

Addition Of Branched Molecules And High Molecular Weight Molecules To Improve Optical Properties Of Linear Low Density Polyethylene Films.

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It is known that addition of 10-20% high pressure low density polyethylene (LDPE) to linear low density polyethylene (LLDPE) can improve the optical properties of LLDPE films. This paper shows that the best LLDPE optical properties are not necessarily obtained by using a clarity-grade LDPE as the minor component. Data is presented showing that "liner grade" LDPE and MMW-HDPE, which have poor optical properties in themselves, show significant improvements in the optical properties of LLDPE. A theory is discussed in which the mechanism for improved optical properties in LLDPE is attributed to disruption of crystallite formation due to the presence of highly branched molecules or high molecular weight molecules.

Thermal Oxidation Behavior Of Polyolefins As Related To Their Composition.

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The thermal oxidation behavior of polyolefins has been well studied over the past thirty years. The influence of polymer composition in terms of tertiary hydrogen content -- and to a lesser extent that of unsaturation -- is well documented. However, the interactive effects of tertiary hydrogen content and unsaturation with catalyst residue impurities are not as well understood. Here we show the importance of polymer composition -- polymer microstructure versus catalyst residue -- under oxidizing conditions at elevated temperatures, and the net effects of chain breakage and chain enlargement reactions below the crystalline melting point of selected polyethylenes. Thermal oxidation in the solid state is compared to that from oxidation in the molten state at temperatures up to 300°C. High-yield, transition metal catalyst currently used in the fluid bed polymerization of polyolefins makes total residue products commercially viable without the need for a separate catalyst removal step. The above studies show that transition-metal catalyzed polyethylenes polymerized under such high-catalyst productivity conditions have acceptable stability to thermal oxidation. Such polyethylenes can quite adequately be formulated to provide excellent melt processing stability, heat aging protection and discoloration resistance.

GRAFT COPOLYMERS AS STABILIZERS OF SAN DISPERSIONS IN POLYETHER-POLYOLS AND ULTIMATELY IN POLYURETHANE FOAMS

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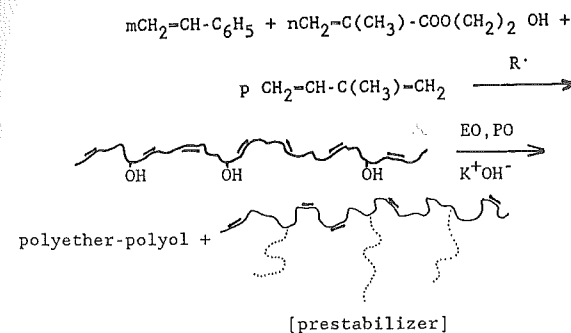
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INTRODUCTION

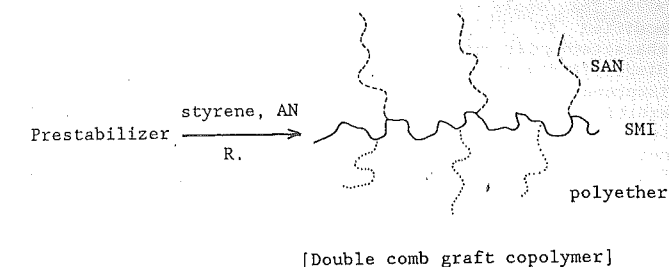
Dispersions of thermoplastic polymers in polyether-polyols are widely used in the field of flexible polyurethane (PU) foams to provide high loading and cell opening effects.^{1,2} Several patents claim that thermoplastic particles, and particularly poly(styrene-co-acrylonitrile) (SAN) particles, can be dispersed in liquid polyether-polyols, using a graft copolymer as a steric stabilizer. As an example, the dispersion polymerization of SAN is carried out in a liquid polyether-polyol and a graft copolymer is expected to result from transfer reactions to polyether.³ Under these experimental conditions, structure and composition of the steric stabilizer are poorly controlled⁴ and make it difficult to correlate the stabilizer characteristics to the main properties of both the dispersion and the final PU foam. In order to draw fundamental structure-property relationships, the macromonomer technique that has been reported elsewhere^{2,4} is a possible approach. This paper reports another technique able to stabilize SAN (80 wt% styrene and 20 wt% acrylonitrile) dispersions in such a way that the in-situ generated stabilizer is very effective and as well defined as possible.

SYNTHESIS OF THE STERIC STABILIZER

The steric stabilizer is an amphipatic copolymer that results from two successive grafting reactions. In a first step, a prestabilizer is synthesized by the so-called "grafting from" method⁵, according to a radical-anionic process. A random copolymer of styrene (main component), 2-hydroxyethylmethacrylate (HEMA) and isoprene, or SMI, is synthesized by a radical way and added with the usual precursors of the polyether-polyols, i.e. ethylene oxide (EO), propylene oxide (PO), glycerol and catalyst (KOH). In the course of the anionic polymerization of epoxides, a grafting occurs from the hydroxyl groups of SMI⁶ and leads to a single comb-graft copolymer.



The prestabilizer-containing polyol is then used as the dispersion medium for the SAN polymerization. The unsaturated isoprene units⁶ of SMI backbone favors the "grafting onto" of SAN and leads to the formation of the actual steric stabilizer, i.e. a double comb graft copolymer.⁷



Most molecular characteristics of the final stabilizer can be modified, such as molecular weight and composition of the SMI backbone, average number and length of polyether and SAN grafts, whereas the extent of the SAN grafting is dependent on isoprene content of SMI and nature and amount of the radical initiator.⁶ The effect that these molecular parameters have on the dispersion stability and viscosity and on the particle size has been investigated as discussed hereafter.

EFFECT OF EXTENT OF POLYETHER AND SAN GRAFTING ON SAN DISPERSION CHARACTERISTICS

30 wt% SAN dispersions have been prepared in a polyether-polyol containing a prestabilizer at a level of 1,8 wt% with respect to the SMI backbone. Molecular characteristics of the prestabilizers have been modified and their effect on SAN dispersions investigated. Table 1A shows that the dispersion stability goes through a maximum when the isoprene content of a prestabilizer containing 6 polyether (PE) chains is increased from 0 to 16 mol%. When the isoprene content of SMI is 4 mol%, a twofold increase in the average number of PE grafts (from 6 to 12) leads to a very high stability, which is poorly affected by a further increase from 12 to 18. Clearly, the stabilizer must contain enough "stabilizing" PE chains to form an effective steric barrier. However too many "anchoring" SAN chains might have a deleterious effect on the coalescence barrier, more likely due to an enhanced compatibility of the stabilizer with SAN particles. According to tables 1A and B, the average particle size parallels the modification noted in the dispersion stability for the series of prestabilizers containing 6 PE chains. The mean diameter of SAN particles becomes essentially independent of the isoprene content when there are 12 PE grafts per SMI-backbone. From tables 1B and C, it appears that surprisingly enough the dispersion viscosity is higher when the SAN particles are bigger. Comparison of tables 1A and C might however indicate a decisive effect of the stability on the dispersion viscosity: a good stability would promote a low viscosity.

It has been observed that a reduction in the molecular weight of the SMI backbone, all the other conditions being kept the same, has a deleterious effect on the dispersion stability.

The SMI composition has also been modified by replacing styrene by methylmethacrylate. Dispersions of a high stability have been obtained; they contain very small particles (ca. 250 nm) but they are prohibitively viscous.

EFFECT OF MOLECULAR CHARACTERISTICS OF THE STABILIZER ON PU FOAM PROPERTIES

Table 2 compares some representative properties of SAN containing PU foams in comparison with the conventional counterpart (i.e. foam prepared from the unmodified polyol). Load bearing is systematically improved upon dispersion of SAN particles within PU matrix. Stable dispersions containing small particles are however more effective in improving load bearing.

The whole set of mechanical properties of SAN modified PU foams do not reflect exactly the main characteristics of the parent SAN dispersions. Indeed, dispersions stabilized by the graft copolymers of 4 mol % isoprene and containing 12 and 18 PE chains, respectively, exhibit the highest stability, a small particle size and a low viscosity. PU foams derived from these dispersions do not however display the best set of mechanical properties. Foam associated to the prestabilizer comprising 6 PE chains and 16 mol % isoprene (in the SMI backbone) is the one that enjoys an improvement of all the mechanical properties. As a rule, tear resistance is improved and elongation tends to decrease when the anchoring of SAN particles to PU matrix is favored (increasing isoprene % at a constant number of PE chains and vice-versa). Improvement in tensile strength levels off rapidly when the average number of PE chains is great enough (12 and 18) or when the isoprene content is high enough (16 mol %) at a lower degree of PE grafting. Depending on the PU foam formulation, optimized stabilizers can actually improve the load bearing by at least 100 %.

CONCLUSIONS

Variations in the molecular characteristics of a double comb graft copolymer used as a steric stabilizer in dispersions of SAN particles in a liquid polyol allow dispersion properties, such as stability, particle size and viscosity to be controlled and optimized. Load bearing property of PU foams is best improved when they are modified by a stable dispersion of rather small SAN particles. These solid polymer/polymer dispersions are actually controlled by the double comb graft copolymer that stabilized the original solid/liquid system. When the mutual anchoring of the solid polymer phases is properly controlled, tear resistance and tensile strength of foams are improved, whereas elongation is kept at an acceptable level.

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Tables 1 - Dispersion characteristics in relation to the polyether and isoprene content of the prestabilizer

Mol % isoprene in SMI Mean Nr of PE chains	Mol % isoprene in SMI			
	0	4	8	16
6	11	6	1,7	5
12	/	0	2	3
18	/	1	/	/

B. Mean particle size (nm)

Mol % isoprene in SMI Mean Nr of PE chains	Mol % isoprene in SMI			
	0	4	8	16
6	720	710	510	1400
12	/	330	375	345
18	/	360	/	/

C. Viscosity at 20°C (mPas)

Mol % isoprene in SMI Mean Nr of PE chains	Mol % isoprene in SMI			
	0	4	8	16
6	10500	8500	4050	4600
12	/	5000	4800	5100
18	/	5500	/	/

Table 2 Modifications (%) in mechanical properties of PU foams modified by SAN particles

Load bearing	+44	+66	+47	+62	(+83)	+63	+66
Tensile strength	-15	+20	+75	+51	+53	+55	+61
Elongation	+40	-10	+5	-16	-25	-42	-14
Tear Resistance	-10	+5	+85	-16	+29	+12	+13
Prestabilizer	Mean Nr of PE grafts	6	6	6	12	12	12
	Mol % isoprene in SMI	4	8	16	4	8	16

A. Stability (Centrifugation test : % of unstable material)

CARBOXYL-FUNCTIONALIZATION OF LINEAR LOW DENSITY POLYETHYLENE

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The utility of carboxyl-containing polymers as compatibilizing agents in the formation of polyblends and multilayer film laminates has recently been reviewed.¹ The polymeric compatibilizers form hydrogen, covalent or ionic bonds with polar functionality or atoms in at least one of the components of the blend or laminate.

The reaction of a molten polyolefin with maleic anhydride (MAH), in the presence of a peroxide catalyst, results in the appendage of individual MAH units, accompanied by crosslinking (LDPE, HDPE), chain scission (PP) or both (EPR). The presence of electron donor compounds which inhibit the homopolymerization of MAH, reduces or prevents these undesirable side reactions.

In view of the increasing interest in linear low density polyethylene (LLDPE), i.e. poly(ethylene-co-1-butene), functionalization with carboxyl groups was investigated. In order to minimize the color development which is generally noted in the crude polyolefin-g-MAH product, the reaction of molten LLDPE with MAH was carried out at 160°C, in the absence as well as in the presence of tri(nonylphenyl and di-nonylphenyl) phosphite (TNPP), using t-butyl peroxoate (tBPO) as catalyst (t_{1/2} 6 sec at 160°C).

EXPERIMENTAL

Reactions were carried out with a 40g charge of antioxidant-free LLDPE (Novacor SG 0218N, melt index 2) in a Brabender Plasticorder at 60 rpm. The polymer was permitted to flux in the chamber, which required about 2 min at 160°C. A mixture of MAH, tBPO and TNPP was added in the form of a paste to the molten polymer, in 4 equal portions at 2 min intervals. After the last addition, the mixing was continued for an additional 2 min. Nitrogen flow through the chamber was stopped during each addition step to prevent loss of MAH.

The MI of crude polymer at 190°C (ASTM D1238, Condition E) was higher than that of polymer from which unreacted MAH had been removed. The latter was obtained by pressing a 5-10 mil film from the crude polymer, suspending the film in boiling water for 2 hr to extract the hydrolyzed unreacted MAH, followed by drying the film in vacuo at 80°C.

The amount of soluble polymer was determined by heating a 5-6g sample of crude polymer in 250 ml 1,2,4-trichlorobenzene (TCB) at 130-150°C for 4 hr. The solution or suspension was filtered through cheese cloth into 1300 ml acetone. The precipitated polymer was filtered, and heated for 45 min at 60°C in 150-200 ml acetone to extract the TCB. The polymer was then filtered, washed with acetone and dried in vacuo at 80°C.

The MAH content of the TCB-soluble polymer was determined by titration of a hot water-saturated xylene solution of the polymer with ethanolic KOH using thymol blue in DMF as indicator.

RESULTS AND DISCUSSION

The reaction of MAH with LLDPE (MI 2) in the presence of 0.0625-0.1875 wt-% t-butyl peroxoate (tBPO) at 160°C, resulted in the formation of a mixture of crosslinked and trichlorobenzene-soluble, acetone-insoluble LLDPE-g-MAH. The latter had an MI of 0.0 and an MAH content ranging from 0.3 to 1.8 wt-% based on LLDPE (Table 1).

The high level of solubility and the 0.0 MI of the product prepared in the absence of MAH, indicates that chain extension rather than crosslinking was dominant under these conditions. Crosslinking increased in the presence of MAH and the TCB-soluble fraction had a 0.0 MI, indicative of chain extension, and MAH contents which increased as the tBPO concentration increased.

Table 1. LLDPE-MAH-tBPO Reaction in Absence of TNPP^a

tBPO g	MAH g	Melt Index	LLDPE-g-MAH	
			TCB-Soluble wt-%	MAH wt-%
0.025	0	0.6	92	-
	1.0	0.0	78	0.62
	2.0	0.0	59	0.86
	3.0	0.0	52	0.58
0.050	4.0	0.0	79	0.34
	0	0.0	94	-
	1.0	0.0	96	1.52
	2.0	0.0	46	1.32
0.075	3.0	0.0	50	1.15
	4.0	0.0	29	0.72
	0	0.0	89	-
	1.0	0.0	72	1.17
	2.0	0.0	60	1.79
	3.0	0.0	61	1.40
	4.0	0.0	66	0.56

^a MAH-tBPO mixture added in 4 shots to 40.0g LLDPE (MI 2) at 160°C; total mixing time 10 min

TNPP has been shown to inhibit the homopolymerization of MAH and reduce crosslinking during the PE-MAH reaction.² The phosphite presumably undergoes oxidation by reaction with the peroxide catalyst and the resultant phosphate is probably the effective electron donor.

The presence of TNPP in the LLDPE-MAH reaction in the presence of tBPO at 160°C increased the MI from 0.0 to values in the range of 0.7 to more than 2. The amount of TCB-soluble polymer increased at higher TNPP concentrations, while the MAH content of the soluble LLDPE-g-MAH ranged from 0.05 to 0.54 wt-%, with most of the results in the 0.2-0.3 wt-% range (Tables 2-4).

Table 2. LLDPE-MAH-tBPO Reaction in Presence of TNPP^a (0.025g tBPO [0.0625 wt-%]/40g MI 2 LLDPE)

MAH g	TNPP g	Melt Index	LLDPE-g-MAH	
			TCB-Soluble wt-%	MAH wt-%
0	0	0.6	92	-
1	0	0.0	78	0.62
	0.5	1.1	60	0.17
2	1.0	0.7	89	0.37
	0	0.0	59	0.86
3	0.5	1.9	50	0.17
	1.0	2.1	84	0.54
4	0	0.0	52	0.58
	0.5	2.1	98	0.28
	1.0	1.6	91	0.27
	0	0.0	79	0.34
	0.5	2.2	85	0.25
	1.0	2.3	93	0.34

^a MAH-tBPO-TNPP mixture added to LLDPE at 160°C