Development of Grafted PE/EVA Nanoclay Composites for Elastomeric Coating Applications

R. Kartik, K. Pavithra

Keywords:

UHMWPE, EVA, MAH, Nanoclay-30B. Elastomeric Coating Applications

Abstract:

Generally to facilitate interaction with a polymer, clay is modified with alkyl ammonium to render the hydrophilic surface, organophilic. However, this organically modified clay does not disperse well in PE (polyethylene) due to its non-polar nature. In this paper, this dispersion is effected by blending PE with EVA (Ethyl Vinyl Acetate). UHMWPE (Ultra High Molecular Weight Polyethylene) was blended with EVA in the ratio of 90:10, 70:30 and 50:50 for imparting polar characteristics to the polyolefin. Due to the immiscibility, 3, 5, 8% of MAH (Maleic Anhydride) was added as the compatibilizer to the above UHMWPE/EVA blendings. The nanoclay, Cl-30B was then added up-to 4%, starting from 1%, to the same. This blending drastically altered the mechanical and the morphological properties. Among the various compositions, optimality was observed for an elastomeric nature. The 70:30 UHMWPE/EVA with 5% MAH and 3 % Cl-30B nanocomposite was found to be optimum in terms of elastomeric nature. It may be potentially used as coatings in the automobile and the marine industry.

Introduction

PE is one of the most widely used polyolefin. However, due to the absence of any polar group in the backbone, the homogeneous dispersion of organically modified (using alkyl ammonium) clay minerals in PE is not realized.

Recently, Jeon reported the intercalated morphology of HDPE (High Density PE) nanocomposites prepared by blending HDPE with naturally modified clay cations, exchanged with protonated dodecylmine in solution. However the presence of fairly large stack indicated poor dispersion. Only when insitu polymerization was performed, PE/clay nanocomposite showed exfoliated morphology [1]. Thus, search continued to find an economical, commercially viable method for the production of PE/clay nanocomposites.

In this paper, a novel idea to create the PE/clay nanocomposites by blending PE and EVA (Before clay dispersion) that may be used for elastomeric coating applications is proposed.

Experiments

UHMWPE/EVA blends in different compositions (90/10, 70/30 and 50/50 wt %) were prepared and designated as UHMWPE/EVA. Grafting percentage was then calculated to ensure uniform grafting [2]. Later, it was melt mixed with 3, 5 and 8 wt% MAH and 1% DCP (Dicumyl Peroxide), designated as Maleic Anhydride grafted UHMWPE/EVA. These direct melt compoundings were carried out in Haake torque rheometer at a rotor speed of 30 rpm and set temperature of 160^{o}c. The UHMWPE/EVA and Maleic Anhydride grafted UHMWPE/EVA were individually melt mixed with the nanoclay-30B, dried in vacuum oven at 60^{o}c, in Haake torque rheometer. Preheating was done to 160^{o}c and the rotor speed was maintained at 5 rpm for about 1 min and then increased gradually to 30 rpm in 60 seconds. This mixing was continued for 15 min, after which, the molten composites were extracted and cooled naturally in air. The two classes of nanocomposites were designated UHMWPE/EVA nanocomposites and Maleic Anhydride grafted UHMWPE/EVA nanocomposites respectively.

The Tensile properties and Elongation at Break, under ASTM D 638 (Type IV specimen), and Flexural Strength, under ASTM D 790, were determined using the Instron UTM. The Impact properties, under ASTM D 256, were determined using a

Tinus olesen model impact 104 (6.8 J hammer and 3.5 m/s impact velocity). On the other hand, the SEM analysis of the impact fractured surface of the specimen was carried out using CARL ZEISS Model; EVO MA 15 scanning electron microscope after coating of the sample with conductive gold using palladium alloys.

Results and Discussions

The amount of EVA, MAH and nanoclay-30B drastically affected the mechanical properties.

As the EVA content in the UHMWPE/EVA blend increased, the tensile, flexural strength and the modulus was found to be decrease. But, the elongation at break and the impact strength increased. This is attributed to the elastomeric nature of EVA.

The addition of MAH and nanoclay-30B to the above blendings, both individually and together, showed a similar response. The tensile, flexural strength and the modulus decreased while the elongation at break and the impact strength increased. These discussions are evident from the Tables, 1 and 2.

Considering the composition analysis, the 70:30 ratio of the UHMWPE/EVA blend had the most optimality in terms of elastomeric nature-Decreased Tensile and Flexural Strength and Modulus, Increased Elongation at Break, Increased Impact Properties. Addition of 5% MAH and 3% Cl-30B amplified this elastomeric response. Hence 70:30 UHMWPE/EVA + 5% MAH + 3% Cl-30B may be rendered to be the most optimum composition.

TABLE 1

TENSILE STRENGTH OF U/EVA, U/EVA WITH NANOCLAY AND U/EVA+5% MAH WITH NANOCLAY

S.No	Sample Identification	Tensile strength MPa	Elongation at break (%)	Tensile Modulus MPa
1	U/EVA (90-10)	6.41853	3.028	-
2	U/EVA (70-30)	2.04457	22.968	-

3	U/EVA (50-50)	2.68465	44.01032	-
4	U/EVA+ 3% MAH (90-10)	4.5	45	-
5	U/EVA+ 3% MAH (70-30)	2.3	2.3	-
6	U/EVA+ 3% MAH (50-50)	3.3	58	-
7	U/EVA+ 5% MAH (90-10)	5.47845	52.5587	-
8	U/EVA+ 5% MAH (70-30)	3.0117	3.556	-
9	U/EVA+ 5% MAH (50-50)	4.28853	64.84383	-
10	U/EVA+ 8% MAH (90-10)	3.6	46	-
11	U/EVA+ 8% MAH (70-30)	2.6	2.3	-
12	U/EVA+ 8% MAH (50-50)	2.3	59	-
13	U/EVA + 1% 30B(90-10)	4	1.2	210
14	U/EVA + 1% 30B(70-30)	2.3	28	45
15	U/EVA + 1% 30B(50-50)	1.6	110	19
16	U/EVA+ 2% 30B(90-10)	4.5	2.5	255
17	U/EVA+ 2% 30B(70-30)	2.8	39	68
18	U/EVA+ 2% 30B(50-50)	1.8	152	25
19	U/EVA+ 3% 30B(90-10)	5	3.948	274.99567

20	U/EVA+ 3% 30B(70-30)	3.1	60.83733	70.4626
21	U/EVA+ 3% 30B(50-50)	2.3	157.44093	28.66327
22	U/EVA+ 4% 30B(90-10)	4.2	3.5	256
23	U/EVA+ 4% 30B(70-30)	2.4	55	62
24	U/EVA+ 4% 30B(50-50)	1.6	145	24
25	U/EVA+ 5% MAH+ 1% 30B(90-10)	6.5	4.3	198
26	U/EVA+ 5% MAH+ 1% 30B(70-30)	3.1	18	69
27	U/EVA+ 5% MAH+ 1% 30B(50-50)	1.8	25	55
28	U/EVA+ 5% MAH+ 2% 30B(90-10)	7.3	4.8	245
29	U/EVA+ 5% MAH+ 2% 30B(70-30)	3.2	29	75
30	U/EVA+ 5% MAH+ 2% 30B(50-50)	2	29	66
31	U/EVA+ 5% MAH+ 3% 30B(90-10)	8.83116	6.72	268.969
32	U/EVA+ 5% MAH+ 3% 30B(70-30)	3.55787	35.004	74.36
33	U/EVA+ 5% MAH+ 3% 30B(50-50)	2.92667	39.8978	72.85586
34	U/EVA+ 5% MAH+ 4% 30B(90-10)	8	5.69	258

35	U/EVA+ 5% MAH+ 4% 30B(70-30)	3.2	30	70
36	U/EVA+ 5% MAH+ 4% 30B(50-50)	1.9	35	65

TABLE 2

FLEXURAL AND IMPACT STRENGTH OF U/EVA, U/EVA WITH NANOCLAY AND U/EVA+5% MAH + NANOCLAY

S.No	Sample Identification	Flexural Strength MPa	Flexural Modulus MPa	Impact properties J/m
1	U/EVA (90-10)	11.48105	406.18817	39.0535
2	U/EVA (70-30)	2.59655	69.9178	79.5452
3	U/EVA (50-50)	6.01176	20.06887	62.17
4	U/EVA+ 3% MAH (90-10)	5	83	146
5	U/EVA+ 3% MAH (70-30)	10	5	43
6	U/EVA+ 3% MAH (50-50)	4	22	126
7	U/EVA+ 5% MAH (90-10)	5	85	150.224
8	U/EVA+ 5% MAH (70-30)	11	325	55.63023
9	U/EVA+ 5% MAH (50-50)	4.5	21	142.418
10	U/EVA+ 8% MAH (90-10)	5	10	142
11	U/EVA+ 8% MAH (70-30)	11	290	48
12	U/EVA+ 8% MAH (50-50)	5	15	136
13	U/EVA + 1% 30B(90-10)	7.3	285	15
14	U/EVA + 1% 30B(70-30)	2.1	96	85.6

15	U/EVA + 1% 30B(50-50)	1.5	35	92
16	U/EVA + 2% 30B(90-10)	8.4	296	17
17	U/EVA + 2% 30B(70-30)	2.9	104	92.3
18	U/EVA + 2% 30B(50-50)	1.6	40	95
19	U/EVA+ 3% 30B(90-10)	9.5	325	20.68495
20	U/EVA+ 3% 30B(70-30)	3.45556	108	119.84875
21	U/EVA+ 3% 30B(50-50)	1.8897	42	149.84875
22	U/EVA+ 4% 30B(90-10)	7.6	320	18
23	U/EVA+ 4% 30B(70-30)	3.1	103	113
24	U/EVA+ 4% 30B(50-50)	1.6	39	168
25	U/EVA+ 5% MAH+ 1% 30B(90-10)	7.36	265	35
26	U/EVA+ 5% MAH+ 1% 30B(70-30)	2.36	105	110
27	U/EVA+ 5% MAH+ 1% 30B(50-50)	1.2	18	163
28	U/EVA+ 5% MAH+ 2% 30B(90-10)	7.9	302	39
29	U/EVA+ 5% MAH+ 2% 30B(70-30)	3.6	110	128
30	U/EVA+ 5% MAH+ 2% 30B(50-50)	1.7	22	172
31	U/EVA+ 5% MAH+ 3% 30B(90-10)	10.25766	311	42.22995
32	U/EVA+ 5% MAH+ 3% 30B(70-	4.8093	114	131.04925

	30)			
33	U/EVA+ 5% MAH+ 3% 30B(50-50)	1.48467	24	185.13
34	U/EVA+ 5% MAH+ 4% 30B(90-10)	6	308	40
35	U/EVA+ 5% MAH+ 4% 30B(70-30)	3.2	100	127
36	U/EVA+ 5% MAH+ 4% 30B(50-50)	1.2	20	175

Morphology is one of the key factors in determining the mechanical properties of the material. For the comparative morphological studies, the SEM images of the composition 90:10, 70:30, 50:50 with optimum amounts of MAH (5%) and nanoclay-30B (3%) were studied.

From the figures 1 and 3, it is evident that the UHMWPE/EVA and UHMWPE/EVA nanocomposite exhibited poor mixing and compatibility. However, in the figure 2, corresponding to Maleic Anhydride grafted UHMWPE/EVA, the compatibilization is clearly visible. Yet the compatibilized blend still had partial miscibility and compatibility only. The figure 4 corresponds to Maleic Anhydride grafted UHMWPE/EVA nanocomposite. Therein, comparatively best instances of good mixing and compatibility characteristics were found. Yet, in the composition 50:50, needle (or) thread like structures were found. This is accounted by the presence of unreacted compatibilizer which results in poor morphology and inferior mechanical properties. Simultaneously, the 90:10 composition showcased poor properties. Also, any phase separation would be masked by the dominant PE matrix. Hence, both the compositions, Viz. 90:10 and 50:50, may be rendered sub-optimum. The 70:30 ratio, on the other hand, may be considered to have optimum properties.

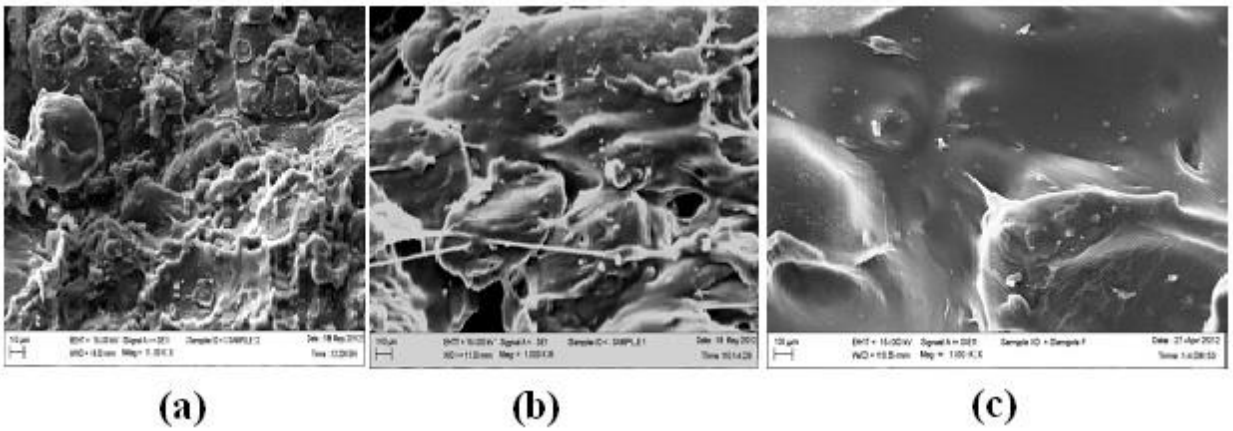

Fig. 1 SEM analysis of UHMWPE-EVA with ratio of (a) 90:10, (b) 70:30, (c) 50:50.

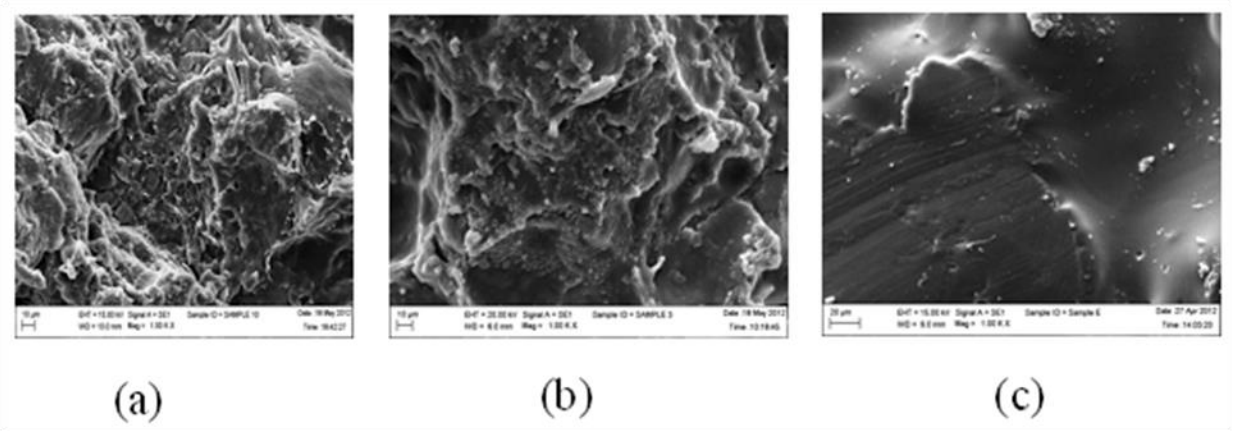

Fig. 2 SEM analysis of UHMWPE-EVA-MAH (5%) with ratio of (a) 90:10, (b) 70:30, (c) 50:50.

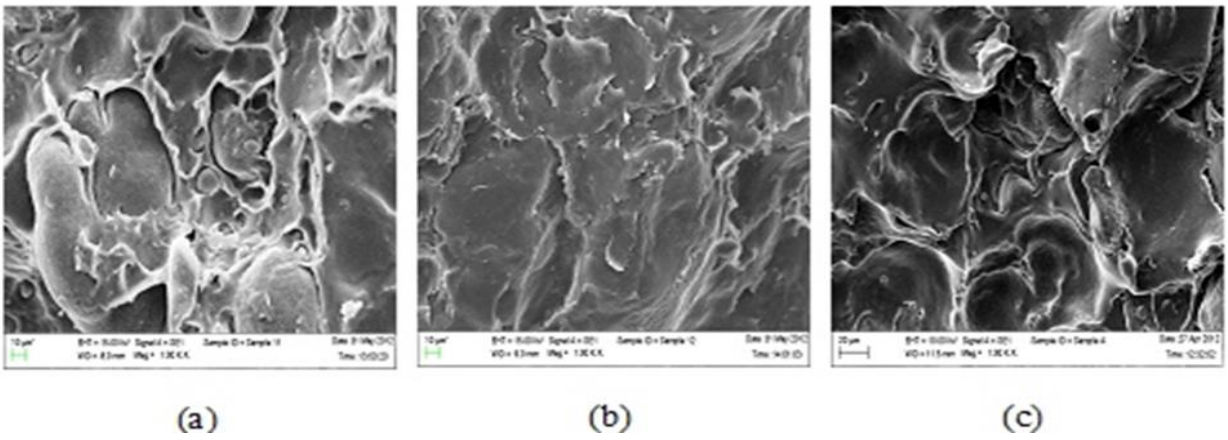

Fig. 3 SEM analysis of UHMWPE-EVA-30B (3%) with ratio of (a) 90:10, (b) 70:30, (c) 50:50.

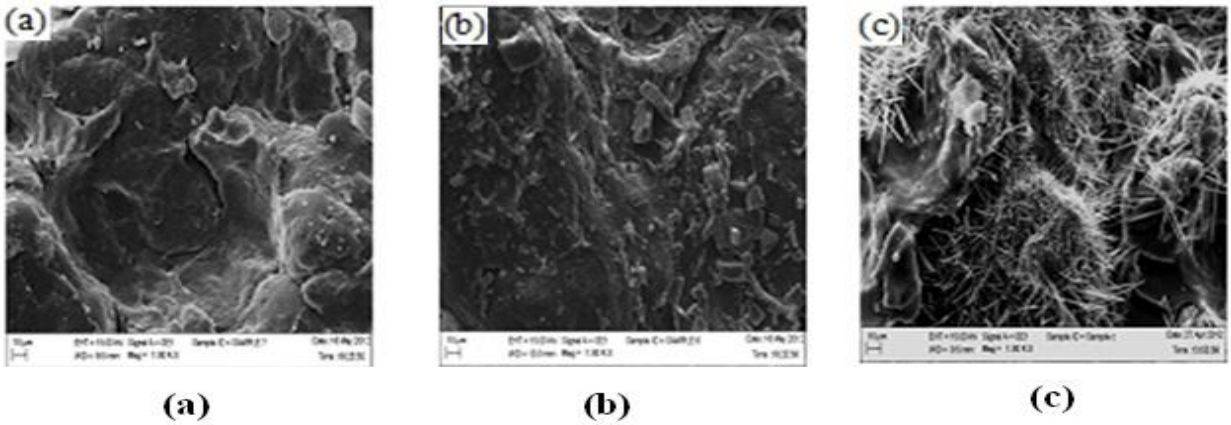

Fig. 4 SEM analysis of UHMWPE-EVA-MAH (5%)-30B (3%) with ratio of (a) 90:10, (b) 70:30, (c) 50:50.

Potential Applications as Coatings

The above Grafted UHMWPE/EVA nanoclay Composites, esp. the optimum 70:30 UHMWPE/EVA + 5% MAH + 3% Cl-30B, may be potentially used as coatings due to their elastomeric nature. They may be

of a huge demand in the automobile and the marine industries.

Conclusion

In this study, UHMWPE-EVA blends were examined in terms of tensile, flexural, impact and morphology along with the addition of the compatibilizer (MAH) and nanoclay-30B in various compositions. The addition of EVA, MAH and nanoclay, Cl-30B, had shown considerable improvement in the elastomeric properties. Among all the compositions, 70:30 UHMWPE/EVA blended with 5% MAH and 3% Cl-30B was found to be the most optimum.

These blends may be used in elastomeric coating applications in the automobile and the marine industries.

REFERENCES

1. Messersmith PB et.al, 1995, Usuki A et.al, 1993, Kojima Y et.al, 1993, Yano K et.al, 1993, Vaia RA et.al, 1995, Biasci L, 1994, Giannelis EP et.al, 1996, Jeon HG, 1998.
2. S.K.Singh,"*Maleic acid grafted low density polyethylene for thermally sprayable anticorrosive coatings"*, Prog. Org. Coat.60 186, (2007)
3. PB. Messermist, EP. Giannelis, *J. Poly. Sci. a: Poly .Chem*, 33,1047 (1965).
4. A. Usuki, T. Kawasum, M. Kojima, Y. Fukushima, A. Okada, T. Kurauchi, O. Kamigaito, *J. Mater. Res*., 8, 1179 (1993).
5. Y. Kojima, A. Usuki, M. Kawasumi, Y. Fukushima, A. Okada, T. Kurauchi, O. Kamigaitor, *J. Mater.Res*., 8,1179 (1993).
6. Jm. Yabi, Am. Ysyju, A. Ijada, T. Kurauch, O. Kamigator, *J. polym. Sci. Part a; polym. chem*., 31, 2493 (1993).
7. RA. Vaia, KD. Jandt, Ej. Kramer, Ep. Giannelis, *Macromoleucules*, 28, 8080 (1995).
8. L. Biasci, M Agliettoe, G. Ruggeri, GF. Ciaredelli, *Polyme*. , 35,3296 (1994).
9. EP. Giannelis, *Adv. Mater*., 8,29 (1996).
10. HG. Jeon, HT. Jung, SW. lee, SD. Hudson, *Poly. Bull*., 41, 10 (1998).

About Authors

- **Kartik R.** was born in New Delhi on 15th of October 1992. He is currently pursuing his bachelors in plastics technology in CIPET, Chennai, India and shall earn his degree in the year 2014.

He has undergone In-Plant Training in many industries to gain knowledge about the processes in the plastic trade. Also his main areas of interest include bioresorbable and biodegradable polymers; synthesis of plastics and their characterization.

Mr. Kartik had also presented review papers and posters in notable conferences and symposiums. His review work on "Bioresorbable Scaffolds" won him the "best student poster" award in the international conference "APM 2012" and also a "2nd prize for paper presentation" in the national level technical symposium "MACRON' 12" organized by B.S. Abdur Rahman University, Chennai, India. He is an ardent follower of application of plastics in the medical industry.

- **Pavithra K**. was born in Gudamalai, Salem district on 25th of November 1994. She is currently pursuing his bachelors in plastics technology in CIPET, Chennai, India and shall earn her degree in the year 2015.

She has also undergone In-Plant Training in many industries to gain knowledge about the processes in a plastic trade. Her main areas of interest include Liquid Crystalline Polymers (LCP), Optoelectronic polymers and synthesis and characterization of blends.

Ms. Pavithra is an ardent participant in many technical symposiums and conferences. Her review poster on "Scaffold Technology" won her a "2st place" in the national level technical symposium "Elastoplaz' 13" organized by MIT, Chennai..