

## Hyperbranched Polyamine as Multipurpose Polymeric Additives for LDPE and Plasticized PVC

Sibdas Singha Mahapatra and Niranjan Karak\*

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

### Abstract

The hyperbranched polyamine based on 4,4'-sulfonyl dianiline was obtained by the earlier reported method and used as multipurpose polymeric additives for low density polyethylene (LDPE) and plasticized polyvinyl chloride (PVC). The effect of this hyperbranched polyamine on the processability, mechanical properties, flammability behavior, *etc.* has been studied. The mechanical properties of the compounded polymers before and after thermal aging and leaching in different chemical media were also studied at dose levels of 1 to 7.5% (w/w) of the additive. SEM study indicates that both polymers exhibit homogenous morphology at all dose levels. The mechanical properties like tensile strength (T.S.) and hardness are improved by incorporation of hyperbranched polymeric additive and these properties increased with the increase of dose level. The flame-retardant behavior as measured by limiting oxygen index (LOI) of all samples indicates an enhanced LOI value compared to the polymer without hyperbranched additive. The processing behavior of all compounded polymers was investigated by measurement of solution viscosity and MFR value. The effect of leaching and heat aging of the polymers on the mechanical properties showed that hyperbranched polyamine is better compared to the commercially used antidegradant, N-isopropyl-N-phenyl *p*-phenylene diamine (IPPD).

### Introduction

Virginity is not a virtue in case of polymers, the usefulness of polymers is obtained by adulteration and the way to adulterate them is very important for their ultimate performance [1]. For adulteration, it is necessary to incorporate some additives with appropriate amount to achieve desirable level of properties into the virgin polymer. Since most of the polymers suffer from heat sensitivity; flammability; attack by oxygen, light, ozone, high energy radiation, mechanical stress during processing; *etc.* So generally anti-degradant (0.2-1 phr, phr = parts per hundred), flame retardant (5-20 phr), heat stabilizer (1-4 phr) process aid (2-5 phr), *etc.* are necessary to incorporate into the virgin polymers [2]. Further, the strength properties of the polymers are generally low and hence it is necessary to incorporate some reinforcing fillers (20-60 phr) into the polymer matrix [2]. Most of the con-

ventional additives suffer from serious problems [3] like leaching, migration, volatility, *etc.* during service period as most of them are small molecular additives. Further, some of them are inorganic in nature, whereas polymers are generally organic in nature, so there is compatibility problem, in these cases. In addition to the above, the amount of conventional small molecular additives generally required is high to get the desired level of properties, which may adversely affect the other properties of the base polymers.

In the last 15 years, the highly branched macromolecules with large numbers of surface functional groups have gain considerable interest to different scientific communities due to their unusual properties [4]. These macromolecules popularly known as dendritic polymers, not only possess large number of surface functionality but also they exhibit unique rheological properties like low melt or solution viscosity because of globular structure with no entanglement [5-8]. This unique architecture of these novel macromolecules makes them interesting candidate as additives for commercial polymers along with many other applications. Since these additives are macro-

\*corresponding author. E-mail: nkarak@tezu.ernet.in

molecular in nature, so they eliminate all the above problems as observed in the case of conventional small molecular additives. Further, because of large number of active functionality on the surface of the dendritic polymers, the effectiveness will be much higher. Thus these additives will be expected to act as a high performance polymeric additives for different base polymers. Many hyperbranched polymers viz. polyphenylene [9], polyesters [10-12], polyetheramide [13], polyamides [14], polyamide-ester [15], *etc.* are utilized to improve desirable level of properties for different well-known polymers. Kim and Webster [9] used hyperbranched polyphenylene to improve processability and thermostability of polystyrene. Voit *et al.* reported the improvement of different properties of commercial linear polymers *e.g.* tensile strength and compression modulus of polycarbonate by blending with hyperbranched polyester [10], homogeneous distribution of dye molecules in polyolefin by modifying with polyester [11], processability of polyamide by mixing with hyperbranched polyetheramide [13], *etc.* Diao *et al.* used hyperbranched polyamide-ester [15] as compatibilizing agent in polypropylene/polyvinyl chloride blend.

In this paper, authors wish to report the utilization of hyperbranched polyamine with s-triazine ring as a multipurpose polymeric additive for commercially available LDPE and plasticized PVC.

## Experimental

### Materials

The hyperbranched polyamine (Fig. 1) was prepared according to the procedure as described in the earlier paper [16]. The detail characterization and a few properties of this polymer were given in the same paper. Low density polyethylene (LDPE) and plasticized poly(vinyl chloride) (PVC) were obtained from local market and 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/c.c.
- PVC: Plasticized with 25% (by volume) of DOP (Diocetyl phthalate), general purpose grade, weight average molecular weight =  $1.2 \times 10^5$ , MFR = 1.5 g/min, density = 1.27 g/c.c.
- IPPD (N-isopropyl-N-phenyl *p*-phenylene diamine) was also obtained from local market and used as received.

### Compounding and molding procedure

The compounding of the polymers was carried out at 145°C for PVC and at 135°C for LDPE in a Bravender plasticorder having mixing chamber of volume 100 cm<sup>3</sup> at dose level of 0 to 7.5 phr of hyperbranched polyamine separately for both the cases. The linear polymers with hyperbranched polyamine 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 pre-shaped sheets of compounded polymers were prepared in the two rolls laboratory size open mill followed by molding at 150°C for 8 min and at 145°C for 10 min for PVC and LDPE based compounds respectively under a pressure of 5-6 tons in a laboratory size electrically heated two platened compression press. The sheets were kept for seven days at ambient conditions and then used to prepare test samples. All the test samples were punched by the punching machine as per the ASTM standard dimensions. For tensile test, the dimension of dumb-bell shaped specimen was as follows. Length = 75 mm, width = 4 mm and thickness =  $2 \pm 0.01$  mm.

### Testing procedure

To determine the properties at least three specimens per test were performed and the average value was reported. Tensile strength (T.S.) and elongation at break (E.B.) were carried out according to the standard ASTM D 412-51 T procedure using dumb-bell shape specimens at room temperature by Zwick Z010 Universal Tensile Machine (UTM) with jaw separation speed of 50 mm/min. The hardness of all samples were measured by Shore A or Shore D type Durometer as per the standard ASTM D 676-59 T procedure. Thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) were carried out in Shimadzu TG 50 and DSC 60 thermal analyzers respectively using the nitrogen flow rate of 30 mL/min and at the heat rate of 10 °C/min. The surface morphology of the compounds 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 Co., 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

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

### ***Aging and leaching procedure***

All dumb-bell shaped specimens were immersed for 10 days in water, for 48 hrs in aqueous 1% NaOH (w/v) and 2% HCl (v/v) solution at *ca.* 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 compounded was performed using melt flow rate (MFR) tester and by 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 plastometer (S.C.Dey & Co., Kolkata) at 190°C for LDPE and 170°C for PVC over a specified time period (10 min). The solution viscosity of PVC and its compounds were measured at concentration of 0.05 g/dL with a suspended level Ubbelohde viscometer at (30±0.1)°C in DMAc. On the other hand, the solution viscosity of LDPE blend is not possible to measure due to poor solubility of LDPE in common organic solvent at experimental conditions.

The density of the compounded polymers was determined by pycnometer in dry toluene at room temperature (*ca.* 30°C) by the conventional liquid displacement method.

## **Results and Discussion**

### ***Morphology study***

The morphology as observed from the fracture surfaces of PVC and LDPE tensile samples exhibit a homogenous distribution of hyperbranched polyamine in the base polymers (Fig. 1). The homogeneous distribution of hyperbranched poly(ether amide) in polyamide-6 matrix was also observed by Huber *et al* [13]. These results indicate that hyperbranched polymers have high 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 the same between two linear polymers. This difference is mainly due to the conformational restrictions on the hyperbranched component [14]. Further, large number of functional groups of the hyperbranched polymer helps in mixing with linear polymer, as the blend is prepared either from solution or in the molten condition [17].

The scanning electron micrographs (SEM) of both polymers suggested that the minor phase domain sizes decrease on increase of the concentration of hyperbranched polyamine. This type of morphology is likely to improve the mechanical properties of the base polymer as the dose level increases, which may be due to uniform distribution of the components as well as better compatibilization at the polymer/polymer interface. Further, a significant change of surface morphology was observed even on mixing at low dose of hyperbranched polymer (1 phr) for both the base polymers. However, from DSC study no conclusion is possible to draw, as there is no significant difference was noticed in the DSC curve for both the cases.

### ***Physical property***

Since the hyperbranched polyamine (Fig. 2) has a large number of active –NH<sub>2</sub> groups (degree of branching, DB = 0.56) and low solution viscosity (inherent viscosity,  $\eta_{inh} = 0.23$  dL/g), so it is expected that this highly branched macromolecule will act as multipurpose polymeric additive. Physical properties like solution viscosity, density, *etc.* of the compounded polymers are given in Table 1. The data show the decrease of the inherent viscosity of the PVC compounds with the increase of the concentration of hyperbranched polyamine. This may be due to the fact that the hyperbranched polyamine has relatively lower viscosity (inherent viscosity 0.23 dL/g) than the linear base polymer, PVC (inherent viscosity 0.87 dL/g). Similar type of result was also reported in case of linear polyamide-6 with hyperbranched poly(ether amide) compounds [13]. Thus the hyperbranched polyamine may act as a process aid. This has been further supported from MFR measurement (Fig. 3) of the compounded polymers, where the MFR value of both PVC and LDPE compounds increases with the increase of hyperbranched polyamine content. These results indicate that this additive is acting as melt viscosity reducer. However, as the values are not significantly changes, so these results confirmed that there is no chemical reaction occurring between the base polymers and the hyperbranched additive,



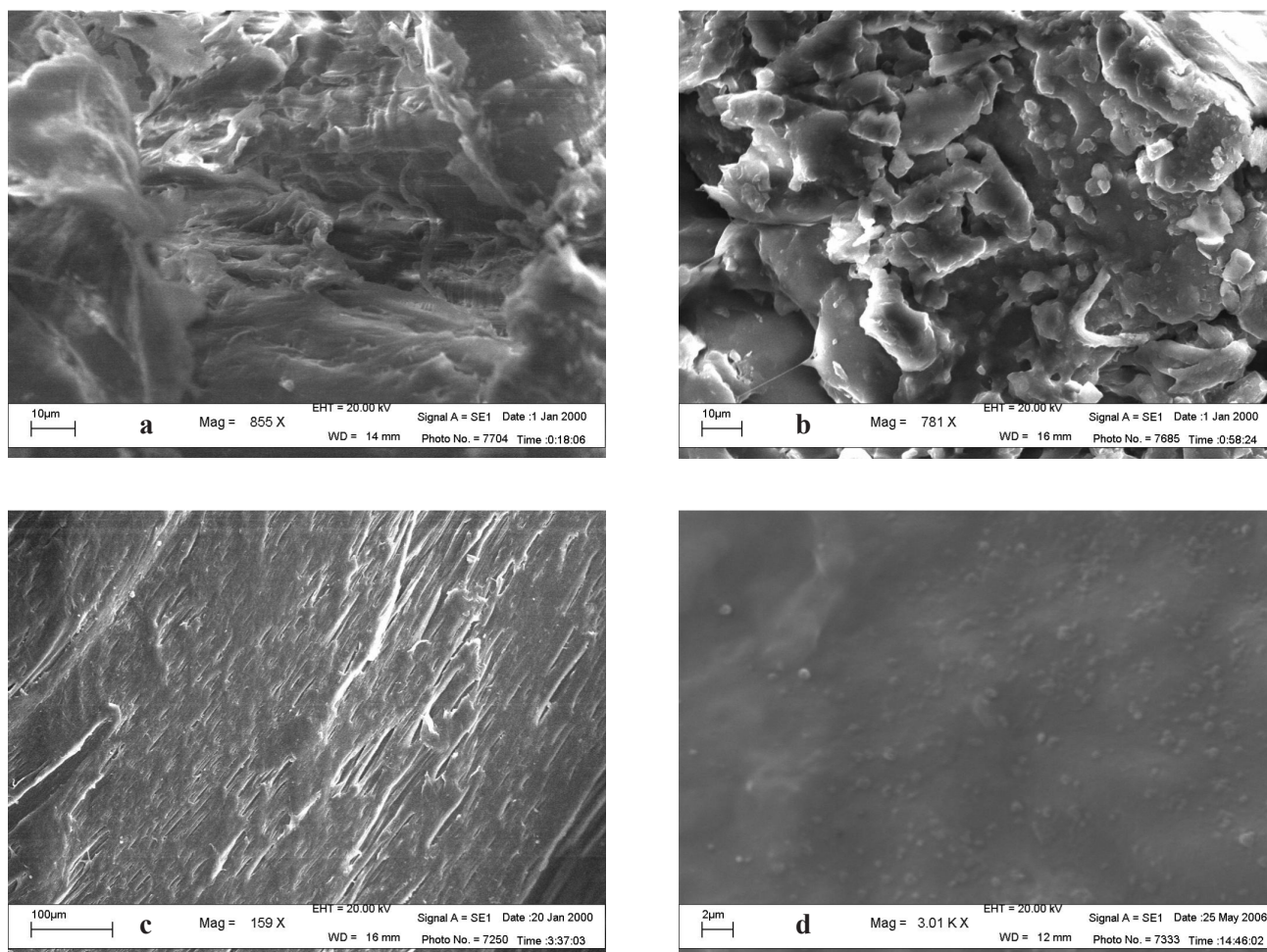


Fig. 1. SEM micrographs of compounds (a) LDPE with 5% hyperbranched polyamine, (b) 100% LDPE, (c) PVC with 5% hyperbranched polyamine, (d) 100% PVC.

otherwise there could have increase of molecular weight, which would increased both solution as well as melt viscosity. However, the change of MFR of PVC based compounds is slightly higher than the LDPE based compounds at same dose level of hyperbranched polyamine. The higher value of MFR of PVC compounds may be due to the better compatibility of plasticized PVC with hyperbranched polymer as supported by SEM study (Fig. 1). This better compatibility may be due to interaction of polar amine groups of hyperbranched polyamine with the polar chlorine atoms of PVC and ester groups of DOP plasticizer. In mixing process it has also been found that the initial rotational screw speed of the mixing equipment increased by 5% to 10% on addition of the hyperbranched polyamine 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 [18], which supports this result. On the other

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

### ***Mechanical properties***

The changes of mechanical properties of the polymers can be explained from the compatibility point of view. As the amine hydrogen atoms of hyperbranched polyamine may interact with the Cl-group of the PVC or/and ester groups of DOP through H-bonding, so these interactions enhance the compatibility between this base polymer and the additive. Further, there is also polar-polar interaction between plasticized PVC and hyperbranched polyamine. However, such interactions are not possible in case of

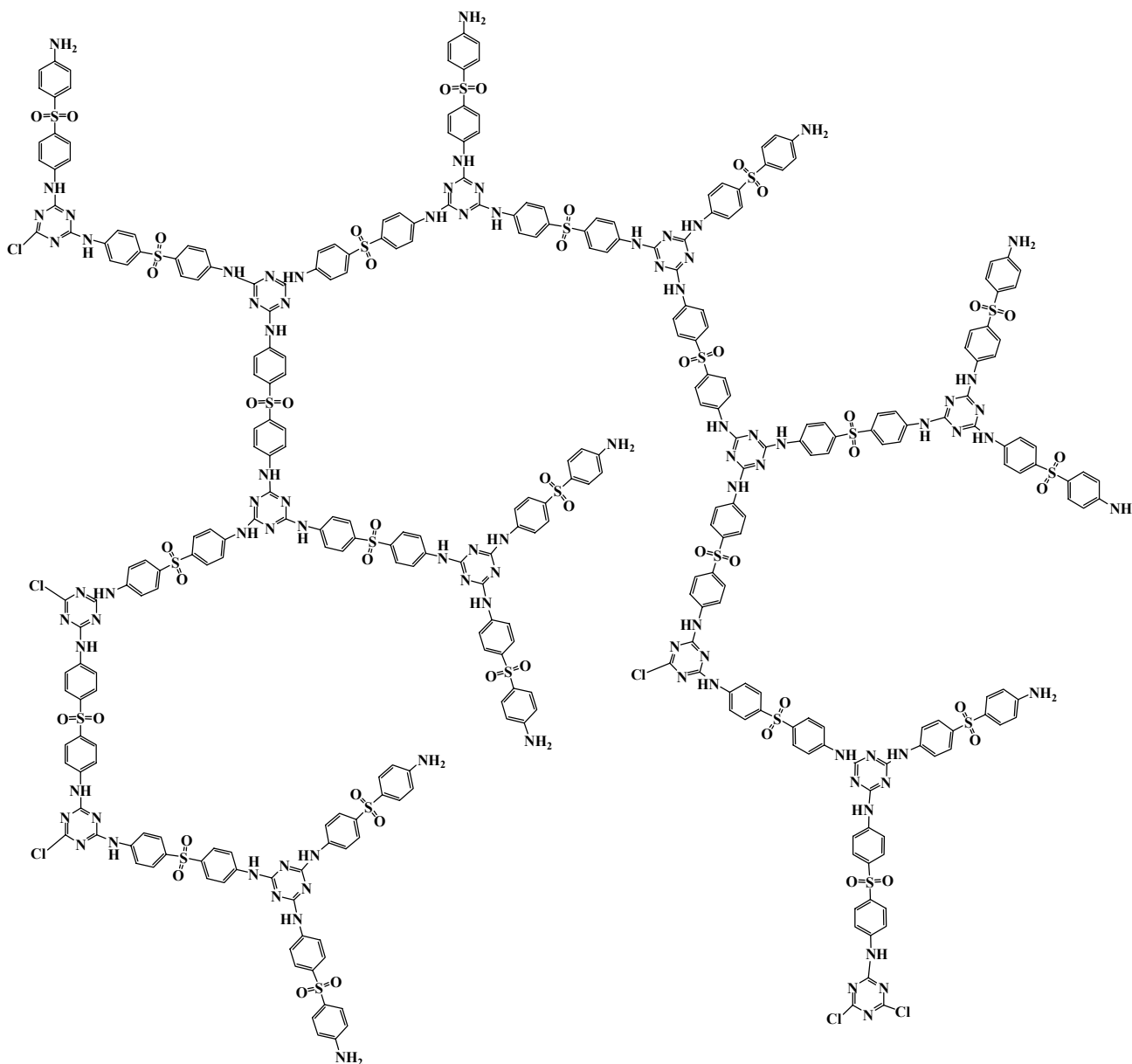


Fig. 2. Structure of hyperbranched polyamine.

**Table 1**

Solution viscosity, density and melt flow rates of PVC and LDPE samples

Physical property	Sample code*							
	P0	P1	P5	P7.5	L0	L1	L5	L7.5
Viscosity, dL/g	0.88	0.87	0.85	0.84	–	–	–	–
Density, g/mL	1.270	1.275	1.28	1.282	0.89	0.90	0.93	0.94
Melt Flow rate, g/10 min	1.57	2.65	3.24	3.46	2.54	2.70	3.01	3.12

\*digit indicates the amount of hyperbranched polymer incorporated in 100 parts of base polymer, and code P is for PVC and L is for LDPE.

LDPE and hyperbranched polyamine. This is supported by SEM studies (Fig. 1). This is also reflected in

their mechanical properties (Table 2 and 3). Thus in case of PVC, the increment of tensile strength is rela-

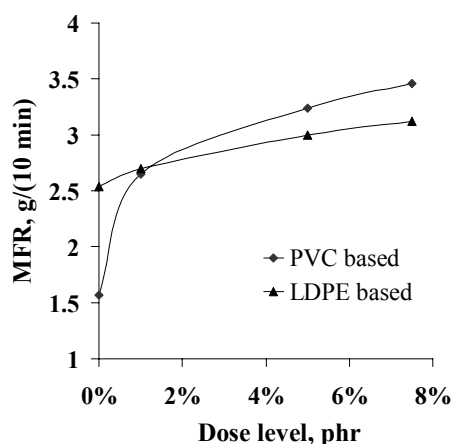


Fig. 3. Melt flow rate of PVC and LDPE based compounds.

tively higher than that of LDPE based material with the increase of amount of hyperbranched additive. Though the tensile strength values decrease at high dose level (7.5 phr) in both the cases and the addition of higher dose than 7.5 was not studied because of commercial point of view as well as due to the fact that a few earlier studies [11,13] showed that mechanical properties of the compounds of hyperbranched polymer with linear polymer decrease at high dose levels may be due to the globular non-entangled structure of the hyperbranched polymers. The higher tensile strength values were also observed for the samples in both the cases at dose level of 5 phr of hyperbranched polymer compared to the conventional antidegradant IPPD (Table 2 and 3). This 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 (Table 4 and 5) for both the polymers indicate that the hyperbranched polyamine acts as antidegradant as well as improves leaching properties. In this case, however, the polymer with IPPD also shows

good retention after heat aging, though the retention after leaching was low than hyperbranched additive containing polymer. These results indicate that even though IPPD is a good antidegradant, but it undergoes leaching problem may be due to small molecular size as well as lesser compatibility with the base polymers compared to hyperbranched polyamine. The better aging properties of the polymers by incorporation of polymeric additive was also reported by Karak and Maiti [19] in case of chloroprene and Natural rubber base polymers with antimony polyether. The hardness of both the polymers increases with the increase of amount of additive, which may be due to rigidity of triazine and aromatic moieties of hyperbranched additive as well as better compatibility. However, the change of hardness with IPPD can not be explained for both the cases. The elongation at break for PVC increases with the increase of hyperbranched polyamine dose level. Whereas in case of LDPE the reverse trend was observed (Table 2 and 3), this may be due to the fact that because of some interactions of PVC chain molecules with hyperbranched polyamine molecules, chains can be extended and as the dose level increases the extensibility also increases. Whereas in the case of LDPE as there is no interaction, so the additive could not help in chain extension rather this remains as free particle, which may deteriorate the elongation capability.

### Flame retardancy

The flame retardancy as measured by LOI value of the samples has increased by 2-5 units for the base polymers by the hyperbranched polyamine additive at dose level of 1 to 7.5 phr, which is not bad. As it has been seen from the other report [20] that even by incorporation of 30 parts of ammonium polyphosphate as flame retardant additive in 70 parts of LDPE

**Table 2**  
Mechanical properties and LOI of plasticized PVC samples before aging

Sample code*	Tensile Strength, N/mm <sup>2</sup>	Elongation at Break, %	Hardness, Shore-A	LOI
P0	10.61±0.055	396±3.14	84±0.44	33.7±0.073
P1	12.47±0.068	452±4.38	85±0.00	35.0±0.056
P5	13.56±0.050	487±4.52	87±0.44	37.5 ±0.032
P7.5	12.91±0.112	532±4.59	88±0.00	38.75±0.046
PIPPD5	12.72±0.110	415±3.87	80±0.77	33.75±0.063

\* digit indicates the amount of hyperbranched polymer or IPPD additive incorporated in 100 parts of base polymer, and code P is for PVC.

**Table 3**  
Mechanical properties and LOI values of LDPE samples before aging

Sample code*	Tensile Strength, N/mm <sup>2</sup>	Elongation at Break, %	Hardness, Shore-D	LOI
L0	10.22±0.072	71±2.19	53±0.00	17.5±0.034
L1	10.49±0.104	51±1.78	55±0.44	18.75±0.042
L5	11.22±0.044	45±1.60	57±0.00	21.25±0.059
L7.5	10.98±0.105	41±1.26	58±0.77	22.50±0.061
LIPPD5	10.41±0.113	54±2.12	50±0.44	18.75±0.039

\* digit indicates the amount of hyperbranched polymer or IPPD additive incorporated in 100 parts of base polymer and L is for LDPE.

**Table 4**  
Effect of Leaching and Heat Aging in the Mechanical Properties of the PVC-Compounds

Sample code*	Sample Treatment**	% Retention of Properties after Treatment		
		Tensile Strength	Elongation at Break	Hardness, Shore-A
P0	HA	94±0.56	93±0.67	97±0.53
	WL	99±0.26	98±0.44	100±0.53
	BL	98±0.46	97±0.59	98±0.65
	AL	98±0.38	98±0.39	97±0.00
P1	HA	96±0.57	95±0.76	98±0.00
	WL	98±0.29	98±0.35	100±0.0
	BL	96±0.52	95±0.82	97±0.51
	AL	98±0.69	98±0.54	97±0.51
P5	HA	98±0.47	97±0.62	98±0.00
	WL	98±0.21	97±0.31	100±0.0
	BL	96±0.36	96±0.71	97±0.51
	AL	96±0.42	97±0.48	97±0.00
P7.5	HA	96±0.78	97±0.44	97±0.51
	WL	97±0.32	98±0.27	99±0.00
	BL	97±0.64	94±0.67	97±0.00
	AL	98±0.53	96±0.56	96±0.51
PIPPD5	HA	95±0.76	85±0.92	98±0.00
	WL	91±0.54	89±0.73	93±0.55
	BL	93±0.63	88±0.58	92±0.00
	AL	92±0.41	89±0.45	93±0.55

\*digit indicates the amount of hyperbranched polymer or IPPD additive incorporated in 100 parts of base polymer, and code P is for PVC.

\*\*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.

**Table 5**  
Effect of Leaching and Heat Aging in the Mechanical Properties of the LDPE-Compounds

Sample code*	Sample Treatment**	% Retention of Properties after Treatment		
		Tensile Strength	Elongation at Break	Hardness, Shore-A
L0	HA	96±0.72	92±0.67	96±0.84
	WL	98±0.51	97±0.45	98±0.00
	BL	94±0.56	93±0.71	94±0.78
	AL	96±0.47	96±0.86	94±0.00
L1	HA	98±0.42	94±0.47	98±0.00
	WL	99±0.21	98±0.61	98±0.00
	BL	97±0.39	96±0.72	97±0.81
	AL	99±0.19	96±0.59	96±0.00
L5	HA	98±0.44	97±0.48	98±0.00
	WL	99±0.37	98±0.45	98±0.00
	BL	98±0.53	97±0.63	99±0.79
	AL	99±0.39	98±0.54	98±0.00
L7.5	HA	97±0.68	95±0.57	98±0.80
	WL	99±0.42	95±0.56	96±0.00
	BL	98±0.49	96±0.71	98±0.00
	AL	99±0.32	97±0.63	96±0.00
LIPPD5	HA	97±0.67	94±0.83	97±0.81
	WL	96±0.55	94±0.77	98±0.00
	BL	95±0.70	93±0.69	98±0.00
	AL	92±0.83	92±0.75	98±0.80

\*digit indicates the amount of hyperbranched polymer or IPPD additive incorporated in 100 parts of base polymer and L is for LDPE.

\*\*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.

the LOI value of the resultant material is 22.6. (Table 2 and 3). The LOI values at 5 phr dose level are much higher with hyperbranched polyamine for both the base polymers compared to the polymers with IPPD. These results indicate that hyperbranched polyamine can function as a flame retardant additive. The high efficiency of hyperbranched polyamine may be due to the fact that it has some special elements such as –Cl, –N and –S in its structure, which are helping flame inhibition of the base polymers [21]. The plasticizer, DOP retards the flame inhibition process of PVC as it is highly flammable compound. However, because of good interactions of the hyperbranched polyamine additive with ester group of DOP as well as –Cl

of PVC, the effect is not prominent. The inhibition to flame may be due to vapor phase mechanism in case of LDPE, whereas it may be combination of vapor phase and condense phase mechanisms in case of PVC as indicated by TG analyses.

The flame retardancy of both the polymers was also investigated from thermogravimetric analysis. The plasticizer, DOP has prominent negative effect on the thermostability of PVC. However, this effect was minimized by the incorporation of hyperbranched additive due to good interaction as described earlier. The TG analysis of PVC samples with 5 phr of hyperbranched polyamine and IPPD (Figs. 4 and 5) indicates better thermostability by incorporation of



hyperbranched polyamine, whereas thermostability decreases with IPPD in the nitrogen atmosphere. This further indicates that there are some interactions of hyperbranched polyamine with PVC and plasticizer molecules. As hyperbranched polymer has thermostable triazine and aromatic moiety [22], so the thermostability of the compounded PVC increased. Whereas thermostability of PVC with IPPD decreases may be due to fact that as there is no interaction with base polymer, so these molecules remain freely and during heating they are vibrating more easily causing higher heat building *i.e.* increasing kinetic energy in the system and thereby facilitates degradation of the polymer. Again in the case of LDPE, the thermostability of the base polymer increases by incorporation of hyperbranched polyamine as well as IPPD compared to the virgin base polymer. This higher thermostability of LDPE on incorporation of additive may be due to the presence of thermostable triazine and aromatic moiety in hyperbranched polyamine and also aromatic moiety in IPPD. In DSC study, as the instrument does not have any cooling arrangement, so it is very difficult to trace the  $T_g$  for both the cases. Also in DSC curves no significant difference is observed for both the cases, except the total heat energy required for melting of LDPE (for pure LDPE  $\Delta H = 166.65$  J/g and for LDPE with 5% hyperbranched polymeric additive  $\Delta H = 129.61$  J/g).

## Conclusions

From this study it has been found that hyperbranched aromatic polyamine with s-triazine moiety

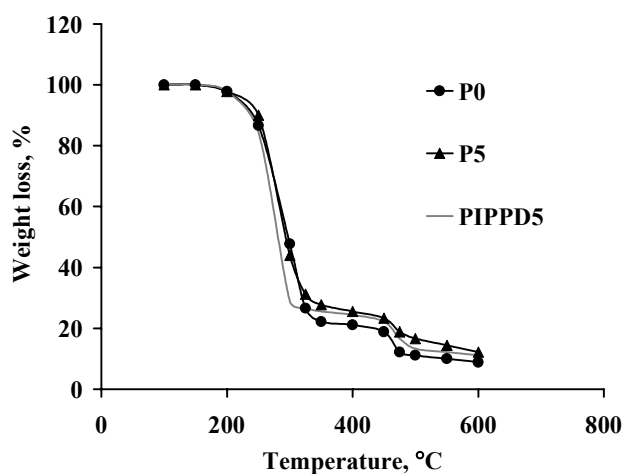


Fig. 4. TG thermograms for PVC based polymer *i.e.* 100% PVC is P0, 5% hyperbranched polyamine with PVC is P5, and 5% IPPD with PVC is PIPPD5.

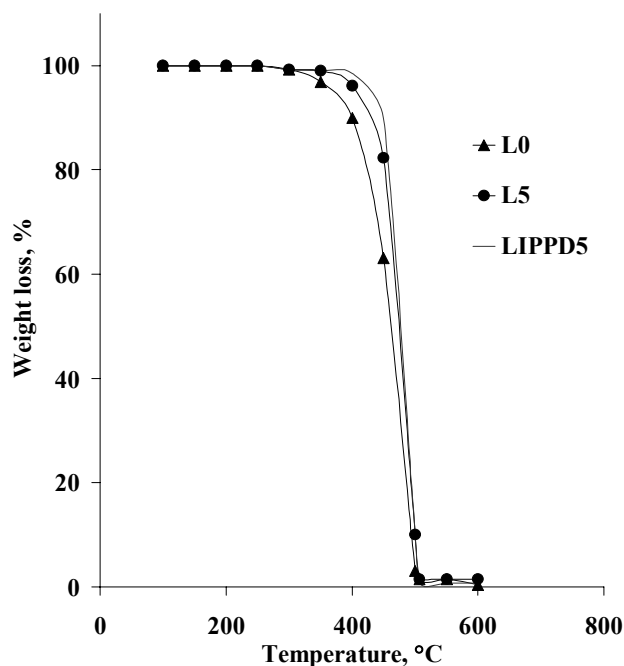


Fig. 5. TG thermograms for LDPE based polymer *i.e.* 100% LDPE is L0, 5% hyperbranched polyamine with LDPE is L5, and 5% IPPD with LDPE is LIPPD5.

can act as a multipurpose polymeric additive for the commercial linear polymers like plasticized PVC and LDPE. The hyperbranched polyamine has good compatible with plasticized PVC and LDPE though the degree of compatibility with PVC is higher than LDPE. This hyperbranched polyamine improved the processability, mechanical properties and flame retardancy for both the base polymers. However, the improvement is higher in case of PVC than LDPE. The retention properties after heat aging as well as after leaching in different chemical media of the polymers also improved. The hyperbranched polyamine has the better capability to prevent degradation, leaching and migration compared to the conventional antidegradant, IPPD.

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