Enhanced Mechanical Properties of Organo-Clay Based UHMWPE Nanocomposite Films

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Abstract: The proposed study investigated the effect of organo-clay contents in ultra-high molecular weight polyethylene (UHMWPE) gel/solution cast films. The organo-clay was loaded in the range of 1 to 5 % (wt. / wt.), based on polymer content, to prepare UHMWPE nanocomposite films. The UHMWPE nanocomposite films were drawn up to 15 times below their melting point. Un-drawn and drawn UHMWPE nanocomposite films were subjected to mechanical and optical characterizations. The enhanced modulus (> 170 % higher than un-drawn films for 5 % organo-clay loadings at draw ratio of 15) and higher force at break (about 150 % higher than un-drawn films) without the loss of inherent optical transparency, even at higher organo-clay loadings, are reported. The findings in this study will broaden the engineering applications of UHMWPE nanocomposite films.

Keywords: UHMWPE, gel or solution casting, modulus, organo-clay, nanocomposite, mechanical properties.

INTRODUCTION

Polymer nanocomposites are made of two-phase systems consisting of polymers (continuous phase) and inorganic/organic fillers (dispersed phase) of which at least one dimension is in the nano-range (1 - 100 nm). The nanoparticles (or nano-fillers) can be one-dimensional nanotubes or nanofibers, two-dimensional clay platelets (layered silicates), or three-dimensional spherical particles [1-5].

The inherent high surface-volume ratio of the nanofillers renders excellent opportunity for the coincidence of fundamental physics, quantum effects, and the length scale of the morphology (nano) which is the basis for improved mechanical, chemical, thermal, magnetic, electrical, biodegradability, optical, scratch/wear resistance, barrier properties, reduced flammability, crystallization rate and functional properties of these nanocomposites, even at low loadings, in comparison to pristine polymers and conventional composites.

Layered silicates (inorganic clays) are the most commonly used inorganic nanoparticles in polymer nanocomposites. To facilitate the dispersion of these clays in the organic polymer matrices the cations present in the galleries of the clays are exchanged with organic surfactants and the resultant clays are generally called organo-clay. In contrast to phase separated composite (microcomposites), improved properties are reported for intercalated and exfoliated organo-clay nanocomposites [1, 2].

UHMWPE possesses excellent physical properties viz. high toughness, self-lubrication, high impact resistance, high abrasion resistance, high chemical resistance and biocompatibility. Among other methods of spinning, gel/solution spinning proved to be rather versatile and successful in producing high strength polyethylene structures, such as films, fibres and tapes [6-8]. In this process, solution spun/cast UHMWPE is drawn in a temperature range close to but below the melting temperature.

Although UHMWPE possesses many excellent properties but its poor adhesion to fillers, lower thermal stability, high melt viscosity and creep are the main hurdles for its vast spread engineering applications. Many researchers have shown that nanofillers can be incorporated into UHMWPE matrix via in-situ polymerization [9, 10], solution casting [11-17] and melt mixing [18-20] to improve thermal, mechanical, electrical, UHMWPE-filler adhesion, fluidity and reduce flammability of the pristine UHMWPE.

The main objective of this research is to add value to the UHMWPE fiber waste from various industries notabily from gloves industries. UHMWPE fiber (DSM Dyneema® fibers) was chopped into very small pieces (5-10 mm) to imitate the gloves industry fiber waste. The chopped fiber was solution casted into UHMWPE and UHMWPE nanocomposite films. The solution casted UHMWPE nanocomposite films showed substantially improved mechanical properties with the retention of inherent transparency of the drawn films. The UHMWPE nanocomposite films may find their

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ISSN: 1814-8085 / E-ISSN: 1927-5129/16

applications in high tech engineering owing to their enhanced mechanical properties in addition to optical transparency which will further broaden their applications.

EXPERIMENTAL

Materials

Ultra-High Molecular Weight Polyethylene (UHMWPE) used in this research was in the form of DSM Dyneema® fibers.

Organo-clay (Nanomer 1.44P MMT - Aldrich), an onium modified montmorillonite (MMT) containing 35 - 45 % dimethyl dialkyl amine as organic modifier, was used after drying at 80 °C for about 5 hours. Xylene (Merck) was used as received.

Preparation of UHMWPE Nanocomposite Films

UHMWPE and UHMWPE nanocomposite films were prepared by the method described below. However an additional step of organo-clay dispersion was needed for UHMWPE nanocomposite films. In all samples the concentration of UHMWPE gel/solution was kept constant to 1 % (W/V).

In the first step of UHMWPE nanocomposite films preparation, the organo-clay in the range 1 to 5 % was added to a sample vial containing xylene. The mixture was mixed under vigorous magnetic bead mixing conditions for about 6 to 8 hours. The mixing was stopped when clear organo-clay dispersion was observed.

In the next step, UHMWPE chopped fibres (5 to 10 mm in length), organo-clay dispersion and the additional volume of xylene were simultaneously charged in a three necked round bottom flask. The flask contents were heated gradually to 135 °C on a silicone oil bath under reflux conditions to avoid the loss of solvent vapor in the laboratory environment. The temperature was maintained for about 8 hours to obtain a clear gel/solution. The gel was poured into an aluminum tray and left for about 30 days which resulted in a uniform UHMWPE nanocomposite film. UHMWPE and UHMWPE nanocomposite films were further dried in a vacuum oven at 60 °C till constant weight. UHMWPE and UHMWPE nanocomposite films thus produced were drawn at two different draw ratios (DR = 8 and 15) below their melting points on a hot shoe. The un-drawn (DR = 1) and drawn UHMWPE and UHMWPE nanocomposite films were used for further characterizations.

Characterizations

Tensile testing of the samples was performed on a Testometric M250-3 CT (Testometric Company Limited; United Kingdom) tensile machine. The gauge length of the samples was kept constant to 150 mm and cross head speed was maintained at 10 mm/min. Average of four test samples are reported for each sample.

The morphology of the un-drawn and drawn UHMWPE and UHMWPE nanocomposite films were observed on Mesdan video analyser 250D -Italy.

RESULTS AND DISCUSSION

Optical Transparency of the UHMWPE and UHMWPE Nanocomposite Films

Optical transparency of the UHMWPE nanocomposite films are compared with UHMWPE films in Figure **1** at two different draw ratios. Un-drawn

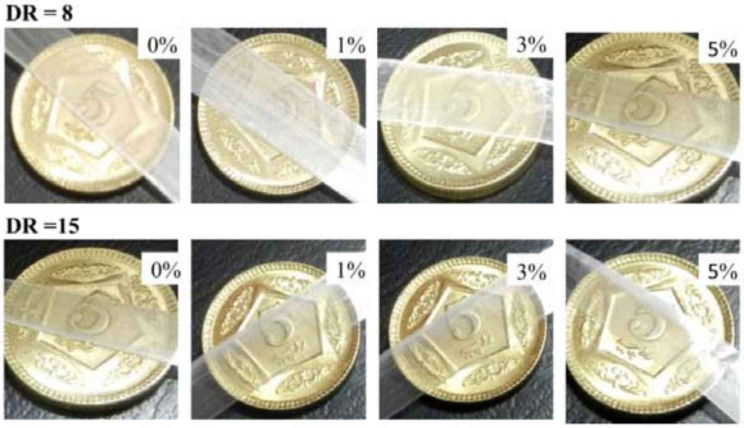

Figure 1: Photographs of UHMWPE and UHMWPE nanocomposite films at various organo-clay loadings and draw ratios, shown on the figures.

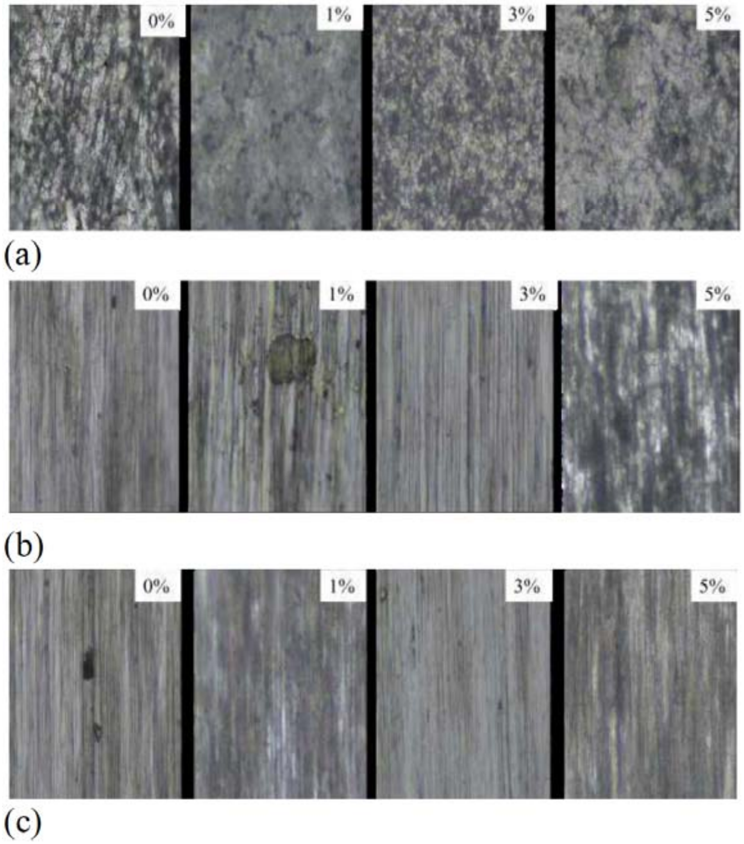

Figure 2: Polarized optical micrograph (POM) of un-drawn and drawn UHMWPE and UHMWPE nanocomposite films at various organo-clay loadings, shown on the figures, and draw ratios: (**a**) DR = 1 (**b**) DR = 8 and (**c**) DR = 15.

samples are translucent, not shown here, whereas the transparency increases with the draw ratio for all organo-clay loadings. It is also interesting to note that even at higher organo-clay loadings the UHMWPE nanocomposite films are comparable to the UHMWPE films.

Polarized Optical Microscopy

Figure **2** shows polarized microscopic micrographs of the UHMWPE and UHMWPE nanocomposite films at three different draw ratios. The development of anisotropy is very apparent in the images. Un-drawn samples showed in Figure **2a** show the lamellar structures [12]. The lamellar structure is transformed into oriented fibrous structure as is evident from the drawn samples 2b and 2c. It is observed that the orientation is increased with the increase in draw ratio as expected by the physics of the deformation of polymer films [21].

Mechanical Properties

The tensile mechanical properties of UHMWPE and UHMWPE nanocomposite films are shown in Figures **3** to **5**.

The effect of various organo-clay loadings on initial modulus at three different draw ratios is shown in Figure **3**. It is apparent that the modulus is higher for UHMWPE nanocomposite films. Furthermore, the initial modulus is increasing with the increase in organo-clay loadings for all samples. The increasing trend of initial

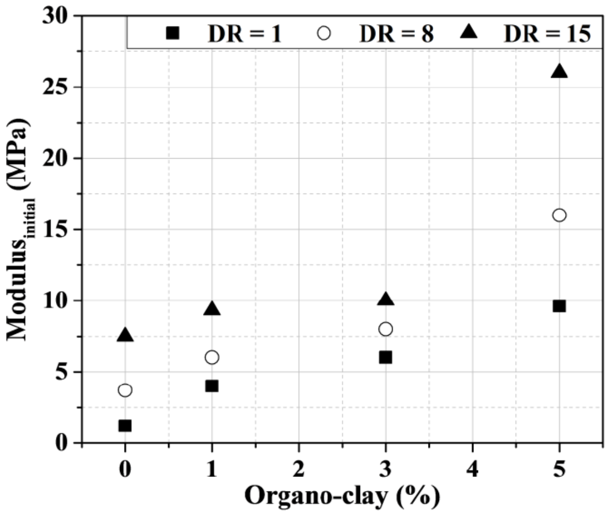

Figure 3: Effect of organo-clay loadings on the initial modulus of UHMWPE and UHMWPE nanocomposite films at three different draw ratios.

modulus is attributed to the resistance exerted by the organo-clay and the oriented polymer chains [22-24]. However, the substantial increase, > 170 % higher than the un-drawn films, is observed for the draw ratio of 15 at 5 % organo-clay loading.

Figure **4** shows the effect of organo-clay loadings on the ultimate breaking force of UHMWPE and UHMWPE nanocomposite films. The force required to break the film samples is higher for the nanocomposite film samples and increases with the increase in organo-clay loadings. The significant increase in the ultimate breaking force, about 150 % higher than the un-drawn films, is observed for higher draw ratio and organo-clay content film samples as expected.

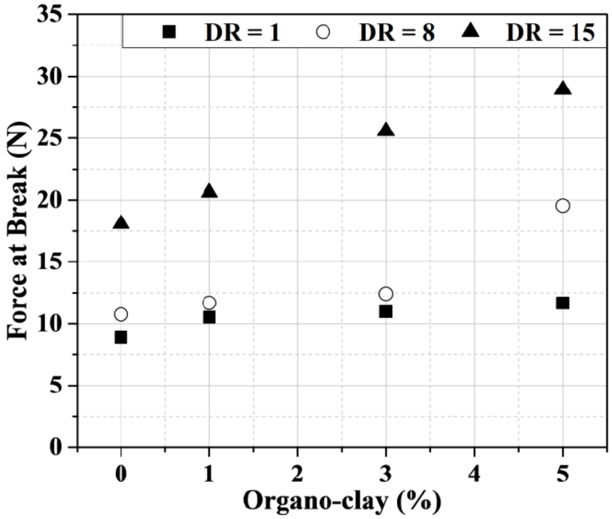

Figure 4: Effect of organo-clay loadings on the force at break of UHMWPE and UHMWPE nanocomposite films at different draw ratios.

The effect of organo-clay loading on the elongation of UHMWPE films at room temperature is shown in Figure **5**. UHMWPE films show higher elongation when compared with UHMWPE nanocomposite films. Furthermore, it is observed that the elongation is almost independent of the organo-clay loadings for the drawn and un-drawn films.

From the observations made in Figures **3** to **5** we conclude that the enhancement of the mechanical properties of UHMWPE nanocomposite films can be attributed to the reinforcement provided by the better dispersion of organo-clay in the polymer matrix in addition to the oriented polymer chains.

CONCLUSIONS

Gel or solution casting was successfully used to prepare UHMWPE and UHMWPE nanocomposite films

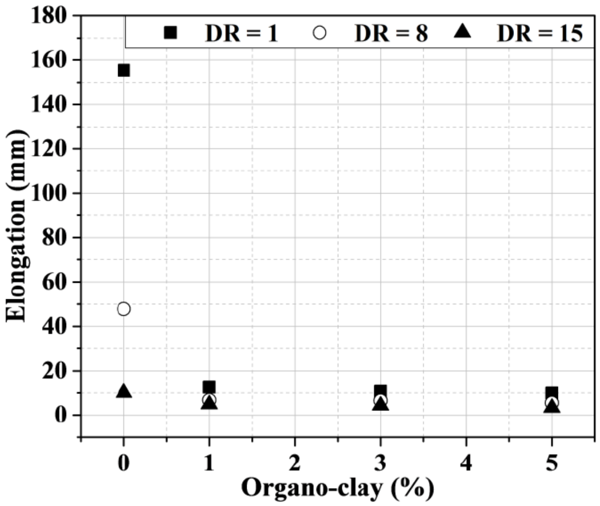

Figure 5: Effects of organo-clay loadings on the elongation of UHMWPE and UHMWPE nanocomposite films at different draw ratios.

with enhanced mechanical properties without the loss of optical transparency even at higher organo-clay loadings. Initial modulus and force at break were increased at least up to 150 % in comparison to the un-drawn film samples for higher draw ratios and organo-clay loadings. However elongation at break was decreased for the drawn samples in comparison to un-drawn film samples as expected. The higher mechanical properties are attributed to the combined effect of organo-clay loadings and draw ratios. The UHMWPE nanocomposite films may find their applications in high tech engineering where higher mechanical properties and optical transparencies are of prime importance.

ACKNOWLEDGEMENTS

Authors are thankful to NED Alumni Association of Southern California (NEDAASC) and MIDAS Safety (Beltexco Company Ltd.) for their generous support for this project.

REFERENCES

[1] Giannelis EP. Polymer Layered Silicate Nanocomposites. Adv Mater 1996; 8: 29. http://dx.doi.org/10.1002/adma.19960080104

[2] Messersmith PB, Giannelis EP. Polymer-layered silicate nanocomposites: in situ intercalative polymerization of epsilon.-caprolactone in layered silicates. Chem Mater 1993; 5: 1064. http://dx.doi.org/10.1021/cm00032a005

[3] Pinnavaia TJ. Intercalated Clay Catalysts. Science 1983; 220: 365. http://dx.doi.org/10.1126/science.220.4595.365

[4] Gilman JW. Flammability and thermal stability studies of polymer layered-silicate (clay) nanocomposites. Appl Clay Sci 1999; 15: 31. http://dx.doi.org/10.1016/S0169-1317(99)00019-8

[5] Pinnavaia TJ, Beall GW. Polymer-Clay Nanocomposite, Wiley, Chichester 2001.

[6] Smith P, Lemstra PJ, Kalb B, Pennings AJ. Ultrahigh-strength polyethylene filaments by solution spinning and hot drawing. Polym Bull (Berlin) 1979; 1: 733. http://dx.doi.org/10.1007/BF00256272

[7] Lemstra PJ, Kirschbaum R. Speciality products based on commodity polymers. Polymer 1985; 26: 1372. http://dx.doi.org/10.1016/0032-3861(85)90315-5

[8] Smith P, Lemstra PJ. Ultra-high-strength polyethylene filaments by solution spinning/drawing. J Material Sci 1980; 15: 505. http://dx.doi.org/10.1007/BF02396802

[9] Alexandre M, Dubois Ph, Sun T, Garces JM, Jérôme R. Polyethylene-layered silicate nanocomposites prepared by the polymerization-filling technique: synthesis and mechanical properties. Polymer 2002; 43: 2123. http://dx.doi.org/10.1016/S0032-3861(02)00036-8

[10] Junges F, Beauvalet MS, Leal BC, Casagrande ACA, Mota FF, Mauler RS, Casagrande Jr. OL. UHMWPE-layered silicate nanocomposites by *in situ* polymerization with tris(pyrazolyl)borate titanium/clay catalyst. J Braz Chem Soc 2009; 20(3): 472. http://dx.doi.org/10.1590/S0103-50532009000300010

[11] Lee EM, Oh YS, Ha S. Ha, Ham MJ, Kim BK. Ultra high molecular weight polyethylene/organoclay hybrid nanocomposites. J Appl Polym Sci 2009; 114: 1529. http://dx.doi.org/10.1002/app.30736

[12] Park HS, Lee JH, Nam J-D. Ultra-drawing of gel films of ultra high molecular weight polyethylene/low molecular weight polymer blends containing BaTiO3 nanoparticles. Macromol Res 2006; 14(4): 430. http://dx.doi.org/10.1007/BF03219106

[13] Shin J, Kim J-C, Chang J-H. Characterizations of ultrahigh molecular weight polyethylene nanocomposite films with organomica. Polym Eng Sci 2011; 679. http://dx.doi.org/10.1002/pen.21870

[14] Zhang W, Hu Z, Zhang Y, Lu C, Deng Y. Gel-spun fibers from magnesium hydroxide nanoparticles and UHMWPE nanocomposite: The physical and flammability properties. Composites: part B 2013; 51: 276. http://dx.doi.org/10.1016/j.compositesb.2013.03.014

[15] Xiong D. Friction and wear properties of UHMWPE composites reinforced with carbon fiber. Mater Lett 2005; 59: 175. http://dx.doi.org/10.1016/j.matlet.2004.09.011

[16] Lemstra PJ, Kirschbaum R, Ohta T, Yasuda H. Developments in Oriented Polymer-2, Elsevier Applied Science Publishers, New York 1987.

[17] Ruan S, Gao P, Yu TX. Ultra-strong gel-spun UHMWPE fibers reinforced using multiwalled carbon nanotubes. Polymer 2006; 47: 1604. http://dx.doi.org/10.1016/j.polymer.2006.01.020

[18] Park S-J, Li K, Hong S-K. J Ind Eng Chem 2005; 11(4): 561.

[19] Zhang Q, Wang Q, Chen Y. J Appl Polym Sci 2013; 3930.

[20] Zhang Y, Yu J, Zhou C, Chen L, Hu Z. Polym Compos 2010; 684.

[21] Lemstra PJ, van Aerle NAJM, Baastiansen CW. Chain-Extended Polyethylene. Polymer J 1987; 19(1): 85. http://dx.doi.org/10.1295/polymj.19.85

[22] Chen L, Wong SC, Pisharath SJ. Fracture properties of nanoclay-filled polypropylene. J Appl Polym Sci 2003; 88: 3298. http://dx.doi.org/10.1002/app.12153

[23] Kojima Y, Usuki A, Kawasumi M, Okada A, Fukushima Y, Kurauchi T, Kamigaito O. Mechanical properties of nylon 6-clay hybrid. J Mater Res 1993; 8: 1185. http://dx.doi.org/10.1557/JMR.1993.1185

[24] Kim JC, Chang JH. Macromol Res 2007; 15: 457.

Received on 19-01-2016 Accepted on 27-04-2016 Published on 12-05-2016

http://dx.doi.org/10.6000/1927-5129.2016.12.34