Analysis and Characterization of U.V Stabilized Metallocene Catalysed LLDPE Films with Conventional Zeiglar-Natta LLDPE

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ABSTRACT

The development of new polyolefins based on metallocene technologies represents a considerable advance in the performance of polyethylene available for a wide range of applications.. The development and progress of the last decade in single-site metallocene catalyst technology finally indicate that the advancing polyolefin industry has moved. The value of metallocene grades of polyethylene compared conventional polyethylene has been examined in UV stabilized film formulations. The exposure to U.V light induces photo degradation in films and causes deterioration of the polymer. Hindered amine Light stabilizers are the best in class to resist the U.V degradation to a considerable level.

The mLLDPE stabilized with 0.5 % HALS 2 systems gave extra ordinary resistance to UV degradation proves that the metallocene catalyst can be a much prone replacement for the conventional LLDPE films that can be used for external applications like in agricultural films, outdoor packaging etc. Also we can optimize that the 1% HALS 1 can be the better formulated UV stabilizer for the conventional LLDPE resins.

INTRODUCTION

The polyethylene industry is a technology intensive industry undergoing a period of major technology renewal. High intensity R&D investment driving this technology renewal extends across a range of technology fronts: catalysis, process engineering, product development, and end-use applications extensions. Some of this technology renewal, principally in the domain of catalysis (metallocene chemistry), has the potential to become revolutionary in scope and impact. They are soluble in hydrocarbons or liquid propene. These properties allow one to predict accurately the properties of the resulting polyolefins by knowing the structure of the catalyst used during their manufacture and to control the resulting molar mass and distribution, comonomer content and tacticity by careful selection of the appropriate reactor conditions.

Metallocenes, in combination with the conventional aluminumalkyl cocatalysts used in Ziegler systems, are indeed capable of polymerizing ethene, but only at a very low activity.Therefore, MAO plays a crucial part in the catalysis with metallocenes.

UV stabilizers are used to prevent or terminate the oxidation of plastics by UV light. They therefore act to protect the moulded product during its life, and are particularly used for building products. To be strictly accurate, UV affects all types of plastics, but a few show better resistances than most. The UV part of sunlight (and in some instances UV light from artificial sources) breaks down the chemical bonds in a polymer in a process called photo degradation, ultimately causing cracking, chalking, colour changes, and loss of physical properties such as impact strength, tensile strength, elongation, and others.

Much attention has centred on hindered amine light stabilizers (HALSs), which are efficient scavengers and function by inhibiting degradation of polymers that have already formed free radicals. Hydro peroxide decomposition and free radical scavenging certainly play a part, as also does the regeneration of HALSs, where UV absorbers are frequently consumed as a result of their operation. There are several theories for how this works - possibly by energy transfer, free radical termination, or peroxide decomposition. Significant stabilization is achieved at relatively low concentrations and it appears that the HALS is actually regenerated by the stabilization process, rather than consumed by it. The effectiveness of HALS systems does not depend on the thickness of the plastics product and they are therefore particularly useful for protection of surface layers and in thin sections. Polymeric HALSs offer superior compatibility, low volatility, excellent resistance to extraction, and contribute to heat stability.

EXPERIMENTAL

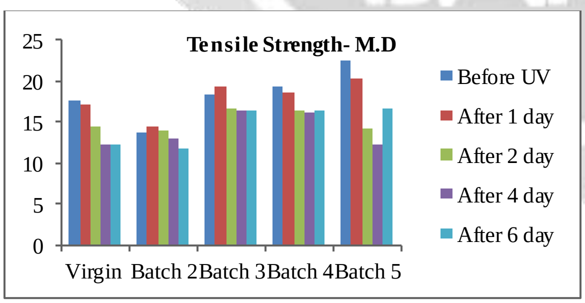
- The materials used in the project are;
  1) Metallocene catalysed LLDPE: ELITE-5401 GS
  2) Linear low density polyethylene(LLDPE): RELIANCE F19010
  3) HALS 1
  4) HALS 2
- Master batches of LLDPE films with each HALS types were formulated and then compounded in a Co-rotating Twin screw extruder, with sections for feed, high shear and high intensity mixing and discharge in a continuous basis. Considering the batch size of 3kg, the various compositions had been prepared for making films.
- Compounding is carried out in the co-rotating twin screw extruder in the temperature range of 160-200^{0}C at 290 rpm with controlling other parameters. Melt strands are cooled by water and cut into pallets by cutter. Total 10 batches are compounded and made ready for processing making them air tight in zipper bags
- The compounded material is final processed out by blown film Process.. The thickness of the films are checked using a guage at intervals and maintained at 40-50 microns

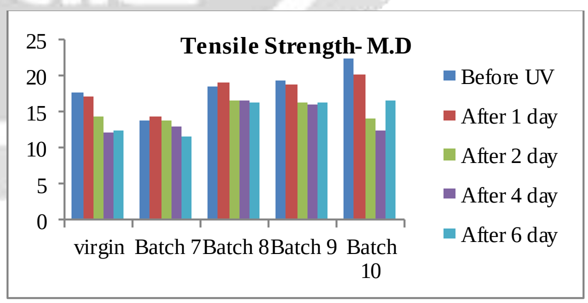
FORMULATIONS OF COMPOUNDED BATCHES

SL no	Batch no	Compositions
1	Batch 1	Virgin mLLDPE
2	Batch 2	99.5% mLLDPE + 0.5% HALS 1
3	Batch 3	99% mLLDPE + 1% HALS 1
4	Batch 4	99.5% mLLDPE + 0.5% HALS 2
5	Batch 5	99% mLLDPE + 1% HALS 2
6	Batch 6	Virgin LLDPE
7	Batch 7	99.5% LLDPE + 0.5% HALS 1
8	Batch 8	99% LLDPE + 1% HALS 1
9	Batch 9	99.5% LLDPE + 0.5% HALS 2
10	Batch 10	99% LLDPE + 1% HALS 2

RESULTS AND DISCUSSIONS

1) TENSILE PROPERTIES





There was a drastic drop in the tensile strength even after 2 day exposure to the U.V and the elongation of U.V stabilized with metallocene LLDPE showed better values compared to the LLDPE before and after same day exposure to samples.

- HALS 1 and HALS 2 stabilized film samples showed better retaining of the strength than virgin polymer and when 0.5% HALS 2 used along with mLLDPE confirms a way better in tensile strength showing a very low % difference in tensile strength after and before UV exposure. Also we can optimize that the 1% HALS 1 can be the better formulated UV stabilizer for the conventional LLDPE resins.

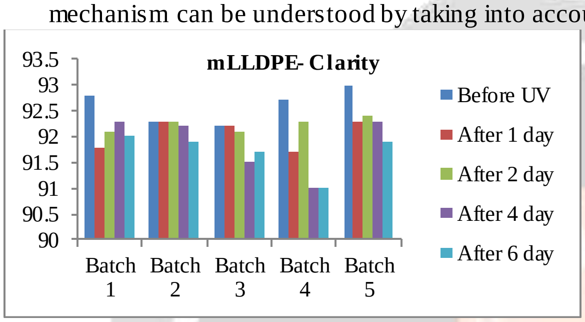
- The mLLDPE stabilized with HALS 1 systems gave extra ordinary resistance to UV degradation proves that the metallocene catalyst can be a much prone replacement for the conventional LLDPE films that can be used for external applications like in agricultural films, outdoor packaging etc.

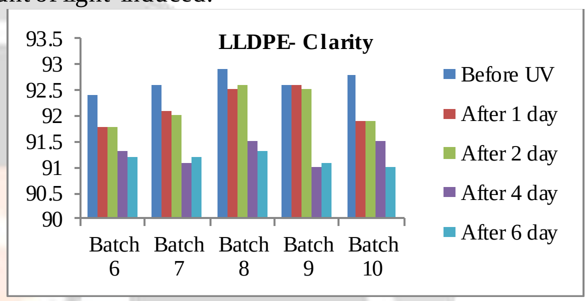
2) TEAR PROPERTIES

Tear Strength of plastic films is adversely affected by the U.V exposure and it showed that tear strength of UV stabilized mLLDPE resins has got attractive properties and those drawn in the transverse direction have got much significant result than that of machine direction. It was the same HALS 2 which proves to be the optimized U.V additive system for mLLDPE and HALS 1 for LLDPE. The mLLDPE tear strength in T.D showed attractive values which makes it very suitable for packaging applications

3) OPTICAL PROPERTIES

LLDPE is widely used for packaging purpose and also undergoes UV exposure. The degradation mechanism can be understood by taking into account of light induced.

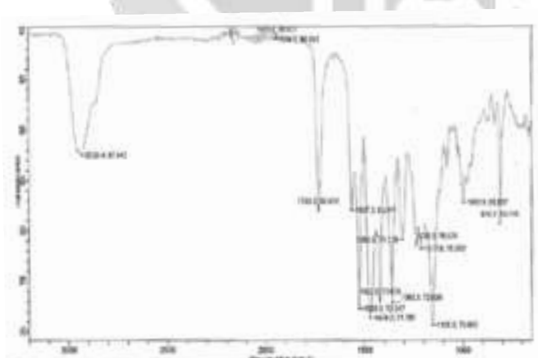




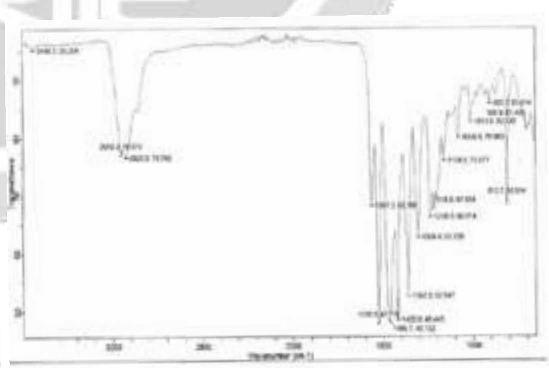
- The luminous transmittance of the mLLDPE sample formulated with 0.5% HALS 2 was retaining while haze almost didn't showed a significant increase in the film. Similar in the case of 1% HALS 1 for LLDPE, it can be seen that the optical properties decreases considerably on exposure except these samples and decrease in property was taking much place in convention LLDPE film samples. It was also seen that on exposure the films becomes tacky and yellowish due to the deterioration of films on exposure to the U.V light.

4) FOURIER TRANSFORM INFRARED SPECTROSCOPY

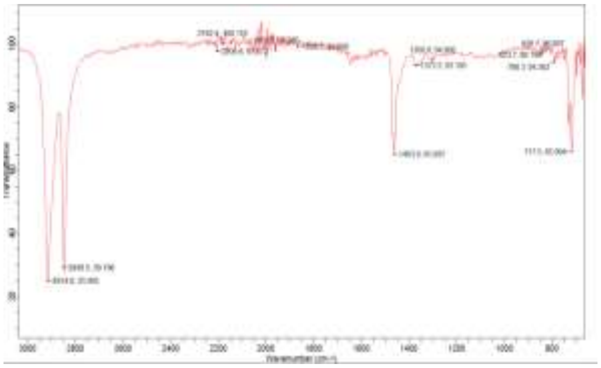
For comparison an infrared spectrum of HALS additives are shown below. Polymer samples become yellow, tacky and opaque during UV exposure.



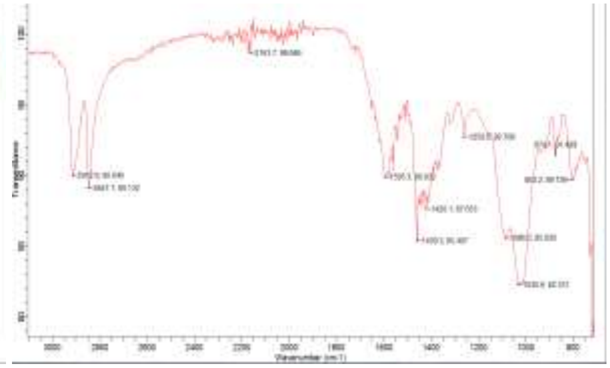
UV Spectra of HALS 1



UV Spectra of HALS



mLLDPE-HALS before U.V



mLLDPE-HALS after U.V

- FTIR study showed that the percentage of U.V degradation was high in LLDPE films rather than mLLDPE films. On increase of time of exposure from day 1 to day 4, the spectrum was showing the evidence of degradation products that consist of carbonyl and oxygen containing low molecular weight compound. The U.V stability was comparatively significant in 0.5% HALS 2 stabilized mLLDPE and 1% HALS 1 stabilized with LLDPE.

CONCLUSION

The thickness of both HALS stabilized metallocene catalyzed LLDPE and Zeiglar Natta catalyzed films were in the range of 40-50 microns.
HALS 1 and HALS 2 stabilized film samples showed better retaining of the strength than virgin polymer and when 0.5% HALS 2 used along with mLLDPE confirms a way better in tensile strength showing a very low % difference in tensile strength after and before UV exposure. Also we can optimize that the 1% HALS 1 can be the better formulated UV stabilizer for the conventional LLDPE resins. The mLLDPE stabilized with HALS 1 systems gave extra ordinary resistance to UV degradation proves that the metallocene catalyst can be a much prone replacement for the conventional LLDPE films that can be used for external applications like in agricultural films, outdoor packaging etc.
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The optical properties of the film sample show the moderate result in comparison to the accepted results in the packaging industry. But a significant reduction of haze was observed in the virgin mLLDPE films and when stabilized with HALS its retention of clarity was remarkable even after 6 days of U.V exposure although incorporation of additives cause slight disturbances in the surface causing slight variations.
From the entire project it is once again proved that metallocene catalyst can be a replacement for the conventionally using Zeiglar-Natta catalyst since the polyolefin industry is growing so fast and continuously looking for property enhancement in an environment friendly and economically; which is the most inevitable factors these days.

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