Blends of Triazine-Based Hyperbranched Polyether with LDPE and Plasticized PVC

Jyotishmoy Borah, Niranjan Karak

Department of Chemical Sciences, Tezpur University, Tezpur, India 784028

ABSTRACT: Triazine-based hyperbranched polyether was obtained by earlier reported method and blended with low density polyethylene (LDPE) and plasticized poly(vinyl chloride) (PVC) separately to improve some desirable properties of those linear polymers. The properties like processability, mechanical properties, flammability, etc. of those linear polymers were studied by blending with 1–7.5 phr of hyperbranched polyether. The mechanical properties were also measured after thermal aging and leaching in different chemical media. SEM study indicates that both polymers exhibit homogenous morphology at all dose levels. The mechanical properties like tensile strength, elongation at break, hardness, etc. of LDPE and PVC increase with the increase of dose level of hyperbranched polyether. The flame retardant behavior as measured by limiting oxygen index (LOI) for all blends indicates an enhanced LOI value compared to the polymer without hyperbranched polyether. The processing behavior of both types of blends as measured by solution viscosity and melt flow rate value indicates that hyperbranched polyether acts as a process aid for those base polymers. The effect of leaching and heat aging of these linear polymers on the mechanical properties showed that hyperbranched polyether is a superior antidegradant compared to the commercially used *N*-isopropyl-*N*-phenyl *p*-phenylene diamine. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 648–654, 2007

Key words: polymer blend; antioxidant; flame retardant; limiting oxygen index (LOI); hyperbranched polyether; PVC; LDPE

INTRODUCTION

In the last 15 years, the highly branched macromolecules with large numbers of surface functional groups have gained considerable interest to different scientific communities due to their unusual properties.[1] These macromolecules popularly known as dendritic polymers not only possess large number of surface functionality but also exhibit unique rheological properties like low melt or solution viscosity because of spherical structure with no entanglement.[2–5] This unique architecture of these novel macromolecules makes them interesting candidate as one of the blend components with different commercial linear polymers along with many other applications. Further, the improvement of many desirable properties of those linear base polymers is expected to be high because of large number of active functionality on the surface of the dendritic polymers. Many hyperbranched polymers viz. polyphenylene,[6] polyesters,[7–9] polycarbonate,[8] poly(ether-amide),[10] polyamides,[10] poly(vinyl chloride) (PVC),[11] etc. were utilized to improve desirable level of properties for different well-known polymers. Kim and Webster[6] used hyperbranched polyphenylene to improve processability and thermostability of linear polystyrene. A lot of works have been reported by Voit and coworkers for improvement of different properties for commercial linear polymers by blending with dendritic polymers e.g., tensile strength and compression modulus of polycarbonate by blending with hyperbranched polyester,[7] homogeneous distribution of dye molecules in polyolefin by modifying with polyester,[8] processability of polyamide by mixing with hyperbranched poly(ether-amide),[10] etc. Diao et al. used hyperbranched polyamide-ester[12] as compatibilizing agent in polypropylene/PVC blend. Blends of hyperbranched polyesters,[7] aryl ester dendrimer,[13] PAMAM dendrimers[11] with commercial linear polymers like polyester, polyamides, polycarbonate, PVC, polyethylene, and polystyrene have also been studied. Massa et al.[8] described fully miscible hyperbranched polyester blends with linear polyester, which exhibit an increase in the tensile strength and compression modulus but loss in toughness. Hong et al.[9] reported the strong effect on rheological behavior of linear low density polyethylene (LLDPE) while blended with hyperbranched aliphatic polyester. Lubricant effects of hyperbranched polymer with polystyrene were also studied by Mulkern and Tan.[14]

In this article, authors wish to report the utilization of a triazine-based hyperbranched polyether as one of

the blend components with commercial linear polymers like low density polyethylene and plasticized poly(vinyl chloride).

EXPERIMENTAL

Materials

The hyperbranched polyether (Fig. 1) was prepared according to the procedure described in the earlier article.[15] The detailed characterization of this polyether was reported in the same article.[15] The physical, chemical, thermal, and dielectric properties are discussed elsewhere,[16] the weight–average molecular weight, M_w, of the polymer is 4450 g/mol. Low density polyethylene (LDPE) and plasticized poly(vinyl chloride) (PVC) obtained from local market (Kumud Enterprise, India) were used as the base polymers. The technical specifications of these polymers are as follows. LDPE: General purpose grade, weight–average molecular weight = 1.0 $\times$ 10^5, MFR = 2.5 g/min, density = 0.90 g/cc. PVC: Plasticized with 25% (by volume) of DOP (dioctylphthalate), general purpose grade, weight–average molecular weight = 1.2 $\times$ 10^5, MFR = 1.5 g/min, density = 1.27 g/cc. IPPD (N-isopropyl-N-phenyl p-phenylene diamine) was also obtained from the local market (Kumud Enterprise, India) and used as received. The specific gravity and ash content of IPPD are 1.03 g/cc and 0.01, respectively.

Compounding and molding procedure

The blending of polymers was carried out at 145°C for PVC and at 135°C for LDPE in a Bravender plasticorder with mixing chamber of volume 100 cm^3 at dose levels of 1, 5, and 7.5 phr of hyperbranched polyether
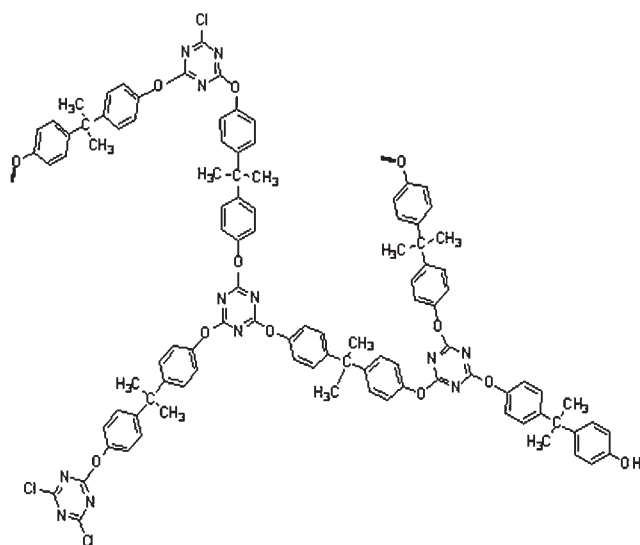

Figure 1 Structure of hyperbranched polyether.

separately for both cases. The linear polymers with hyperbranched polyether were mixed with screw speed of 60–65 rpm for 3–4 min in each case. Both the base polymers were also mixed with 5 phr of IPPD in the same way, separately. The preshaped sheets of compounded polymers were prepared in the two rolls laboratory size open mill followed by molding at 150°C for 8 min for PVC and 10 min for LDPE, respectively, under a pressure of 5–6 tons in a laboratory size electrically heated two platened compression press. The sheets were kept for 7 days at ambient condition for maturation before further studies.

Testing procedure

To determine the properties at least three specimens per test were performed and the average value was reported. Tensile strength (TS) and elongation at break (EB) were carried out according to the standard ASTM D 412-51 T procedure using dumbbell-shaped specimens at room temperature by Zwick Z010 universal tensile machine (UTM) with jaw separation speed of 50 mm/min. The hardness of all samples was measured by Shore A- or Shore D-type durometer as per the standard ASTM D 676-59 T procedure. Thermogravimetric (TG) analysis was carried out in Shimazdu TG 50 thermal analyzer using the nitrogen flow rate of 20 mL/min and at the heat rate of 10°C/min. The surface morphology of blends was studied by using SEM of SU-SEM probe analytical scanning microscope. The flame retardancy test of all samples were carried out by measurement of limiting oxygen index (LOI) value by a flammability tester (S.C. Dey, Kolkata) as per the standard ASTM D 2863-77 procedure for self-supported samples. The minimum concentration of oxygen required in the oxygen–nitrogen gas environment just sufficient to sustain the flame for 30 s was used for calculating LOI value using the following formula

$$LOI = \frac{\text{volume of oxygen}}{\text{volume of nitrogen} + \text{volume of oxygen}} \times 100$$

Aging and leaching procedure

All dumbbell-shaped specimens were immersed for 10 days in water and for 48 h in aqueous 1% NaOH (w/v) and 2% HCl (v/v) solution at 30°C. The heat-aging test was carried out at 70°C for 7 days in an electrically heated air-circulating oven as per the standard ASTM D 573 procedure.

Processability testing

The processability of the compound was performed using melt flow index/rate (MFI/MFR) tester and by
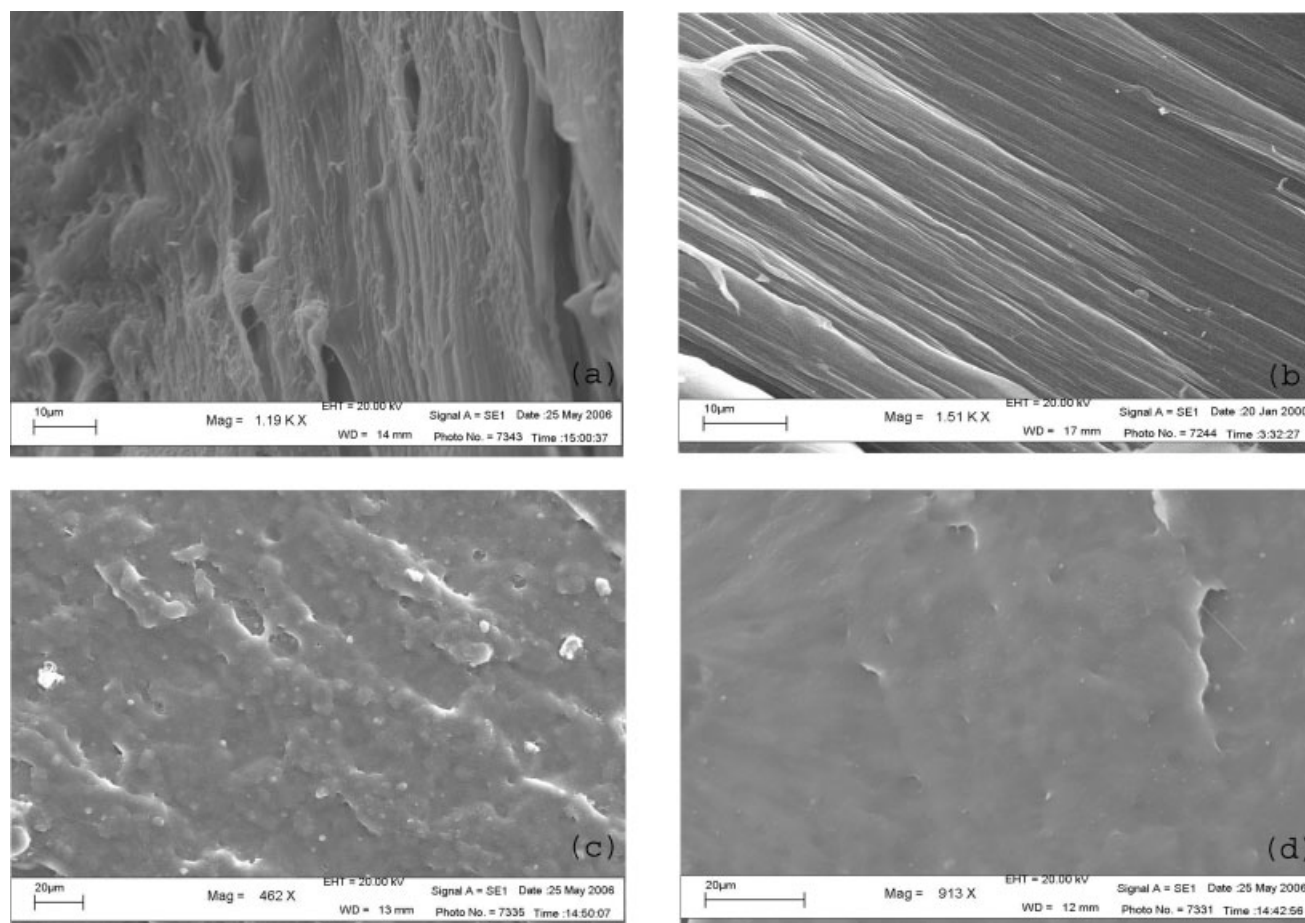
Figure 2 SEM micrographs of blends: (a) LDPE with 5% hyperbranched polyether, (b) 100% LDPE, (c) PVC with 5% hyperbranched polyether, and (d) 100% PVC.

solution viscosity measurement. The MFR value was measured as the amount in gram of the material extruded by piston action through the standard orifice under the standard plastimeter (S.C. Dey, Kolkata) at 190°C for LDPE and at 170°C for PVC over a specified time period (10 min). The solution viscosity of PVC and its blends were measured with a suspended level Ubbelohde viscometer at (25 ± 0.1)°C in 0.05 g/dL DMAc. On the other hand, the solution viscosity of LDPE blend could not be possible to measure due to the poor solubility of LDPE in common organic solvent at experimental conditions.

RESULTS AND DISCUSSION

Morphology study

The morphology as observed from the fracture surfaces of the PVC and the LDPE blends exhibit a homogenous distribution of hyperbranched polyether in the base polymer matrix (Fig. 2). The homogeneous distribution of hyperbranched poly(ether-amide) in polyamide-6 matrix was also observed by Huber et al.[10]

These results indicate that hyperbranched polymers have higher capability to compatibilize with linear polymers. The mixing behavior of a linear polymer with the highly branched polymer at molecular level is expected to be quite different from that between two linear polymers. This difference is mainly due to the conformational restrictions on the hyperbranched component.[11] Further, large numbers of functional groups of the hyperbranched polymer help in mixing with linear polymer, as the blend is prepared either from solution or from the molten condition.[18]

The scanning electron micrographs (SEM) of both blends suggested that the minor phase domain size decreases on increase of the concentration of hyperbranched polyether. This type of morphology is likely to improve the mechanical properties of the blends as the dose level increases, which may be due to uniform distribution of the blend components as well as the compatibilization at the polymer/polymer interface. Further, a significant change of surface morphology was observed even on blending with low dose of hyperbranched polyether (1 phr) for both the base polymers.

TABLE I
Physical Properties of Commercial Polyolefins Blended with Hyperbranched Polyether

Physical property	Composition of blend (phr)							
	PVC (100)	PVC/HBP (100/1)	PVC/HBP (100/5)	PVC/HBP (100/7.5)	LDPE (100)	LDPE/HBP (100/1)	LDPE/HBP (100/5)	LDPE/HBP (100/7.5)
Viscosity (dL/g)	0.87	0.84	0.80	0.79	–	–	–	–
Density (g/mL)	1.26	1.27	1.31	1.34	0.91	0.92	0.95	0.96
Melt flow rate (g/10 min)	1.57	2.74	3.30	3.50	2.54	2.62	2.99	3.09

Physical property

Physical properties like solution viscosity, density, etc. of the blends are given in Table I. The data show a decrease of the inherent viscosity of the PVC-based blends with the increase of the concentration of hyperbranched polyether, which may be due to the fact that the hyperbranched polyether has relatively lower viscosity (inherent viscosity 0.60 dL/g) than the linear base polymer, PVC (inherent viscosity 0.87 dL/g). This result indicates that no chemical reaction occurred between the two polymers, as the viscosity of the blends is lower than PVC. Similar type of result was also reported in case of linear polyamide-6 with hyperbranched poly(ether-amide) blends.[10] Thus, the hyperbranched polyether may act as a lubricating agent or process aid. This has been further supported from MFI measurement (Fig. 3) of the blends, where the MFI value of both PVC and LDPE blends increases with the increase of hyperbranched polyether content. However, the change of MFI of PVC-based blends is slightly higher than the LDPE-based blends at same dose level of hyperbranched polyether. The higher value of MFI of PVC blends may be due to the better compatibility of PVC with hyperbranched polymer as supported by SEM study (Fig. 2). In mixing process, it has also been found that the initial rotational screw speed of the mixing equipment was increased by 5–10% on addition of the hyperbranched polyether for both cases. The improvement of processability by incorporation of hyperbranched polymer is also reported in case of blends of linear polystyrene and hyperbranched polyester,[14] which supports this result.

On the other hand, in compounds of both PVC and LDPE with 5 phr of IPPD, no change in the viscosity or screw speed was observed, which indicates that IPPD cannot act as a process aid for these base polymers. This result confirmed that this hyperbranched polyether could be employed to improve processability for linear polymers like LDPE or PVC.

Mechanical properties

The changes of mechanical properties of the blends can be explained from the compatibility point of view. The better compatibility of PVC with hyperbranched

polyether may be due to the polar–polar interaction between PVC and hyperbranched polyether. However, such interactions are not possible in case of LDPE and hyperbranched polyether. This reflects in higher improvement of mechanical properties (Table II) in case of PVC blends compared to LDPE blends. Thus, in case of PVC blends, the increment of tensile strength is relatively higher than that of LDPE blends with the increase of amount of hyperbranched polyether. The tensile strength value decreases at high dose level (7.5 phr) in both the cases, and the addition of higher dose than 7.5 phr was not studied because of economical point of view, as well as due to the fact that a few earlier studies[8,14] showed that mechanical properties of the blends of hyperbranched polymer with linear polymer decrease at high dose levels, which may be due to the globular nonentangled structure of the hyperbranched polymer. The higher tensile strength values of the samples in both cases at 5 phr of hyperbranched polyether compared to the conventional antidegradant IPPD (Table II) may be due to the fact that hyperbranched additive has better compatibility than IPPD with both the base polymers. The retention of mechanical properties after heat aging and leaching in different chemical media (Tables III
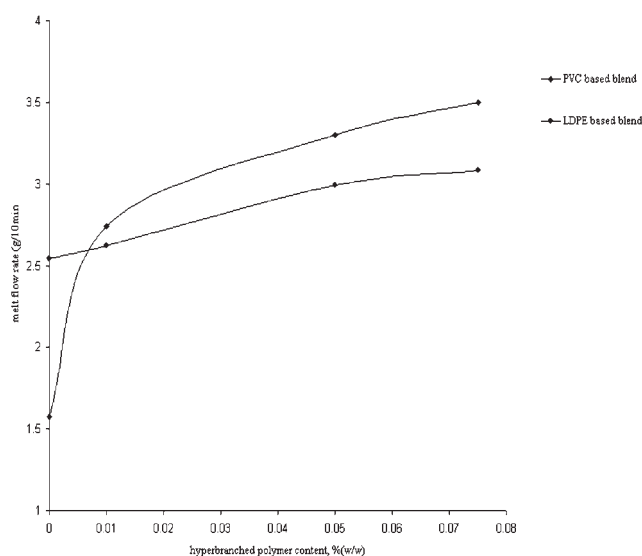

Figure 3 Melt flow index of PVC- and LDPE-based blends.

TABLE II
Mechanical Property of Hyperbranched Polyether Blended with LDPE and PVC

Composition of blend materials (phr)	Tensile strength (N/mm^2)	Elongation at break (%)	Hardness (Shore A & D)[a]	Limiting oxygen index (LOI)
LDPE (100)	10.2 ± 0.055	73 ± 4.55	53 ± 0.24	17.5 ± 0.07
LDPE/HBP[b](100/1)	10.4 ± 0.065	55 ± 5.02	54 ± 0.45	20 ± 0.08
LDPE/HBP (100/5)	11.1 ± 0.045	56 ± 3.55	56 ± 0.35	25 ± 0.05
LDPE/HBP (100/7.5)	11.2 ± 0.10	57 ± 4.85	56 ± 0.34	26.2 ± 0.06
PVC (100)	10.6 ± 0.046	503 ± 4.50	84 ± 0.14	33.7 ± 0.08
PVC/HBP (100/1)	12.7 ± 0.045	551 ± 3.72	85 ± 0.25	35 ± 0.06
PVC/HBP (100/5)	13.8 ± 0.055	561 ± 3.85	87 ± 0.04	37.5 ± 0.07
PVC/HBP (100/7.5)	13.2 ± 0.074	571 ± 4.75	87 ± 0.37	38.7 ± 0.08
PVC + 5% IPPD	12.7 ± 0.065	515 ± 5.60	80 ± 0.54	33.7 ± 0.09
LDPE + 5% IPPD	10.4 ± 0.082	54 ± 5.25	50 ± 0.50	18.7 ± 0.10

[a] PVC and PVC-blend were measured in Shore A scale
[b] HBP = hyperbranched polyether

and IV) for both polymers indicates that the hyperbranched polyether can act as an antidegradant and also it has good leaching characteristics. In this case, the polymers with IPPD also show good retention after heat aging, though the retention after leaching was lower than hyperbranched polyether. These indicate that even though IPPD is a good antidegradant, it undergoes leaching problem, which may be due to small molecular size as well as lesser compatibility with the base polymers compared to hyperbranched polyether. The better aging properties of the polymer blends by incorporation of polymeric additive was also reported by Karak and Maiti[17] in case of chloroprene and natural rubber blends with antimony polyether. The hardness of both polymers increases with the increase of the amount of hyperbranched polyether, which is mainly due to rigidity of triazine and its aromatic moiety as well as good compatibility. However, the change of hardness with IPPD cannot be explained for both the cases. The elongation at break for PVC

TABLE III
Effect of Leaching and Heat Aging in the Mechanical Properties of the LDPE-Blends

Composition of blend materials (phr)	Sample treatment[a]	% Retention of properties after treatment		
		Tensile strength (N/mm^2)	Elongation at break (%)	Hardness
LDPE (100)	HA	96 ± 0.055	92 ± 0.052	98 ± 0.063
	WL	98 ± 0.065	119 ± 0.075	98 ± 0.056
	BL	94 ± 0.046	63 ± 0.045	94 ± 0.043
	AL	96 ± 0.065	66 ± 0.046	94 ± 0.044
LDPE/HBP (100/1)	HA	98 ± 0.076	114 ± 0.083	96 ± 0.076
	WL	96 ± 0.035	127 ± 0.025	98 ± 0.084
	BL	97 ± 0.047	115 ± 0.063	96 ± 0.051
	AL	96 ± 0.058	134 ± 0.059	94 ± 0.062
LDPE/HBP (100/5)	HA	98 ± 0.035	75 ± 0.087	96 ± 0.075
	WL	98 ± 0.065	87 ± 0.045	96 ± 0.058
	BL	91 ± 0.068	52 ± 0.075	94 ± 0.045
	AL	92 ± 0.075	67 ± 0.035	94 ± 0.053
LDPE/HBP (100/7.5)	HA	97 ± 0.038	70 ± 0.073	98 ± 0.065
	WL	98 ± 0.054	96 ± 0.043	96 ± 0.015
	BL	96 ± 0.034	85 ± 0.076	94 ± 0.025
	AL	97 ± 0.016	84 ± 0.025	94 ± 0.056
LDPE/IPPD[b] (100/5)	HA	97 ± 0.087	99 ± 0.065	100 ± 0.023
	WL	96 ± 0.029	98 ± 0.043	98 ± 0.055
	BL	99 ± 0.046	99 ± 0.032	98 ± 0.034
	AL	96 ± 0.058	98 ± 0.056	98 ± 0.076

[a] HA, heat aging for 7 days at 70°C; WL, leaching with water for 10 days at room temperature; BL, leaching with 1% NaOH solution; AL, leaching with 2% HCl solution.
[b] N-isopropyl-N-phenyl-p-phenylene diamine.

TABLE IV
Effect of Leaching and Heat Aging in the Mechanical Properties of the PVC-Blends

Composition of blend materials (phr)	Sample treatment[a]	% Retention of properties after treatment		
		Tensile strength (N/mm^2)	Elongation at break (%)	Hardness
PVC (100)	HA	94 ± 0.055	93 ± 0.039	97 ± 0.035
	WL	99 ± 0.087	98 ± 0.075	100 ± 0.05
	BL	98 ± 0.064	103 ± 0.038	98 ± 0.055
	AL	98 ± 0.054	98 ± 0.046	97 ± 0.028
PVC/HBP (100/1)	HA	91 ± 0.052	91 ± 0.051	97 ± 0.036
	WL	96 ± 0.057	101 ± 0.051	98 ± 0.025
	BL	91 ± 0.035	99 ± 0.063	97 ± 0.049
	AL	94 ± 0.067	109 ± 0.050	98 ± 0.047
PVC/HBP (100/5)	HA	95 ± 0.042	101 ± 0.038	98 ± 0.068
	WL	98 ± 0.062	99 ± 0.055	98 ± 0.028
	BL	94 ± 0.035	102 ± 0.057	96 ± 0.063
	AL	96 ± 0.075	101 ± 0.045	97 ± 0.058
PVC/HBP (100/7.5)	HA	98 ± 0.084	100 ± 0.035	97 ± 0.075
	WL	98 ± 0.055	100 ± 0.055	98 ± 0.055
	BL	91 ± 0.055	100 ± 0.055	96 ± 0.055
	AL	98 ± 0.055	101 ± 0.055	97 ± 0.055
PVC/IPPD (100/5)	HA	97 ± 0.055	85 ± 0.055	98 ± 0.055
	WL	95 ± 0.005	89 ± 0.055	93 ± 0.036
	BL	98 ± 0.015	88 ± 0.021	92 ± 0.075
	AL	93 ± 0.025	98 ± 0.081	93 ± 0.056

[a] HA, heat aging for 7 days at 70°C; WL, leaching with water for 10 days at room temperature; BL, leaching with 1% NaOH solution; AL, leaching with 2% HCl solution.

increases with the increase of hyperbranched polyether dose level, whereas in case of LDPE the reverse trend was observed (Table II). This may be due to the fact that because of better compatibility of plasticized PVC with hyperbranched polyether, as supported by SEM study, these interactions help in chain extension of PVC compound and as the dose level increases, the extensibility also increased, whereas in the case of LDPE, as the system is less compatible, the hyperbranched additive could not help in chain extension, rather these remain more as separate phase, which may deteriorate the elongation.

Flame retardancy

The flame retardancy values of the blends containing hyperbranched polyether and IPPD are shown in Table II. The values indicate that hyperbranched polyether improved LOI values for both blends. However, the LOI values of the blends at 5 phr dose level of hyperbranched polyether is much higher compared to polymers with IPPD at same dose level in both cases. These results indicate that hyperbranched polyether can function as a better flame retardant additive than IPPD. The high efficiency of hyperbranched polyether is mainly due to the fact that it has some special elements such as —Cl (coming from defects in the structure) and $\rangle$N— (coming from triazine moiety) in its structure, which are helping in flame inhibition of the base polymers. The inhibition to flame by both the polymers may be due to vapor phase mechanism in case of LDPE, whereas it may be combination of vapor phase and condense phase mechanism in case of PVC as indicated by TG analysis.

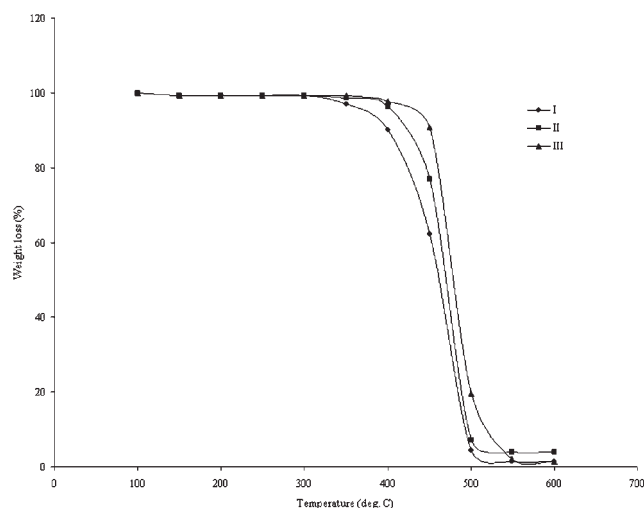The flame retardancy of all blends was also investigated from thermogravimetric analysis. The TG analy-

Figure 4 TG thermograms for LDPE blends (I = 100% LDPE; II = LDPE with 5% hyperbranched polyether; III = LDPE with 5% IPPD).
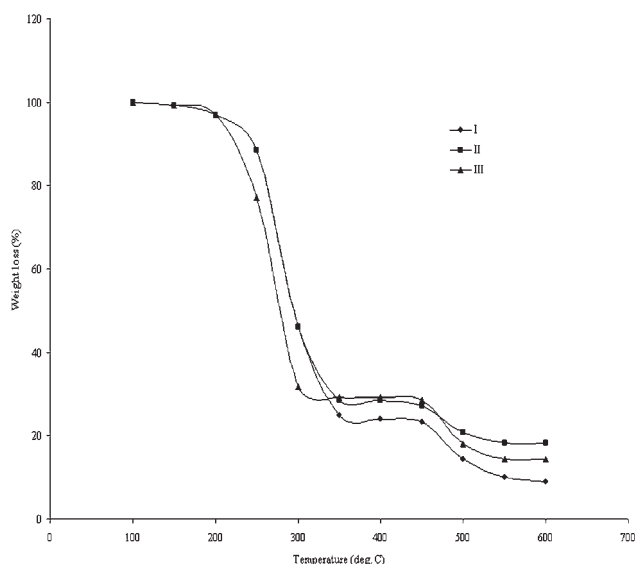
Figure 5 TG thermograms for PVC blends (I = 100% PVC; II = PVC with 5% hyperbranched polyether; III = PVC with 5% IPPD).

sis of the samples with 5 phr of hyperbranched polyether and IPPD in both cases (Figs. 4 and 5) indicates that the thermostability of PVC remains constant, though the same increases for LDPE by incorporation of hyperbranched polyether, whereas thermostability decreases by incorporation of IPPD for PVC though the same increases for LDPE. This further indicates that there are some interactions of hyperbranched polyether with PVC molecules. This higher thermostability of LDPE on incorporation of blend component is mainly due to the presence of thermostable triazine and aromatic moiety in hyperbranched polyether and also aromatic moiety in IPPD. Whereas thermostability of blend of PVC with IPPD decreased may be due to poor compatibility of the components, high volatility of plasticizer, DOP and the liberated HC1 gas may react exothermically to the amino groups of IPPD.

CONCLUSIONS

From this study, it has been found that hyperbranched aromatic polyether with s-triazine moiety can effectively act as multipurpose blend component for the commercially important linear polymers like PVC and LDPE. The hyperbranched polyether has good compatible with PVC and LDPE though the degree of compatibility with PVC is higher than LDPE. This hyperbranched polyether improved the processability, mechanical properties, and flame retardancy for both types of blends. However, the improvement is significant in case of PVC-based blends. The retention properties after heat aging as well as after leaching in different chemical medium of the blends also proved the better capability to prevent degradation, leaching, and migration of hyperbranched polyether compared to the conventional antidegradant, IPPD.

References

1. Voit, B. I. C R Chim 2003, 6, 821.
2. Hult, A.; Johansson, M.; Malmstrom, E. Adv Polym Sci 1999, 143, 1.
3. Mourey, T. H.; Turner, S. R.; Rubinstein, M.; Frechet, J. M. J.; Hawker, C.; Wooley, K. L. Macromolecules 1992, 25, 2401.
4. Stutz, H. J Polym Sci Part B: Polym Phys 1995, 33, 333.
5. Malmstrom, E.; Hult, A. J Macromol Sci Rev Macromol Chem Phys 1997, 37, 555.
6. Kim, Y. H.; Webster, O. W. Macromolecules 1992, 25, 5561.
7. Schmaljohann, D.; Potschke, P.; Hassler, R.; Voit, B. I.; Froehling, P. E.; Mostert, B.; Loontjens, J. A. Macromolecules 1999, 32, 6333.
8. Massa, D. J.; Shriner, K. A.; Turner, S. R.; Voit, B. I. Macromolecules 1995, 28, 3214.
9. Hong, Y.; Cooper-White, J. J.; Mackay, M. E.; Hawker, C. J.; Malmstrom, E.; Rehnberg, N. J Rheol 1999, 43, 781.
10. Huber, T.; Potschke, P.; Pompe, G.; Habler, R.; Voit, B.; Grutke, S.; Grubler, F. Macromol Mater Eng 2000, 280/281, 33.
11. Nunez, C. M.; Andrady, A. L.; Guo, R. K.; Baskir, J. N.; Morgan, D. R. J Polym Sci Part A: Polym Chem 1998, 36, 2111.
12. Diao, J. Z.; Ba, W. W.; Ding, T. H.; Niu, J. T. Iran Polym J 2005, 14, 287.
13. Carr, P. L.; Davies, G. R.; Feast, W. J.; Stainton, M. N. Polymer 1996, 37, 2395.
14. Mulkern, T. J.; Tan, N. C. B. Polymer 2000, 41, 3193.
15. Borah, J.; Karak, N. Polym Int 2004, 53 2024.
16. Borah, J.; Mahapatra, S. S.; Saikia, D.; Karak, N. Polym Degrad Stab 2006, 91, 2911.
17. Karak, N.; Maiti, S. J Appl Polym Sci 1998, 98, 927.
18. Monticelli, O.; Oliva, D.; Russo, S.; Clausnitzer, C.; Potschke, P.; Voit, B. Macromol Mater Eng 2003, 288, 318.