

EFFECTS OF GRAFTING ON PROPERTIES OF LOW DENSITY POLYETHYLENE

By

Muhammad Sarfraz*, Sajid Naseem and M. Aamir Shehzad

Abstract

In order to improve essential properties of polyethylene, polar monomers such as acrylic acid, acryl amide, and methacrylic acid can be introduced onto polyethylene. In this work binary mixture of methacrylic acid and styrene monomers, in presence of benzoyl peroxide as an initiator, were grafted onto low density polyethylene. Characterization of the grafted polyethylene was accomplished using Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimeter (DSC), and melt flow indexer (MFI). Presence of carbonyl peaks in the spectra of grafted polyethylene, low MFI value as compared to pure polyethylene, and higher endothermic peaks in thermogram of grafted polyethylene affirmed grafting of methacrylic acid and styrene onto polyethylene. MFI values at different loads further led towards the rheological study of virgin and grafted polyethylene grades.

Keywords: polyethylene, grafting, rheology, differential scanning calorimeter (DSC), Fourier transform infrared (FTIR)

1. PAPER OBJECTIVE

Polyolefins are not only abundantly employed as cheap thermoplastics possessing much improved bulk characteristics but also in a wide range of commodity applications^[1-5]. Although they are versatile, but the lack of some special surface properties e.g. printability, poor dispensability with inorganic fillers, hydrophilicity, lubricity, roughness, wettability, and selective permeability are not present in these worthy commercial thermoplastics on account of their inertness as well as non-polar nature^[2-3]. These deficiencies limit the application of these beneficial materials for special uses such as printed circuit, coating for diffusion barrier, coating for decorative purposes, membrane separation, conducting polymers etc.^[5-6]. For these reasons comprehensive studies have been made on surface modification techniques of polyolefins during last fifty years^[7].

A wide variety of modification theories and techniques e.g. blending, copolymerization, grafting, and curing have been nominated to successfully modify the surface of polyolefins. The existing modification techniques of polyolefins emphasize grafting as an enthralling method to chemically attach a number of functional groups on to the backbone chain of polyolefins^[6, 8-9]. A number of researchers have contributed to develop novel co-polymerization techniques by grafting different monomers on to the polyolefin backbone. Amongst the notable techniques chemical, radiation, photochemical, plasma-induced and enzymatic grafting are of great value^[6]. The present research work engages free radical grafting of two monomers i.e. methacrylic acid and styrene on to polyethylene main chain by using benzoyl peroxide as an initiator. Number of researchers^[10-13] has reported chemical grafting of exclusively one monomer on to polyethylene but minor work has been done on binary monomer mixture grafting especially by using a mixture of two monomers namely methacrylic acid and styrene.

2. EXPERIMENTAL

2.1. Materials

Fundamental materials utilized in these experiments were low density polyethylene (LDPE), methacrylic acid (MAA), styrene, and benzoyl peroxide (BPO). This particular LDPE grade, having MFI of 0.7 (g/10min) and specific gravity of 0.94-0.97, plays the role of base polymer and

*Department of Polymer & Process Engineering, University of Engineering & Technology, Lahore-Pakistan.

was imported from Qatar Petrochemical Company Ltd. 98% pure methacrylic acid used as monomer was obtained from Acros Organic. Co-monomer styrene of 99% purity was furnished by Alfa Aesar. Benzyl peroxide (98% pure) used as initiator was taken from Sigma Aldrich.

2.2. Synthesis of grafted polyethylene

Weighed amounts, as cited in Table 1, of all ingredients exclusive initiator were charged into a round bottom flask equipped with a stirrer. The whole mixture was heated up to 93 °C. As soon as the required temperature was attained the initiator was added to the mixture and thorough agitation was carried out. The mixture was kept on agitating for a time period of 3 hours at the reaction temperature. After the reaction completion, grafted product was purified by first washing with 0.1 N NaOH solution, dried, and then washed with distilled water. To neutralize any alkaline contents, material was then washed with 0.1 N HCl solution, dried and then again washed with distilled water. The sample is then finally dried in an oven at 110 °C and further analysis was carried out.

Table 1: Grafting mixture composition

Materials	Amount	
	Phr	%
PE	100	48.8
Methacrylic acid	30	14.6
Styrene	3.5	1.7
BPO	1.5	0.7
Water	70	34.1
Total	205	100

2.3. FTIR spectroscopy

The FTIR spectrums were recorded on JASCO FT/IR-4100 infrared spectrometer. Potassium bromide was used as an inert background material to get the spectra of both pure and grafted samples of polyethylene. The analysis was done in the region of 400 to 4000 cm^{-1} .

2.4. Differential scanning calorimetry

Thermograms were obtained at heating rate of 10 °C min^{-1} in Shimadzu DSC 60-A apparatus. Both pure and grafted samples were analyzed against aluminum as reference material. The temperature range for the experiment was selected to be 180 °C.

2.5. Rheological testing

MFI of the grafted and pure samples were determined by using KARG Industrietechnik apparatus according to ASTM D 1238-04 varying load from 2.16 to 21.6 having die diameter of 2.095 mm under temperature of 190 °C.

3. RESULTS & DISCUSSION

3.1 FTIR spectroscopy

Quantitative proof of the grafting of methacrylic acid and styrene monomers onto polyethylene is provided by the infrared spectroscopy. Figure 1 demonstrating FTIR spectrum of virtuous polyethylene clearly indicates methylene group rocking and session vibrations at characteristic peaks of 721 and 1642 cm^{-1} respectively. In addition symmetric and asymmetric methylene group stretching was observed at characteristic peaks of 2844 and 2918 cm^{-1} respectively.

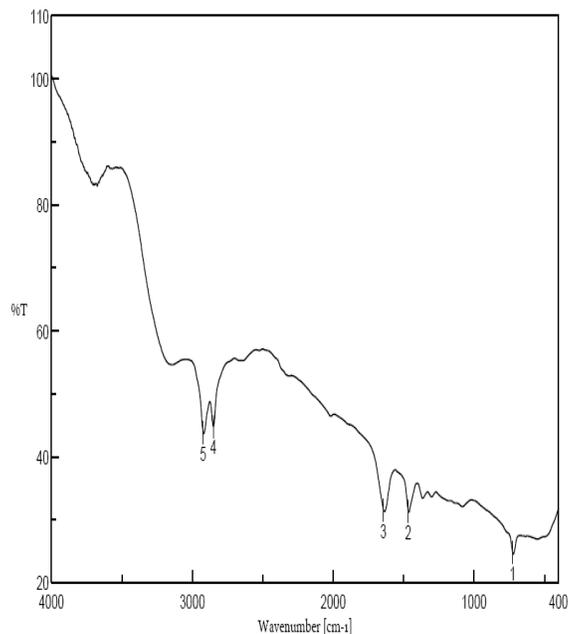


Figure 1: FTIR spectrum of ungrafted polyethylene

In Fig. 2, the spectrum of grafted polyethylene, the characteristic peak observed at 1697 cm^{-1} is of vital importance which affirms the presence of carboxylic (-COOH) group. This COOH group peak is due to the compoment of methacrylic acid confirming grafting of methacrylic acid onto polyethylene backbone chain.

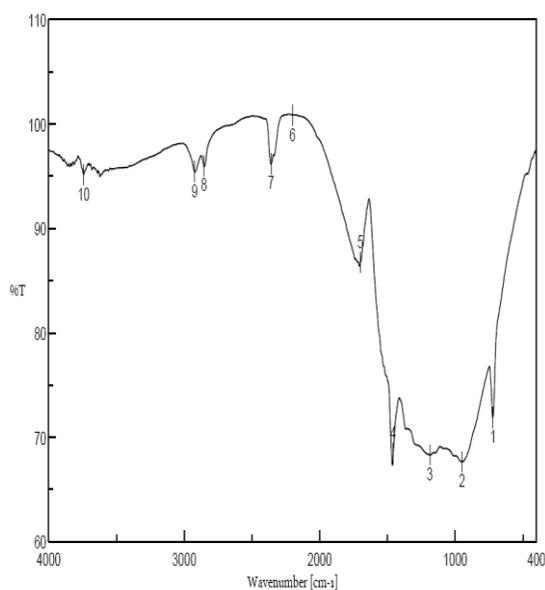


Figure 2: FTIR spectrum of grafted polyethylene

3.2 Differential scanning calorimetry

Figure 3 shows thermograms of ungrafted and grafted polyethylene grades. From this melting peak of LDPE was found to be 110.09°C while for grafted polyethylene melting point was observed at 111.15°C which is higher than that of the ungrafted polyethylene. This increase in melting point can be attributed to the presence of polar groups generated after grafting. Another important point is that this change in melting point, however, is relatively low and can be ascribed to low level of grafting. On a molecular level, the grafted chains are relatively difficult to move, rotate, and oscillate as compared to ungrafted ones; thus elevating the melting point of

the grafted material. Another interesting point to be noted here is that the portion of thermogram of grafted polyethylene prior to melting point peak is not as smoother as that in case of ungrafted polyethylene. This non-uniformity can be ascribed to early movement of grafted side chains; which means a little bit more amount of energy is required for the movement of grafted side chains before the movement of main chains. Conversely, we can infer two types of movements of the chains are occurring there: (a) those of small grafted acrylic acid and styrene side chains; (b) those of main backbone chains. In the first case a small quantity of heat is absorbed to melt the smaller side chains, but a large quantity of heat is engaged in the second case.

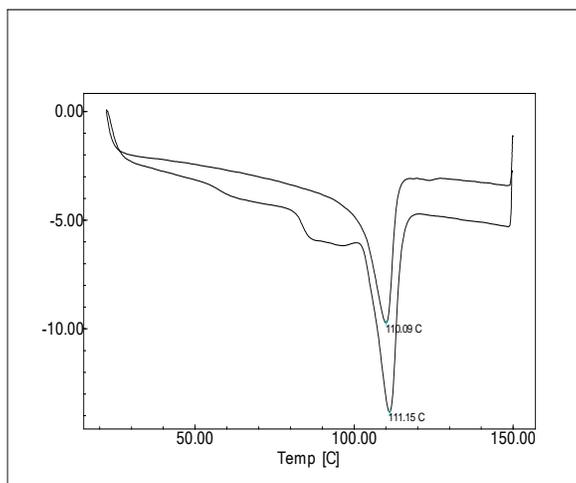


Figure 3: DSC curves of (a) virgin polyethylene (*upper curve*) and (b) grafted polyethylene (*lower curve*)

3.3 Rheological properties

Rheological measurements are very important for quality control of raw materials, optimization of manufacturing processes and forecasting the performance of a material [14]. Melt flow index (MFI) is a good indicator of flow properties of the material under consideration. Figure 4 shows MFI of both grafted and ungrafted polyethylene grades at different loads. It is evident from the Fig. that MFI value of ungrafted polyethylene is higher than those of grafted polyethylene under the same test loads. This decrease in MFI of LDPE after grafting is associated with the greater degree of branching of grafted polyethylene as compared to ungrafted counterpart. Presence of branches diminishes the flow properties in polyethylene up to much extent. This drop off in MFI is also an indication of efficient grafting of MAA and styrene on polyethylene.

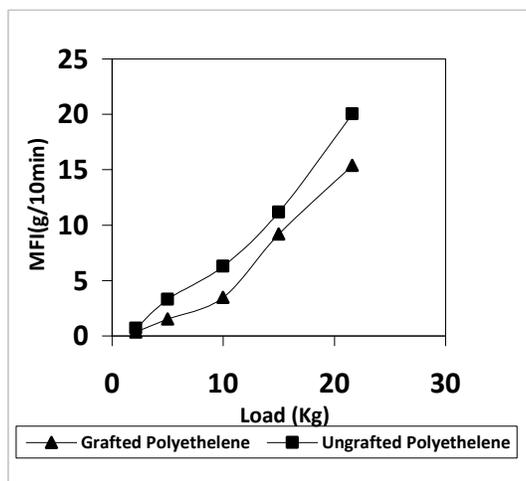


Figure 4: MFI of pure and grafted LDPE as a function of load

Shear stress and strain rate can be calculated by using Eqs. (1) and (2) respectively ^[14]:

$$\tau = \frac{R_N F}{2\pi R_p^2 L_N} \quad (1)$$

$$\gamma = \frac{4Q}{\pi R_N^3} \quad (2)$$

where R_N is the radius of nozzle (0.105 cm), L_N is nozzle length (0.8 cm), R_p is piston radius (0.4737 cm), Q is flow rate (cm^3/sec) and F is test load ($\text{kg} \times 9.087 \times 10^5$ dyne). Stress strain curves obtained from MFI data are represented in Fig. 5. By increasing the strain rate, stress for both the grafted as well as ungrafted polyethylene increases accordingly, the relative difference between stresses for grafted and ungrafted counterparts being small at zero strain rate. But as the strain rate exceeds zero, grafted polyethylene requires extra amount of stress than its ungrafted counterpart to make the same amount of deformation. In case of grafted polyethylene, resistance offered by ungrafted chains to flow and deform is the major reason of higher stress value. It is evident from Fig. 5 that the behavior of both grafted and virgin polyethylene resembles pseudoplastic with yield stress.

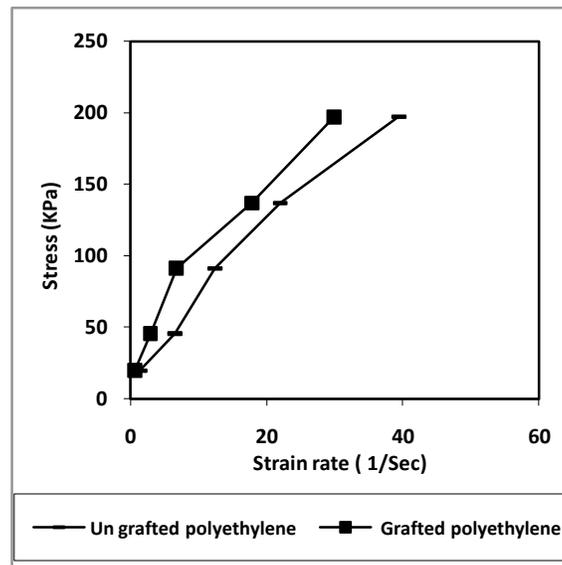


Figure 5: Strain rate (sec^{-1}) as a function of stress (kPa)

For the case of flow polymer through circular die, a correction is normally applied to take into account the pseudoplasticity of the melt which implies that the assumed parabolic profile in the die actually illustrates more plug flow behavior ^[15]. This correction is generally expressed as:

$$\gamma_{true} = \frac{4Q}{\pi R^3} \frac{(3n+1)}{4n} \quad (3)$$

Viscosity can be calculated from the Eq. (4):

$$\eta_a = m \gamma^{n-1} \quad (4)$$

Dependence of true viscosity on true strain rate is illustrated in Fig. 6. From the Fig. it is apparent that viscosity decreases with the increase in strain rate for both the virgin as well as grafted polyethylene grades. The viscosity of grafted polyethylene is approximately one and half times the viscosity of virgin counterpart at zero strain rate.

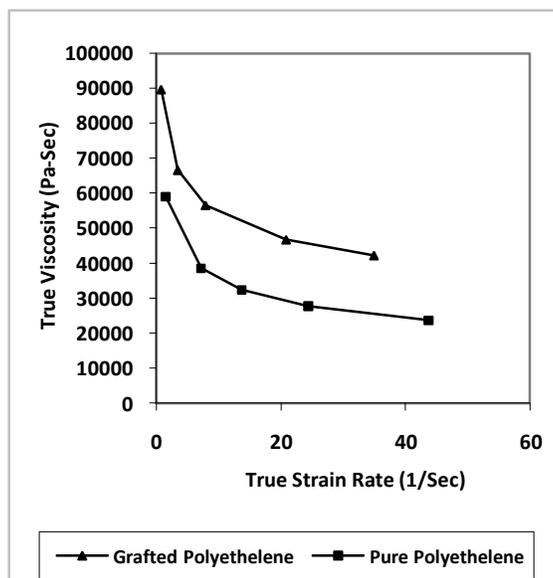


Figure 6: True strain rate (sec^{-1}) as a function of true viscosity (Pa-sec)

Although the magnitude of viscosity for both the grades varies with strain rate, relative difference between the viscosity of grafted and pure polyethylene counterparts remains almost same for the entire range of strain rate. Higher viscosity of grafted polyethylene than virgin polyethylene is attributed to the presence of branches in grafted polyethylene which offer more hindrance to align themselves in flow direction on applying stress as compared to the more flexible straight chains in ungrafted polyethylene. Grafted chains make some sort of physical entanglements among themselves which stand firm against applied stress, thus increasing melt viscosity. This decrease in viscosity with increasing strain rate reveals rheopectic behavior for both the grades, the grafted polyethylene demonstrating more rheopecticity (fluid consistency index = 0.6) than the virgin polyethylene counterpart (fluid consistency index = 0.7).

4. CONCLUSION

From above discussion it can be inferred that reasonable grafting can be achieved by using binary monomer mixture of styrene and methacrylic acid. FTIR analysis shows presence of COOH group in grafted polyethylene confirming grafting of methacrylic acid and styrene. Rheological properties have been changed due to grafting process which is indicated by lower value of MFI of grafted polyethylene as compare to virgin polyethylene. For same strain rate, higher stress is required for grafted polyethylene as compared to virgin polyethylene due to resistance in flow offered by branched chains. Viscosity also increases by introduction of branches. From DSC analysis it is concluded that melting point of polyethylene increases after grafting.

5. ACKNOWLEDGEMENT

The author is thankful to the Department of Polymer and Process Engineering, University of Engineering and Technology Lahore-Pakistan for furnishing laboratory equipment and related chemicals and materials.

6. NOMENCLATURE

F	test load	kg
L_N	nozzle length	cm
m	fluid consistency index	N-sec-m^{-2}
n	fluid behavior index	dimensionless
Q	flow rate	cm^3/sec
R_N	radius of nozzle	cm
R_P	piston radius	cm

Greek letter

$\dot{\gamma}$	strain rate	sec^{-1}
$\dot{\gamma}_{\text{true}}$	true strain rate	sec^{-1}
η_a	true or apparent viscosity	kP-sec
τ	shear stress	kPa

7. REFERENCES

- [1]. Daniel J. Burnett, Frank Thielmann, Rose A. Ryntz, Correlating thermodynamic and mechanical adhesion phenomena for thermoplastic polyolefin, Springer Boston, 2007.4(2):PP 211-215.
- [2]. Shrojal M. Desai, R. P. Singh, Advances in polymer science, Springer Berlin / Heidelberg, 2004.169: PP 231-294
- [3]. S. K. Singh, S. P. Tambe, A. B. Samui, V. S. Raja, Dharendra Kumar, Maleic acid grafted low density polyethylene for thermally sprayable anticorrosive coatings, Progress in organic coatings, 2006.55(1):PP 20-26
- [4]. Gilberto de O. Meraes, Adriana N. Geraldos, Heloisa A. Zen, Duclerc F. Parra, Ademar B. Lugao, Preliminary study of styrene grafting on Polyethylene films, International Nuclear Atlantic Conference ,2007
- [5]. A. Shojaei, R. Fathi, N. Sheikh, Adhesion modification of Polyethylene for metallization using radiation induced grafting of vinyl monomers, Surface & coating technology, 2007.201: PP 7519-7529
- [6]. A. Bhattacharya, B. N. Misra, Grafting; a versatile means to modify polymers techniques, factors and applications, Progress in polymer science, 2004.29: PP 767-814
- [7]. Franjo Ranogajec, Effect of solvent on radiation grafting and crosslinking of polyethylene, Radiation physics & chemistry, 2007.76: PP 1381-1384
- [8]. Yoshikimi Uyama, Koichi Kato and Yoshito Ikada, Surface modification of Polymers by grafting, Advances in polymer science, Springer Berlin/Heidelberg, 1998.137: PP 1-39
- [9]. A. Baran Teke, S. Hamarat Baysal, Immobilization of urease using glycidyl methacrylate grafted nylon-6 membranes, Process biochemistry, 2007.42: PP 439-443
- [10]. K Yamada, T Kimuro, H Tsutaya, M. Hirata, Hdrophilic and adhesive properties of methacrylic acid grafted polyethylene plates, Journal of applied polymer science, 2003.(44)1: PP 993-1001
- [11]. Ging-Ho Hsiue, Wen-Kuei Huang, Preirradiation grafting of acrylic and methacrylic acid onto polyethylene films: Preparation and properties, Journal of applied polymer science, 2003(30) 3: PP 1023-1033
- [12]. J. P. Lawler, A Charlesby, Grafting of acrylic acid onto polyethylene using radiation as initiator, Radiation physics & chemistry, 1980.(15)5: PP 595-602
- [13]. O. N. Tretinnikov, Analysis of photo induced graft polymerization of acrylic acid onto polyethylene films by attenuated total reflectance IR spectroscopy, Journal of applied spectroscopy, 2010.(76)6: PP 898-901
- [14]. Shenoy AV and Saini DR, Thermoplastic melt rheology and processing, CRC Press, 1996
- [15]. Cogswell F. N, Polymer melt rheology : a guide for industrial practice, G. Godwin, 1981