |
| 80/20/3 | -37 | -45 | - |
| 80/20/5 | -44 | - | - |
| 70/30/0 | -43 | -64 | 26.16±1.5 |
| 70/30/3 | -42 | -55 | - |
| 70/30/5 | -54 | - | - |



**Scheme 1** Purposed reactions between NR and MA and between LLDPE and MA.

*Melt strength of LLDPE and LLDPE/NR blends*

During the tubular blown film experiment, at fixed blow up ratios, the take up speed was increased until the tubular film was broken, where the tensile force exerted by increasing draw ratio exceeded a critical value that the tubular bubble could no longer withstand. Such critical force may be termed *ultimate melt strength.*The term melt strength of polymer is referred to maximum draw ratio and the maximum blow up ratio of tubular blown film process. From Table 2 addition of 10 %wt NR leads to an enhancement of melt strength due to an increase in long chain branching in the matrix of LLDPE. Blow ability (maximum BUR) of LLDPE with 10 %wt NR was 6 (Table 2) which was greater than that of pure LLDPE (BUR=5).

**Table 2** Melt viscosity of LLDPE, NR and LLDPE/NR blends

| **Materials** | **Shear viscosity (Pa.s) @ 100 $s^{-1}$** | **Shear viscosity (Pa.s) @ 500 $s^{-1}$** | **Maximum Draw ratio** | **Maximum Blow up ratio** |
|---|---|---|---|---|
| LLDPE/NR/MA | | | | |
| 100/0/0 | 1,368 | 534 | 6 | 5 |
| 0/100/0 | 1,455 | 521 | * | * |
| 90/10/0 | 1,413 | 513 | 5 | 6 |
| 90/10/3 | 1,614 | 546 | 6 | 6 |
| 80/20/0 | 1,355 | 541 | * | * |
| 80/20/3 | 1,676 | 584 | 7 | 6 |
| 80/20/5 | 1,673 | 560 | 7 | 6 |
| 70/30/0 | 1,530 | 462 | * | * |
| 70/30/3 | 1,724 | 555 | * | * |
| 70/30/5 | 1,809 | 592 | * | * |

Note * can not process in blown film extrusion

*Melt viscosity of LLDPE and LLDPE/NR blends*

In this work, the apparent shear viscosities of LLDPE/NR blends were measured at 100 and 500 $s^{-1}$, respectively. Results are shown in Table 2. The shear viscosities of the blends are greater than that of LLDPE. This implies that after addition of NR and MA into LLDPE, the adhesion between two phases is enhanced. Intuitively, the higher shear viscosity of the blends indicated better blowability.

*Molecular orientation*

It is known that the blown film process imparts biaxial molecular orientation to the products. Figure 2 shows molecular orientation functions of the LLDPE film as a function of DR. The film was broken at DR above 5, which corresponded to its maximum or ultimate melt strength. The crystalline orientation function ($f_c$ or $F_c$ in Figures 2-3) increased rapidly upon extension. This indicated segmental orientation of the crystalline structure of LLDPE, which was aligned parallel to the stretching direction. On the other hand amorphous orientation ($f_{am}$ or $F_{am}$ in Figures 2-3) was slightly lower than the crystalline orientation at low DR. The amorphous segments resided in the interlamellar region existed in various forms: tie chains, cilia, loops and unattached chains. Generally the tie chains interconnected between the crystal blocks, was expected to orient more than cilia, loops and unattached chains that relaxed more rapidly. At BUR 5 and DR 5, $f_c$ and $f_{am}$ of LLDPE film were about 0.5. High BUR (=5) leads to more balanced orientation as well as high degree of planar orientation in both MD and TD.

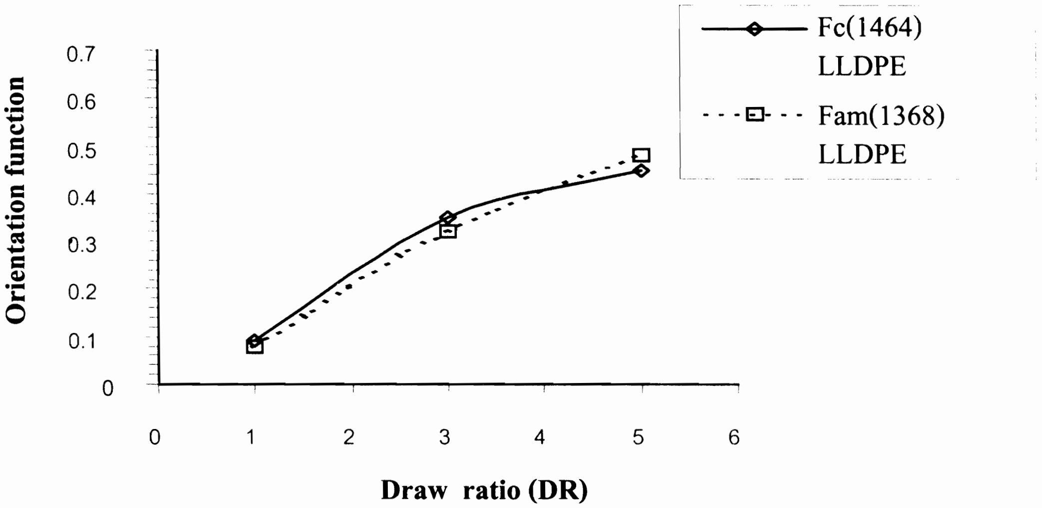


**Figure 2** Crystalline ($F_c$) and amorphous ($F_{am}$) orientation functions of LLDPE at BUR 5 and DR 1, 3 and 5

The $f_c$ and $f_{am}$ of LLDPE phase in LLDPE/NR blends at the composition 90/10 %wt is shown in Figures 3. Table 1 shows that degree of crystallinity decreases with increasing NR content. NR molecules of the blends are in the amorphous layers. The ungrafted NR molecules in the blend act like the unattached chains in the system. During the drawing process, these unattached chains tend to recover to the initial state relatively faster than the attached chains, resulting in decreasing orientation. It is interesting that $f_c$ and $f_{am}$ increased with increasing MA content. This indicated that MA played a significant role in the orientation of both crystalline and amorphous segments. This implies that MA performs as a compatibilizer to enhance adhesion between NR and LLDPE so that the unattached chains, which relax easily, are reduced and the imposed orientation is sustained during the solidification process.

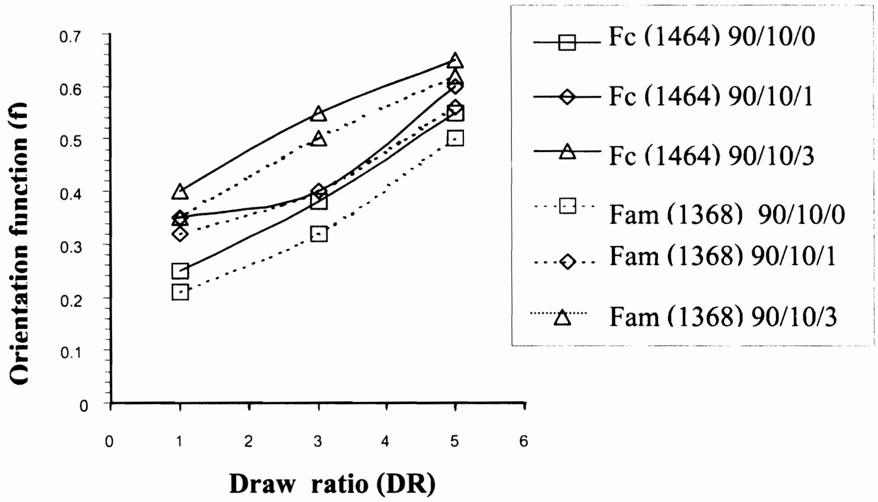


**Figure 3** Crystalline ($f_c$) and amorphous ($f_{am}$) orientation functions of LLDPE/NR blown films at composition 90/10 %wt at BUR 5 and DR 1, 3 and 5

*Mechanical properties*

Figure 4 shows tensile strength at break of the LLDPE film as a function of draw ratio. The strength of sample increases with increasing draw ratio which corresponds to higher molecular orientation. Besides the drawing process conditions, the strength of LLDPE/NR blend films are also dependent on NR and MA content. In Figure 5, addition of 10 %wt NR without MA showed a negative effect on the tensile strength at break of the films. This was due to the lack of interfacial adhesion between LLDPE and NR phases. The poor adhesion between the NR dispersed phase and the LLDPE matrix resulted in higher actual stresses in the LLDPE matrix for a given applied load and caused a rapid failure of the film. On the contrary, addition of 1-3 %wt MA caused a significant increase of tensile strength in both MD and TD of the films. For example at DR = 5, tensile strength for LLDPE/NR blends at the composition 90/10 %wt without MA exhibited value around 9 MPa and 7.2 MPa in MD and TD, respectively. After addition of 1 %wt MA an increase of tensile strength to about 18 in both MD and TD is observed. Further addition of MA (up to 3 %wt) caused an increase in the tensile strength of blend films to 19 MPa in both MD and TD. At DR = 5 the tensile strengths at break in MD and TD are unaffected which shows a more balanced molecular orientation in both directions. It can be concluded that MA can improve the interfacial adhesion and thus increase the tensile strength of the films.

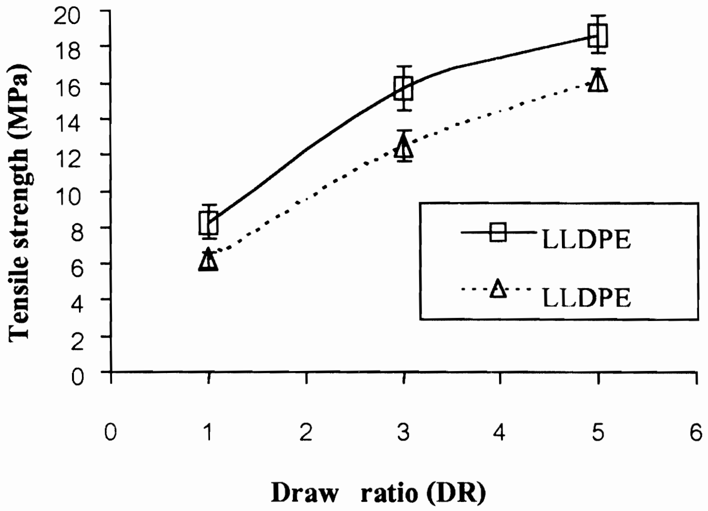


**Figure 4** Tensile strength at break for LLDPE blown films at BUR 5, DR 1, 3 and 5

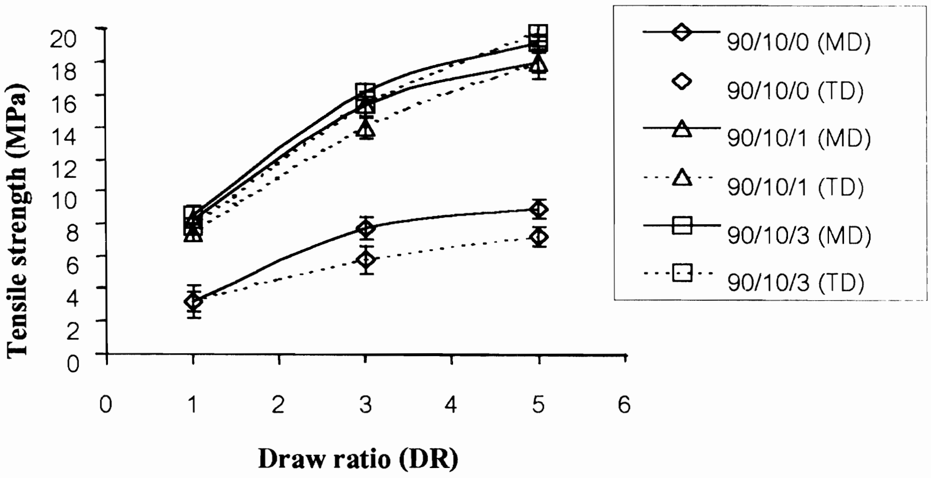


**Figure 5** Tensile strength at break for LLDPE/NR blown films at composition 90/10 wt% in MD and TD at BUR 5, DR 1, 3 and 5

*Impact Strength*

The effect of drawing on impact strength of the 90/10 blends with and without MA compared with that of pure LLDPE film can be seen in Figure 6. All samples show the same trend; i.e. impact strength decreases when DR increases. This implies that when a sudden load is applied, the failure of film becomes easier with chain alignment (increasing DR). This is probably due to the less number of tie molecules to provide toughness and strong connection between crystalline blocks. For 90/10 LLDPE/NR blend without MA, the impact strength is not improved at all but it is greatly improved with MA content. This indicates the enhancement of adhesion between two phases such that the rubber toughening function is obtained.

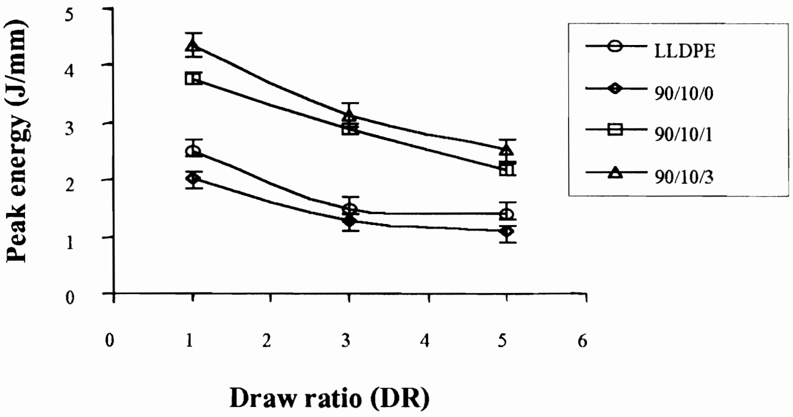


**Figure 6** Impact strength of LLDPE/NR blown films at composition 90/10 wt% at BUR 5 and DR 1, 3 and 5

## Other reactive blending of polyethylene

Polymer blending of HDPE and poly(vinyl chloride) (PVC) can be achieved by reactive blending of HDPE and methyl methacrylate (MMA) with dicumyl peroxide (DCP) as an initiator. The product of the reaction is expected to be MMA-grafted HDPE (see Figure 7) which makes HDPE to be reactive. Following the reactive step is the addition and mixing of another polymer component (PVC or silk fibers) until steady torque is obtained.

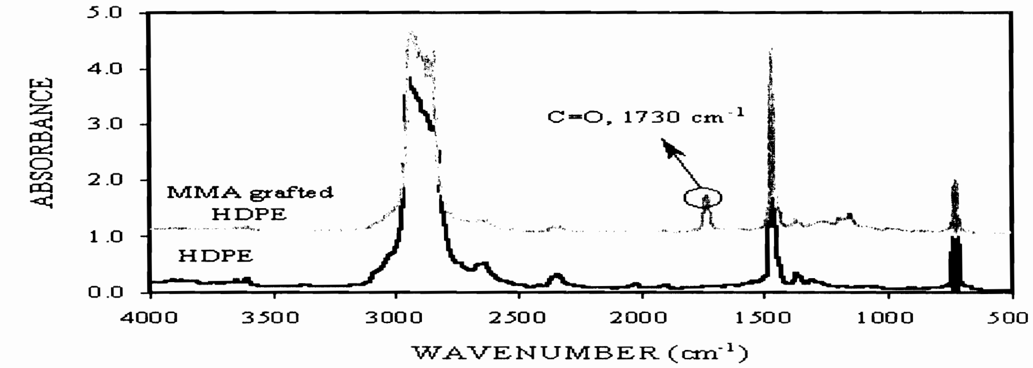


**Figure 7** FTIR spectra of pure HDPE and purified MMA-grafted HDPE from reprecipitation of crude blended sample/*o*-dichlorobenzene solution in acetone

The flexural modulus of HDPE/Silk/MMA blend and tensile modulus of HDPE/PVC/MMA blend as functions of composition and initiator content are shown in Figures 8-9. The moduli of the reactive blends are higher than those of the simple binary blends. Effect of fiber loading on the flexural modulus of the HDPE/SF/MMA blend shows a reduction in the modulus at 10 %vol fiber loading and an increase at higher fiber loading. At low concentration of fiber, instead of being a reinforcing fiber, silk fiber acts as a defect such that a high strain is localized in the matrix causing a debonding between silk fiber and matrix. This phenomenon refers to the matrix diluted by non-reinforcing and debonded fiber called "Dilusion Effect".(Akhtar, *et al. 1986*) Moreover, for HDPE and SF blends, one-pot blending (preparing a reactive blend of HDPE and MMA with DCP in an internal mixer and then mix it with SF for 10 minutes at 160°C) is superior to two-step blending (HDPE, purified MMA-g-HDPE, and SF was mixed 15 minutes at 160°C on two–roll mill and further mixing in twin screw extruder at 130°C for feed zone to 190°C at die for another 10 minutes) so that the dilution effect is less pronounced and relatively higher modulus is obtained. In addition, the two-step blending took longer processing time at high temperature and thus SF is more susceptible to degrade.(Tsukad, 1988)

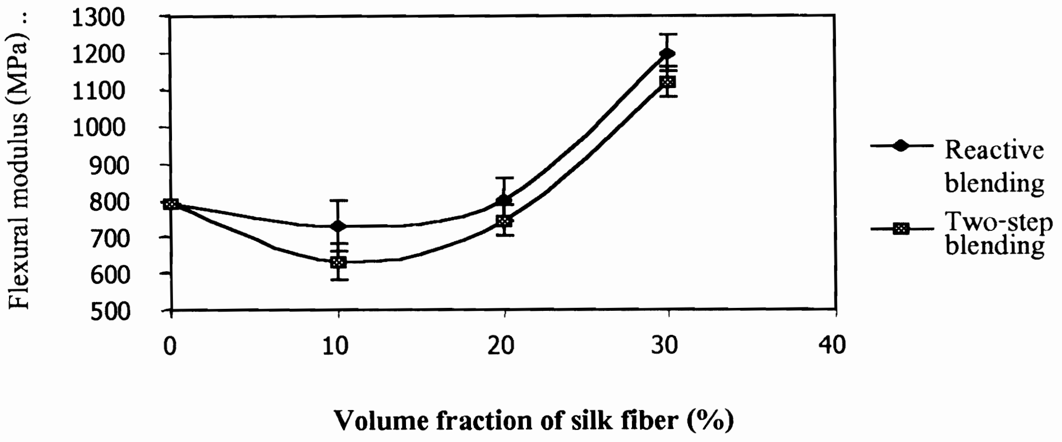


**Figure 8** Effect of fiber loading on flexural modulus of MMA-g-HDPE/Silk blends with 10, 20, 30 % SF.

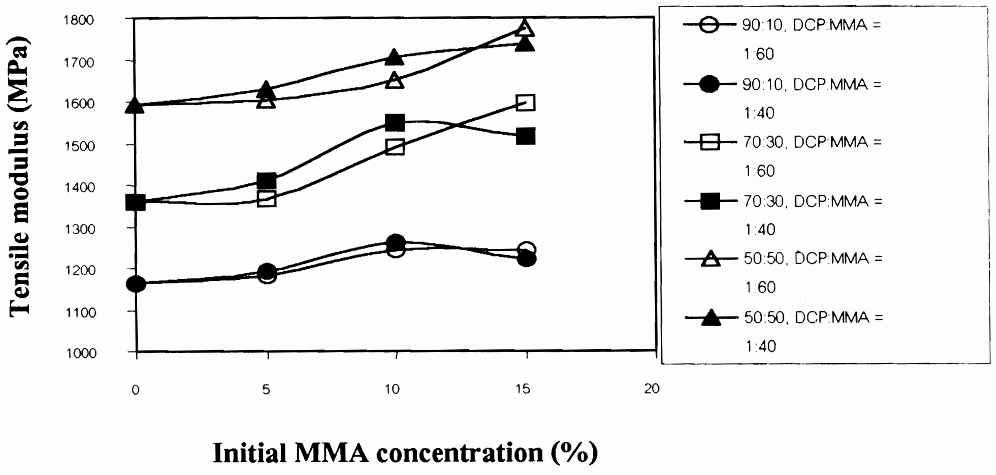


**Figure 9** Tensile modulus of HDPE/PVC blends with DCP and MMA.

Tensile modulus of the HDPE/PVC/MMA blend (Figure 9) increases with PVC content (a rigid phase) and MMA content indicating better adhesion between two phases by MMA-g-HDPE (see Figure 7). In other words, PVC and PMMA is miscible to some extent (Dompas, *et al. 1997*) and due to this miscibility induced by MMA-g-HDPE and PVC, it makes HDPE/PVC blend compatible. However, the high DCP and MMA content leads to gel formation (0.25 %wt obtained at 1:40 DCP:MMA for 15 %initial MMA by refluxing with *o*-dichlorobenzene) causing reduced modulus. The increment of tensile modulus due to high ratio of DCP and MMA is more obvious at high PVC content due to better interaction between MMA and PVC.

## Conclusions

Reactive blending of polyethylene with small reactive molecules (MA and MMA) can be performed either with or without initiator dependent on reaction mechanisms. The reaction products act as *in-situ* compatibilizer to enhance adhesion and reduce interfacial tension between the two phases. The reactive blending produces compatibilized polymer blends and composites which can bring about improved physical and mechanical properties.

Addition of MA to the LLDPE/NR blends strongly affected the melt viscosity and morphology of LLDPE/NR blends. The size of NR dispersed phase decreased while the melt viscosity increases with increasing MA content. Molecular orientation and mechanical properties including impact resistance of the binary blend LLDPE/NR are weaker than those of pure LLDPE, but these properties can be enhanced by varying DR and the reaction with MA. Modulus of HDPE/PVC/MMA increases with PVC and DCP:MMA content. For HDPE/SF blends the one pot blending is relatively better than two-step blending.

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