

Polymer-bound hindered amine light stabilizers for improved weatherability in multi-phase polymer systems

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Hindered amine light stabilizers (HALS) have been bound to both the rubber and matrix phases of acrylonitrile-EPDM-styrene (AES) terpolymers. The stabilizers were incorporated by reaction of either 4-aminotetramethylpiperidine or 4-aminooxamidetetramethylpiperidine with anhydride functionality incorporated into the EPDM or SAN. This method permits control of the phase location of the stabilizers in multi-phase polymer systems. Thereby the phase most susceptible to degradation can be positively stabilized. The polymers were evaluated via accelerated weathering. These studies show that the primary function of HALS in AES is to inhibit degradation of the EPDM rubber phase. Superior weathering performance results when HALS is both bound to the rubber phase and melt blended into the product.

INTRODUCTION

The protection of polymeric substrates against aerobic oxidation has traditionally involved the blending of anti-oxidants, such as hindered phenols, into the polymer during processing. For the protection of polymers used in outdoor (weatherable) applications a successful new class of anti-oxidants, hindered amine light stabilizers (HALS), have emerged.¹⁻⁵ Structurally, a hindered amine light stabilizer consists of one or more tetramethylpiperidine rings attached to a variety of organic functional groups. Perhaps the most common of this new class of stabilizers is Ciba Geigy's Tinuvin 770, shown below. Recently, the major reactions by which HALS polymeric stabilize substrates have been elucidated.^{6,7} These light stabilizers are most often used in combination with an efficient UV light absorber such as a benzotriazole. As in the case of the hindered phenol anti-oxidants, these stabilizers are normally melt blended into the polymer in a post-polymerization step.

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When stabilizers are melt blended into a multiphase polymer system each of the stabilizers partitions between the different phases. For instance, in AES the stabilizers partition between the EPDM rubber and the SAN phases. This can lead to disadvantages. In the case of Tinuvin 770 in AES, solubility parameters predict, and recent NMR experiments confirm, that the majority of the stabilizer partitions into the SAN phase due to the higher weight fraction of this phase. The EPDM phase, however, is believed to be more sensitive to oxidation. This deficiency leads to the second disadvantage, stabilizer efficiency. To ensure that the EPDM phase is sufficiently stabilized more stabilizer must be blended in than may really be necessary. The additional stabilizer present in the SAN phase can also be detrimental to physical properties such as heat distortion temperature.

Recently, there has been great interest in the use of polymer-bound stabilizers to control the location of the stabilizers in polymer systems.⁸⁻¹⁰ In particular, this approach has been used to control the leaching of stabilizers from polymers, and is particularly useful in coatings systems. The polymer-bound HALS is believed to enhance weatherability due to its non-fugitive nature and the even distribution of the stabilizer throughout the resin.⁸⁻¹⁰ Acrylic coatings have been developed employing a bound hindered amine light stabilizer. These coatings exhibit superior weatherability over similar acrylic coatings using free HALS.¹¹⁻¹⁴ Interestingly, work with the acrylic system showed that the best weatherability resulted when a combination of bound and free HALS were employed as the stabilizer package. In this situation the advantages of the former are combined with the mobility of the latter to give superior weatherability. To our knowledge, polymer-bound stabilizers have not previously been used to control the placement of stabilizers in multi-phase polymer systems.

This paper will describe the attachment of HALS to the rubber and matrix phases of AES terpolymer. We feel this approach is especially applicable to a two phase system such as AES where a quantity of HALS could be attached directly to the more sensitive EPDM phase, ensuring stabilization and increasing the efficiency of the stabilizer package. The weatherability of these polymers will be compared with polymers in which the HALS have been melt blended, giving insight into the weathering process. The reagents used to deliver the HALS functionality were aminotetramethylpiperidine or amino HALS, 1, and aminooxamidetetramethylpiperidine or hydrazine HALS, 2, (HA-R100) supplied by Atochem, North America.



EXPERIMENTAL

All polymerizations were performed in a resin reactor equipped with an efficient mechanical agitator. A heating profile was used that maintained a constant polymerization rate with time. The polymerization heating profile consisted of 105°C for 100 min., ramp to 108°C over 20 min, ramp to 112°C over 60 min., ramp to 120°C over 60 min., and ramp to 125°C over 60 min. The amino HALS, 1, was purchased from Aldrich Chemical Co. and the hydrazine HALS, 2, was supplied by Atochem, North America. Maleic anhydride grafted EPDM rubber, RoyalTuf 465, and pure EPDM rubber, Royalene 505, were supplied by Uniroyal Chemical. RoyalTuf 465 contained approximately 1.1% maleic anhydride. Samples for infrared analysis were prepared by hot pressing small pieces of polymer into thin films.

EPDM functionalization: amino HALS

In a typical preparation 160 g of RoyalTuf 465 was dissolved into 11 toluene by shaking overnight. To the resulting viscous solution was added 5.6 ml of the amino HALS, 1, followed by an additional two hours on the shaker. This resulted in an additional rise in viscosity to give a gel. The gel was sectioned into several devolatilization pans, allowed to stand in a hood overnight and devolatilized in a vacuum oven at 125° C for 2 h. The product was then cooled in the oven under vacuum overnight.

EPDM functionalization; hydrazine HALS

The procedure used was identical to that used above for the amino HALS. RoyalTuf 465, 160 g, was used to 4.35 grams of the hydrazine HALS, 2. This reaction did not result in the formation of a gel. The solution was poured into the devolatilization pans and worked up as described above.

SAN functionalization; hydrazine HALS

A polymerization feed consisting of 712.5 g of toluene, 458.7 g styrene, 152.9 g acrylonitrile, and 6.95 g maleic anhydride was placed into the polymerization reactor with 7.35 g of a 12.5%1,1-di-(*t*-butylperoxy)cyclohexane initiator solution. A progressing temperature profile was used to maintain a reasonable polymerization rate. A second and third addition of maleic anhydride (3.47 grams in 60 ml toluene each) was added after 1 h 30 min and 3 h, respectively. After a total polymerization time of 6.5 h the temperature was lowered to 90°C, the pressure vented and 34.3 g of **2** in 400 ml of 50/50 toluene/cyclohexanone was added to the reactor. No rise in viscosity was observed. After 45 min at 90°C the reactor was emptied and the polymer devolatilized at 215°C for 3-4 h. The product was cooled in the oven overnight under vacuum.

SAN functionalization; amino HALS

When the amino HALS, 1, was used in a procedure identical to that above, a large increase in the polymer viscosity was observed upon addition of 1. This resulted in setting up the polymerization reactor with gel. However, the polymer was recovered and worked up as described above.

Bound HALS AES polymerization using functionalized EPDM

In this polymerization 1251.8 g of a rubberized feed (10.9% RoyalTuf, 51.7% toluene, and 37.4% styrene) was added to a polymerization reactor. At the start of the polymerization 155.8 g of acrylonitrile and 7.32 g of a 12.5%1,1-di-(t-butylperoxy)cyclohexane solution was added to the reactor through an addition tank. After 5 h 40 min the temperature was cooled to 106°C. When this temperature was reached (after 6 h 5 min) the pressure was vented and 3.72 g of 2 (in a minimum amount of toluene) was added through the reactor head. The polymerization temperature was ramped back up to 120°C over 45 min and the polymer dumped after a total time of 7 h and 20 min. The polymer was devolatilized under vacuum at 215°C for a little over 1 h and then oven cooled overnight under vacuum.

Bound HALS AES polymerization using functionalized SAN

For this polymerization 1214.5 g of rubberized feed consisting of 11.4% Royalene 505, 49.4%toluene, 38.9% styrene, and 0.3% maleic anhydride was added to the polymerization reactor. At the start of the polymerization 157.4 g of acrylonitrile and 7.40 g of a 12.5%solution of 1,1-di-(*t*-butylperoxy)cyclohexane was added to the reactor through an addition tank. After approximately 1 h and $15 \min 3.3 \text{ g}$ of maleic anhydride in 47.4 g of toluene was added through an addition tank. At this point the total feed composition was 9.72% Royalene 505, 45.5% toluene, 33.2% styrene, 11.07% acrylonitrile, and 0.5% maleic anhydride with 650 ppm peroxide. After a total time of 4 h and 35 min (reaction at 41.5% solids) a slurry of 18.04 grams of 2 in 60 g cyclohexanone was quickly added to the reactor through the addition tank. The polymer was dumped after an additional hour stirring (reaction at 49.8% solids for a rubber level of $\sim 18.5\%$). The polymer was devolatilized under vacuum at 190° C for approximately 2 h with the oven cooling to room temperature overnight under vacuum.

Weathering study sample preparation

Samples including controls were prepared for accelerated weathering studies. All samples contain Tinuvin 328, a benzotriazole UV light absorber. All samples were melt blended using a Farrel two roll mill. The rolls were operated at 33 rpm with roll temperatures of 200°C for the front roll and 175°C for the back roll. After the polymer was banded on the rolls stabilizers were sprinkled onto the polymer on the front roll while milling continued. Each polymer sample was cut from the roll several times and rotated 90° to insure good dispersion of the added stabilizers. To prepare AES polymer from functionalized SAN, blends were prepared using grafted EPDM rubber obtained from Uniroyal Chemical prepared by suspension polymerization. This grafted rubber is approximately 50% EPDM in SAN. The compositions of samples prepared for weathering studies are presented in Table 1.

Samples were compression molded for weathering studies. Accelerated weathering was carried out in an Atlas Ci65 Weatherometer with xenon arc source. Irradiance was 0.35 W/m^2 at 340 nm with black panel temperature of 63°C and wet bulb depression of 10°C. Borosilicate inner and outer filters were used. Irradiation was 24 h light with 18 min water spray every 2 h. The conditioning water temperature was 45°C.

Weatherability was evaluated by comparing results of chip (unnotched) impact, (ASTM D 4508-85) gloss retention, and color change with emphasis on yellowing. Samples were pulled for analysis after exposures of 500 h, 1000 h, 1500 h, 2000 h and 3000 h irradiation in the xenon arc. Samples were wiped with Kimwipes under tap water before each reading.

Table 1. Samples prepared for weathering studies

Sample	Component	Amount
Α	AES control (lab prepared) Tinuvin 770 Tinuvin 328	0∙3 phr 0∙5 phr
В	AES control (lab prepared) Hydrazine HALS, 2, (melt blended) Tinuvin 328	0-3 phr 0-5 phr
С	AES control (lab prepared) Amine HALS, 1, (melt blended) Tinuvin 328	0·3 phr 0·5 phr
D	AES with SAN bound Hydrazine HALS, 2 Tinuvin 328	0·5 phr
E	AES with EPDM-bound Hydrazine HALS, 2 Tinuvin 770 Tinuvin 328	0-3 phr 0-5 phr
F	AES with EPDM-bound Hydrazine HALS, 2 Tinuvin 328	0·5 phr
G	SAN 880 SAN Grafted EPDM Rubber Tinuvin 770 Tinuvin 328	to 20% Rubber 0·3 phr 0·5 phr
Н	SAN with bound Hydrazine HALS, 2 SAN Grafted EPDM Rubber Tinuvin 328	to 20% Rubber 0·5 phr
I	SAN 880 SAN Grafted EPDM Rubber Hydrazine HALS, 2 Tinuvin 328	to 20% Rubber 0·3 phr 0·5 phr
J	SAN with bound Amine HALS, 1 SAN Grafted EPDM Rubber Tinuvin 328	to 20% Rubber 0·5 phr

RESULTS AND DISCUSSION

EPDM functionalization

Incorporation of hindered amine light stabilizers into a polymer via a post-polymerization step first requires that a reactive site be either copolymerized or grafted into the polymer backbone. The reactive functional group chosen for this study was cyclic anhydrides, which readily react with amine and hydrazine derivatives. Maleic anhydride was shown to quickly react with 1 and 2 at 0°C, and was picked as the anhydride of choice. Maleic anhydride is easily grafted into polyolefins, including EPDM, by using extrusion techniques or can readily copolymerize with a variety of monomers such as styrene and acrylonitrile.^{15,16} Importantly, polymer bound MA can readily be converted into the imide by reaction with a variety of primary amines. As the main focus of the project was to develop methods for attaching HALS functionalities directly to the more sensitive EPDM phase of AES, work was first aimed towards EPDM functionalization. A sample of EPDM-g-MA was obtained from Uniroyal, sold under the trademark of RoyalTuf 465. RoyalTuf 465 contains approximately 1.1% maleic anhydride and is a toluene soluble rubber.

Addition of the amino HALS, 1, to a toluene solution of RoyalTuf 465 at room temperature, (generalized in Fig. 1), quickly results in the formation of a thick gel. This gel is believed to arise from an ionic cross-coupling in the intermediate amic acid as shown in Fig. 2. Devolatilization of this intermediate gel in a vacuum oven at 125°C for 2 h regenerates soluble rubber. In the infared spectrum of a sample of RoyalTuf 465 five carbonyl stretches are observed; 1860 cm^{-1} , 1788 cm^{-1} , 1745 cm^{-1} , 1714 cm^{-1} , and 1692 cm^{-1} . The first two CO stretches are assigned to the grafted MA and the peak at 1692 cm⁻¹ probably arises from the corresponding diacid (succinic acid has a v_{co} at 1694 \cdot 7 cm⁻¹). The assignment for the remaining two peaks, 1745 cm^{-1} and 1714 cm^{-1} , are uncertain at this time. The IR spectrum upon reaction with 1 followed by devolatilization shows three peaks in the CO stretching region at 1785 cm^{-1} , 1743 cm^{-1} , and 1710 cm^{-1} . The 1785 cm⁻¹ and 1710 cm⁻¹ peaks, characteristic of maleimide carbonyl stretches,^{17,18} confirms the ring closed structure shown in Fig. 2. The ring closure is believed to occur during devolatilization. The anhydride appears to have reacted completely with the amino HALS.

In light of the thick gel formed during the intermediate stage in the reaction of **1** with RoyalTuf 465, it is interesting to note that the reaction of RoyalTuf 465 with **2** shows no rise in viscosity at any stage of the reaction. The IR spectrum of the devolatilized hydrazine HALS functionalized EPDM shows three CO stretches at 1790 cm^{-1} , 1736 cm^{-1} , and 1678 cm^{-1} . The first two stretches are consistent with other amino imide structures and again indicate that ring closure has occurred as shown in Fig. 2. The 1678 cm^{-1} peak is characteristic of the oxamide carbonyls which link the HALS moiety to the polymer bound imide, Fig. 2. At this time it is not clear why ionic cross-linking is not observed



Fig. 1. Generalized polymer functionalization by HALS derivatives 1 and 2.

during the intermediate amino amic acid stage in the reaction of RoyalTuf 465 with 2. It is possible that the driving force for ring closure in amino amic acid derivatives is greater than for the amic acid derivatives (Sargent, J. D., 1991, pers. comm.). However, it is hard to believe that the dehydration and ring closure would occur at room temperature. Therefore, the absence of a viscosity increase at room temperature when 2 is added to the RoyalTuf 465 solution is most likely due to much weaker intermolecular ionic cross-linking in the amino amic acid intermediate.



Fig. 2. Ionic cross-coupling in amic acid intermediate.

The IR data clearly demonstrates that the reaction of either of the HALS derivatives, 1 or 2, with RoyalTuf 465 generates an EPDM rubber with a bound hindered amine light stabilizer. The reactions are relatively fast and appear to be quantitative by IR spectroscopy. The difference in viscosity between the amic acid and the amino amic acid intermediates indicates that the hydrazine HALS will be much easier to work with and is the best choice for use in the AES functionalization.

SAN functionalization

The successful functionalization of EPDM by both HALS derivatives 1 and 2 indicated that SAN could be functionalized in a manner similar to EPDM. To accomplish this 1% maleic anhydride was added to a SAN polymerization to provide for the active functionalization site. In all cases the HALS functionalization was carried out in the polymerization reactor after high solids were reached. Slow addition of 1 to a reactor containing the S/AN/MA terpolymer at 125°C resulted in a rapid rise in viscosity which finally

set up the reactor after all of the amino HALS was added. However, the functionalized polymer could be recovered and devolatilized at 210°C. The IR spectrum of the devolatilized polymer shows carbonyl stretches at 1779 cm^{-1} and 1700 cm⁻¹, again characteristic of a ring closed imide structure as shown in the generalized scheme, Fig. 1. Undoubtedly the ionic crosscoupling caused the reactor to gel up. It is surprising that this occurred at such a high temperature, in fact the same temperature that the EPDM/amino HALS reaction was devolatilized and the maleamic acid dehydrated giving the ring closed imide structure. It appears that for the amino HALS, 1, vacuum or some water removal scheme is necessary to drive the dehydration to completion. No such method was available in the standard reactor used in these reactions.

In contrast to this above observation, addition of hydrazine HALS, 2, to the S/AN/MA ter-polymer again gave no rise in viscosity. However, interpretation of the IR spectrum of this devolatilized (215°C) polymer, is not as clear as the previous spectra. The v_{co} peaks at 1857 cm⁻¹ and 1780 cm⁻¹, as seen earlier, are characteristic of polymer bound maleic anhydride. The strong peak at 1679 cm^{-1} is again assigned to the oxamide carbonyls. This leaves the two shoulders at 1735 cm^{-1} and 1706 cm^{-1} to be assigned. The later peak is assigned to the amino imide carbonyl stretch. It is at a slightly lower wavenumber than the amino imide CO stretch seen in the hydrazine HALS functionalized EPDM but is well within the literature range for imide and amino imide carbonyl stretches.^{17,18} The assignment for the weak shoulder at 1735 cm^{-1} is not clear at this time. The oxamide carbonyls in free hydrazine HALS occur at 1641 cm^{-1} . Therefore, the IR data indicates that the hydrazine HALS has reacted completely with the co-polymerized MA and is bound to the polymer in the amino imide form.

AES polymerization with functionalized EPDM and SAN phases

The synthesis of HALS functionalized AES was accomplished by a very similar technique to that used for the SAN functionalization described above. Because of the viscosity difficulties which arise when the amino HALS, 1, is used as the HALS source, only the hydrazine HALS, 2, was used in the AES functionalization experiments. The HALS addition to AES was also done in the polymerization reactor after high solids were reached.

To generate AES with a HALS functionalized rubber phase, RoyalTuf 465 was used as the rubber source instead of Royalene 505. Addition of 2 after high solids were obtained and devolatilizing the polymer at 215°C gave AES with a HALS functionalized EPDM phase, where the oxamide group links the HALS moiety to the polymer backbone. The IR spectrum of this devolatilized polymer shows the following assignments: oxamide carbonyls at 1678 cm⁻¹ and the amino imide carbonyls at 1778 cm⁻¹ and 1738 cm⁻¹.

The functionalization of the SAN phase in AES was accomplished by adding three aliquots of maleic anhydride to a standard AES polymerization using Royalene 505 EPDM rubber. Addition of hydrazine HALS, 2, to the reactor after high solids were reached and devolatilizing at 190°C gave AES with the HALS moiety attached to the SAN phase, again via the oxamide linking group. In this product the grafted SAN is also functionalized.

WEATHERING STUDY

In order to evaluate the effects of bound stabilizers on weathering it is most convenient to look at the data in small groups of samples.

Comparison of samples A, B and C shows the relative effectiveness of the three hindered amine light stabilizers (HALS) used in this study. In these samples the stabilizers are simply blended into the polymer in equal weight concentrations and are not bound to the polymers. Comparison of the chip impact data in Fig. 3 shows essentially no difference among the samples. The gloss data in Fig. 4 again shows little difference but indicates that Tinuvin 770 (Sample A) shows a slight advantage over the amino HALS, 1, and the Hydrazine HALS, 2, which give comparable results. Figure 5 compares the yellowing results and once again shows very little difference among the samples. These results are important in that they indicate that the HALS samples which were bound to the polymers have no inherent advantage over Tinuvin 770.

Having established the HALS equivalence when blended into the AES samples, we can now



Fig. 3. Chip impact vs time. \Box , sample A; \bigcirc , sample B; \triangle , sample C.



Fig. 4. Gloss vs time. □, sample A; ○, sample B; △, sample C.



Fig. 5. B* vs time. \Box , sample A; \bigcirc , sample B; \triangle , sample C.



Fig. 6. Chip impact vs time. □, sample A; ◇, sample D; ∇, sample E; ■, sample F.

evaluate if binding the HALS to the rubber or matrix phase offers any advantage. The effects of HALS binding are evaluated in samples A, D, E, and F. Sample A is the control containing Tinuvin 770. In sample D, the hydrazine HALS, 2, is bound to the SAN and grafted SAN phase. In Sample F the hydrazine HALS, 2, is bound to the EPDM rubber phase, and in sample E hydrazine HALS, 2, is bound to the EPDM phase and Tinuvin 770 is blended into the sample. Figure 6 shows the chip impact performance of these samples. Comparing sample D to sample A shows that binding the HALS to the SAN phase is a slight disadvantage. When the HALS is bound to the EPDM phase (sample F) the performance is equivalent to the blended HALS (sample A). When the HALS is both bound to the EPDM phase and blended into sample (sample E) the chip impact the



Fig. 7. Gloss vs time. □, sample A; ◇, sample D; ▽, sample E; ■, sample F.



Fig. 8. B* vs time. □, sample A; ◊, sample D; ∇, sample E; ■, sample F.

weathering performance is improved. Figure 7 shows the gloss performance of these samples, and the results parallel the chip impact performance. When the HALS is bound to the SAN phase (sample D) the performance is poorer than the control (sample A). Note that the gloss starts to fall off sooner with the SAN-bound sample. When the HALS is bound to the rubber phase (sample F) the performance is equivalent to the control. However, when the HALS is both bound to the EPDM and blended into the sample (sample E), the gloss is maintained for a longer period of time. Figure 8 compares the effects of weathering on yellowing for these samples. All four of the samples appear to be equivalent for yellowing performance.

The last set of samples (G, H, I, and J) show the effect of binding HALS to the SAN phase

100000-

80000

E 20000 500 1000 1500 2000 2500 3000 TIME (HOURS IN XENON ARC)

Fig. 9. Chip impact vs time. ●, sample G; ▲, sample H;
◆, sample I; ▼, sample J.



Fig. 10. Gloss vs time. ●, sample G; ▲, sample H; ◆, sample I; ▼, sample J.

when the grafted rubber is prepared independently. These samples compare blending Tinuvin 770 (sample G) or hydrazine HALS, 2, (sample I) with samples having SAN-bound hydrazine HALS, 2, (sample H) or amino HALS, 1, (sample J). The chip impact data in Fig. 9 confirms that samples with SAN-bound HALS are inferior to samples in which the HALS is simply blended in. The gloss data for these samples is shown in Fig. 10. The sample with Tinuvin 770 blended in (sample G) shows superior performance to the SAN-bound samples as well as the sample with hydrazine HALS, 2, blended in (sample I). This figure also indicates that SAN-bound hydrazine HALS, 2, is better than SAN-bound amino HALS, 1. As in Fig. 8, Fig. 11 indicates that there is little difference in vellowing performance due to bound HALS.



Fig. 11. B* vs time. ●, sample G; ▲, sample H; ◆, sample I; ▼, sample J.

CONCLUSIONS

The addition of the amino HALS, 1, or the hydrazine HALS, 2, to RoyalTuf 465 (EPDM-g-MA) or to a styrene, acrylonitrile, maleic anhydride terpolymer readily affords, after devolatilization, EPDM and SAN with hindered amine light stabilizers attached directly to the polymer backbone. AES with stabilized EPDM or SAN phase can be made accordingly. In all cases the HALS group appears to be attached to the polymer via an imide or amino imide structure depending on whether 1 or 2 were used as the HALS source respectively. The amino HALS is more difficult to work with due to a large rise in the solution viscosity. The viscosity increase is believed to be due to an ionic cross-linking between adjacent polymer chains in the maleamic acid intermediate. It is not clear at this time why the hydrazine HALS does not experience a similar viscosity rise.

The weatering data confirms that the primary function of the HALS is to inhibit degradation of the EPDM rubber phase. Thus, it can be advantageous to bind the HALS to the rubber phase. When the HALS is bound to the SAN phase, poorer weathering performance results. Superior weathering performance results when the HALS is both bound to the rubber phase and blended into the product.

The weathering data can also help us understand the mechanistic path to weathering degradation. The data indicates that loss of gloss and physical properties (impact strength) are largely due to degradation of the rubber phase. Thus, when the HALS is bound to the SAN phase these properties degrade faster. The yellowing, however, appears to take place primarily in the SAN phase. We have also seen that the HALS does not appear to effectively inhibit this yellowing.

This work illustrates the concept and utility of the use of bound stabilizers to control stabilizer location in multi-phase polymer systems. Bound stabilizers permit the location of the stabilizers in the phase most susceptible to degradation. In this work we have illustrated the concept in a rubber reinforced system with light stabilizers. The concept should also find utility in many multi-phase systems such as polymer blends where stabilizer partitioning can be a problem. In addition to light stabilization it should also be useful for thermal stabilization.

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