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The effects of epoxy resin nano particles on shrinkage behavior and thermal stability of talc-filled polypropylene

Yousef Jahani · Morteza Ehsani

Abstract   Reactive mixing of epoxy resin with polypropylene (PP) and talc were carried out on a co-rotating twin screw extruder. The prepared samples were injection molded to produce the specimens for the measurements of the shrinkage rate. The microstructure of the composites was studied by scanning electron microscope and correlated to the orientation of filler particles and shrinkage behavior. The nano size epoxy resin particles are obvious in SEM images both in the PP matrix and also adhered on the talc powders. The shrinkage measurement revealed that, using epoxy resin in the formulations, leads to a reduction of 14.3% in the shrinkage rates which is isotropic in both flow and transverse directions. The oven aging test at 100 °C showed a significant effect of epoxy resin on increasing the thermal stability of composites. The stabilization effect of epoxy resin was more pronounced at higher epoxy resin content. It is believed that the metallic impurities on the surface of talc powder deactivated by the functional groups of epoxy resin and the degradation reaction rate decreased.

Keywords   Polypropylene · Talc · Epoxy resin · Melt flow ability · Shrinkage

Introduction

Polypropylene (PP) is the most important commodity plastic, with wide range of grades available for various applications. Low price, excellent chemical resistance, acceptable range of tensile strength and modulus, good impact strength and processability made it an attractive candidate for many engineering applications

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[1, 2]. It is possible to improve some of properties of PP, to meet the requirements of particular cases. Low stiffness is one of the most important deficiencies prohibiting neat PP replacing more expensive engineering thermoplastics. The combination of PP with rigid fillers such as talc, exhibit increased stiffness and dimensional stability, which however due to increased contact and surface interaction between these irregularly shaped particles, lead to drastically decrease in melt viscosity and the deterioration of processability. Talc is used massively in PP and this composite has been widely studied [3–8].

One of the reasons for the use of mineral fillers in the PP semi-crystalline thermoplastic is to reduce the shrinkage [6]. Platy shape talc powders have generally been found to be the most effective in reducing the shrinkage of PP. The shrinkage of PP–talc commercial compounds at 30 or 40% of talc, are higher than the shrinkage of parts manufacture by amorphous thermoplastics such as acrylonitrile butadiene styrene (ABS) with the same thickness [1]. It may be attractive in some cases for making parts, to shift to cheaper raw materials without making a new mold; therefore the shrinkage rate is the crucial factor for the accuracy of molded parts dimensions. The improved melt flowability, lower processing temperature and lower injection pressure are the potential advantages of this replacement and may leads to increased mold durability. The combinations of polypropylene with thermosetting resin such as epoxy and polyester were the subject of some researches [9–11]. Jiang et al. [10] in their study on dynamically cured epoxy–PP blends have been reported that the epoxy resin in 70/30 PP/epoxy blend, dispersed as spherical particles. Wan et al. [9] have been studied on the effects of peroxide cross-linked polyester on polypropylene through reactive mixing. Some types of epoxy resins use as stabilizer/co-stabilizer in various plastics [12]. It has been also fond that, epoxy resin improves the thermal stability of Polypropylene filled with epoxy-resin-grafted nanosilica [13].

Up to now, there are not available any released reports and publications considering the talc-filled polypropylene treated by epoxy–polyester thermosetting resin.

In this study, the reactive mixing of epoxy resin with talc and PP were carried out on a twin screw extruder. We looked at the need for high stiffness and therefore high filler fraction with improved rheological behavior as dictated by the processing requirements and isotropic low shrinkage and improved thermal stability. The epoxy resin in a novel way is used with talc filled PP to reduce the shrinkage of composites to the level of amorphous thermoplastic polymers.

Experimental

Raw materials

The specification of the materials used in this study are surveyed in Table 1. The polypropylene was a standard injection grade homo polymer, with melt flow rate (MFR) of about 15 g/10 min (ASTM D1238 @230 °C/2.16 kg). The highly lamellar talc with mean particle size of 10 μm, and specific surface area of 3.2 m^2/g,

Table 1 The specifications of the materials used in the study

Materials	Grade and description	Company
PP-homopolymer	Ceetec-J801R	Hyundai
Talc	1445	Luzenac
Antioxidant	Irganox 1010	Ciba
Epoxy resin	Kukdo YD013	Kukdo
Polyester resin	Uralac 5142	DSM

and the epoxy resin with 750 (g/equivalent weight), and curing time of 6 min at 190 °C, for 50/50 epoxy/polyester resins ratio, were used in the experiments. The polyester resin was used as cross-linking agent for epoxy resin. As a processing stabilizer, 0.2 part of Ciba Irganox 1010 antioxidant, per 100 parts of compounds was added to all formulations.

Sample preparation

The compounding was performed on a Coperion Werner Pfleiderer, ZSK25-WLE twin screw extruder. It is a co-rotating, intermeshing, twin screw machine, with modular 25 mm screw and 40 L/D. The ZSK25 extruder was equipped with a twin screw side feeder, which was used to intrude the talc and the epoxy resin in the barrel. The screw elements configuration and ventilation ports locations on the barrel are shown in Fig. 1.

To feed the material into twin screw compounder, four Brabender gravimetric dosing units have been used. The antioxidant and polypropylene pellets, according to recipes, fed into main hopper by gravimetric feeders. One feeder was allocated to dose the resin. The epoxy resins were premixed with polyester resin, by a turbo mixer, and the particles passed through a 10 micron sieve. To study the effect of epoxy–polyester hybrid resin 2.5, 5 and 10 weight percentages of resin were added to PP–talc composites with 20, 30 and 40% of filler content. The epoxy–polyester curing reaction release water [11]. The moisture of talc powder and the water byproduct generated due to resin curing reaction were removed efficiently by two free devolatilizing ports and one vacuum degassing port. The mixing operation was carried out at 750 rpm screw speed, with approximate residence time of about 4.5 min of the material in the barrel. The temperature profile on the barrel was 170, 170, 180, 185, 190, 200, 195, 195, 195, 190, 190 °C from the hopper to the die head which is shown by ten heating zone Z1–Z10 on the Fig. 1. The melt temperature was about 215 °C on screw tip.

Measurement of the properties

Shrinkage behavior

The dumbly shape specimens for tensile test, were used for the measurement of dimensional changes and shrinkage. The specimens were injection molded, at the
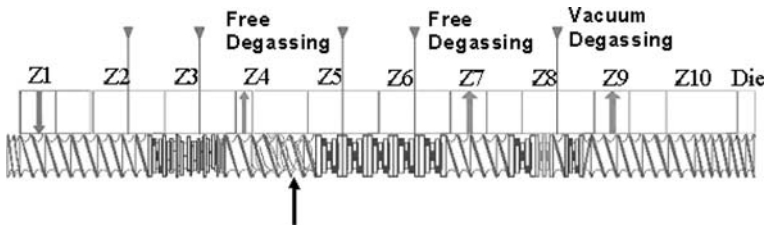
Fig. 1 Screw arrangement and degassing ports of twin screw compounder

temperature of 175–195 °C, from hoper to nozzle of injection machine. The mold temperature is controlled at about 35 °C during the injection process. The thickness of specimens was 4 mm, and the width in measuring section was 10 mm.

Melt flow rate

The melt flow rate of the composites was determined by a Zwick melt-flow analyzer, according to ASTM D1238 on the pre-dried granules. To evaluate the shear rheological behaviour of the samples, two loads of 2.16 kg and 10 kg at 230 °C were used in the measurement.

Scanning electron microscopy

The injection moulded samples were fractured in cross direction to melt flow in the liquid nitrogen. The morphology of fractured, gold coated surfaces of the samples were studied by Cambridge 360, scanning electron microscopy (SEM), using a voltage of 15 kV.

Oven aging test

The oven aging test was carried out on the injection molded specimen of tensile test. The service temperature of PP–talc composites are normally under 100 °C. The dumbbell specimens were aged at 100 °C in an oven with circulating air with 2 °C accuracy in a time period of four weeks. After 150, 350, 500 and 700 h the tensile properties of aged specimens were measured by a universal testing machine. The test results were calculated by the average of three runs.

Results and discussion

The effect of epoxy resin on shrinkage behaviour

The shrinkages of neat PP and the PP–talc composites with, and without resin were shown in Table 2. The shrinkage of neat PP in flow and cross the flow directions were 1.67 and 1.56% respectively. PP shrinks freely along the thickness of the part and exhibit anisotropic shrinkage along and across the flow directions. The frozen

Table 2 The shrinkage data of composites at various amounts of talc and epoxy resin

Material	Shrinkage along the flow (%)	Shrinkage across the flow (%)
PP	1.67 ± 0.03	1.56 ± 0.038
PP + 20% talc	1.23 ± 0.02	1.04 ± 0.027
PP + 20% talc + 2.5% resin	1.18 ± 0.012	1.03 ± 0.018
PP + 20% talc + 5% resin	1.13 ± 0.01	1.03 ± 0.013
PP + 20% talc + 10% resin	1.01 ± 0.01	0.96 ± 0.015
PP + 30% talc	1.03 ± 0.025	0.92 ± 0.031
PP + 30% talc + 2.5% resin	0.98 ± 0.01	0.9 ± 0.014
PP + 30% talc + 5% resin	0.90 ± 0.01	0.83 ± 0.016
PP + 30% talc + 10% resin	0.78 ± 0.01	0.72 ± 0.012
PP + 40% talc	0.81 ± 0.015	0.8 ± 0.022
PP + 40% talc + 2.5% resin	0.70 ± 0.01	0.7 ± 0.012
PP + 40% talc + 5% resin	0.64 ± 0.01	69 ± 0.01
PP + 40% talc + 10% resin	0.50 ± 0.01	0.49 ± 0.01

outer layer of molded part, prevent the free shrinkage over the length and width of samples [14, 15].

PP as a semi-crystalline thermoplastic, exhibit a considerable shrinkage on cooling. The inclusion of mineral fillers reduces the overall level of shrinkage and the fillers with isotropic particles prevent the warpage problem [16]. Platy fillers such as talc have generally been found to be the most effective in giving the highest levels of shrinkage reduction consistent without sacrificing the other properties [17].

The 20 wt% talc–PP composite without epoxy resin showed a shrinkage rate of 1.22% and decreased to 0.81% for the composite with 40 wt% talc. In the talc filled PP the shrinkage rate were decreased due to lower volume fraction of matrix resin and also due to increased interfacial contact between the plate-like talc particles and PP matrix. It is observed that, treating composites with small amount of the epoxy resin decreased the shrinkage rates of 40% talc–PP composite down to about 0.71% that is close to the normal range of the shrinkage of amorphous thermoplastic polymers such as ABS resins. The modulus, and heat distortion temperature of PP + 40% talc composite is comparable with ABS resin with acceptable range of mechanical properties consistent with lower price. It may be attractive in some cases to shift to cheaper raw materials without making a new mold, and the shrinkage rate is the crucial factor for the accuracy of molded parts dimensions. The improved melt flowability, lower processing temperature and lower injection pressure are the potential advantages of this replacement and may leads to increased mold durability.

The shrinkage behaviors of composites at various talc content (Fig. 2) and resin/talc ratios (Fig. 3) indicated that the shrinkage rates decrease by increasing the percentages of talc powder and epoxy resin in the composites. The variation of shrinkage rates of composites against PP percentages in the composites with and without resin, in Fig. 4 shows that the shrinkage rate of composites containing epoxy resin decreased by about 14.3% (the incline of 0.024 against 0.021)
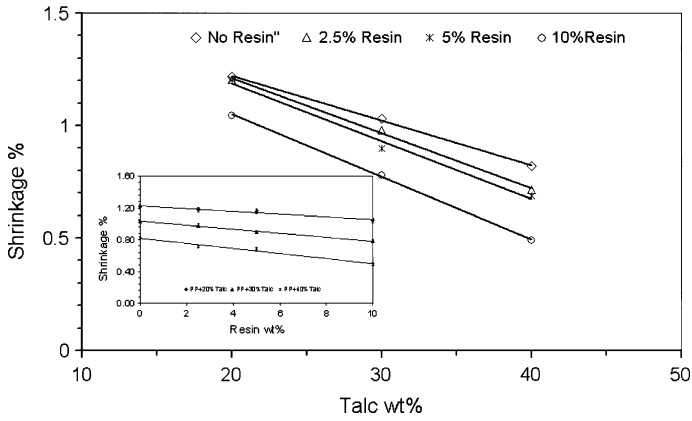
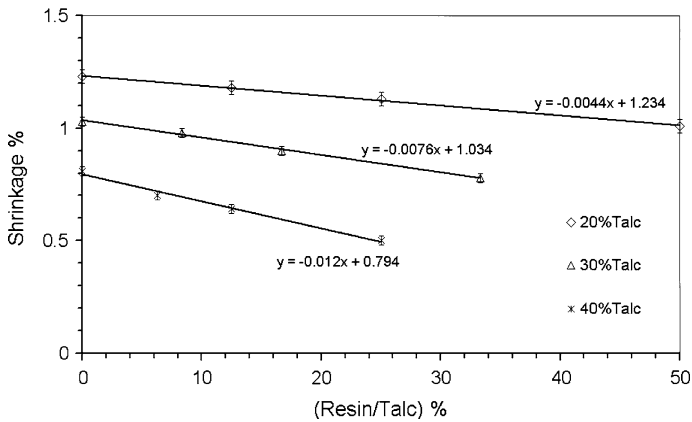**Fig. 2** The effect of talc and epoxy resin on the shrinkage of composites

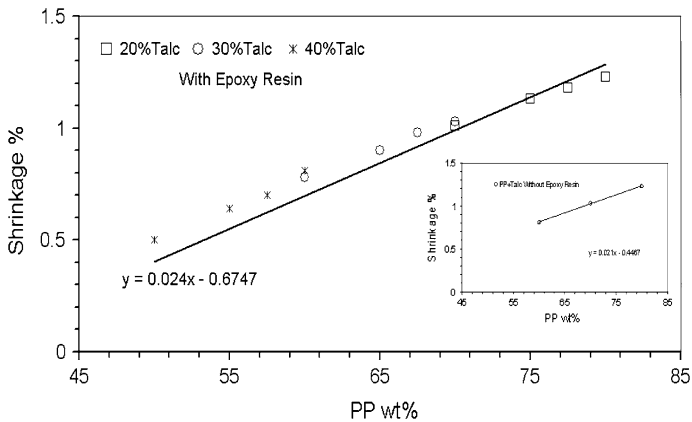**Fig. 3** The correlation of shrinkage behaviors with resin/talc ratios

Fig. 4 The shrinkage rates of composites with and without resin

comparing with the composites without resin. The difference in the slope of lines may be attributed to the nano size of cured epoxy resin particles in the PP matrix.

The effect of epoxy resin on melt shear flow behavior

The effect of epoxy resin on the melt shear flow behavior was evaluated by MFR test. The shear flow measurement at 10 kg load comparing with 2.16 kg showed a substantial change in the trend of MFR data with and without epoxy resin. It is observed that the melt flow behavior of PP + talc composite (without epoxy resin) at both loads of 2.16 and 10 kg are similarly decreased by increasing talc weight percentages (Fig. 5), while the composites containing epoxy resin showed opposite trends at 10 kg load, and the melt flow increased by increasing talc and epoxy resin content. It is believed that, the agglomerates break down at higher shear stress (due to 10 kg applied load) and the nano size resin particles as balls facilitate the sliding and movement of the talc particles and the PP melt layers. As it can be seem in Fig. 6, the incline of MFR curve up to 2.5 wt% resin for 40% talc composite is steeper than 30 and 20% talc and it can be concluded that, the effect of epoxy resin on increasing the melt flow at higher shear stresses are more pronounced up to around 2.5 wt% of resin, and in the composites with higher talc content.

Morphology and its correlation with shrinkage behavior and shear flow

The SEM images of fractured surfaces of the injection molded samples are shown is Fig. 7. Most of particles in the fractured surface have platy structure oriented in flow direction with various particle sizes. The sizes of bigger particles are close to mean particle size of talc which is about 10 μm. There are many other smaller nano-size particles with average diameter of about 200 nm, visible in the SEM micrographs of Fig. 7b and c, which are the cured epoxy resin particles.
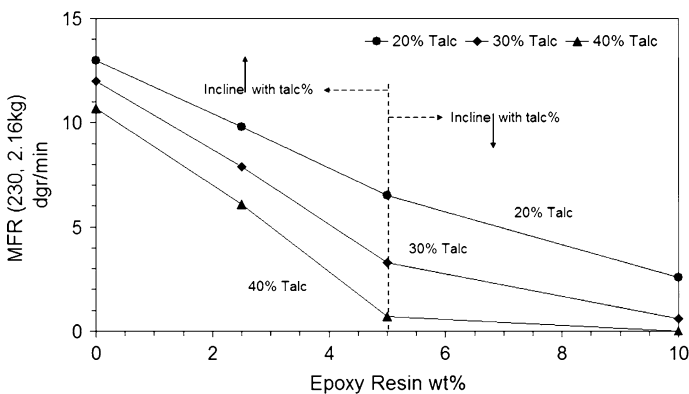

Fig. 5 Effect of the epoxy resin% on the melt flow rate of composite at low load of 2.16 kg
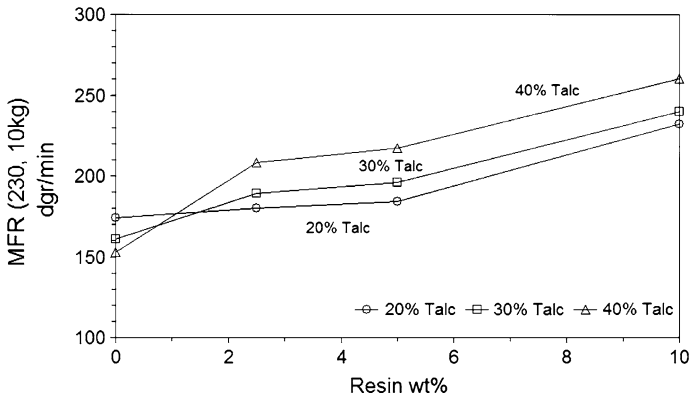
Fig. 6 The effect of talc content on the melt flow rate at high load of 10 kg

Lim and White [18] were found that plate-like particles such as talc in the thermoplastic matrix-based on the analysis made on the 3-mm thick specimens-orient so that their major surfaces lie parallel to the metal walls of the die or mould prescribing the flow. Similarly, Suh and White [19, 20] were found that talc flakes showed preferred alignment parallel to the surface of blow-molded and thermo-formed polyolefin parts. Medina [21] by using X-ray diffraction and scanning electron microscopy on 6-mm thick plaques showed that, for talc-filled polypro-pylene compounds in the skin region of injection mouldings the long axis of the talc platelets aligned parallel to the molding surface, whereas through the molding thickness orientation was more random [18]. By presenting an SEM image in Ref. [2], it has been expressed that, the talc particles align in the direction of applied stress and keeps the random form in the boundary layer in the skin region. It has been shown in SEM images of our previous report [22] that, the talc plate-like particles were aligned with an angle, in the direction of flow even close to the skin of molded part. It is generally accepted that the fillers particles will separate when internal stresses, induced by viscous drag, exceed a certain value equal to the attractive cohesive force [23, 24]. According to this concept, in shear flow, the maximum separating force due to viscous drag on the particles to overcome the attractive cohesive force of filler particles will be obtained at an orientation of 45° relative to the direction of applied shear [25].

The talc powder, and also epoxy resin nano size particles induce isotropic shrinkage in the molded parts. It is found a minor negligible difference in shrinkage rates of the composites modified by epoxy resin in the flow and cross-flow directions at higher percentages of talc (Table 2). The epoxy resin nano size particles were induced isotropic shrinkage rates, in the PP matrix.

As it can be seen in the SEM images, a fraction of epoxy resin interacted with, and adhered on the talc particles, which this may alter talc surface chemistry and change the talc–PP interaction. A part of cured resin also dispersed in the PP matrix and as balls facilitated the movement of melt layers on each other and sliding on the
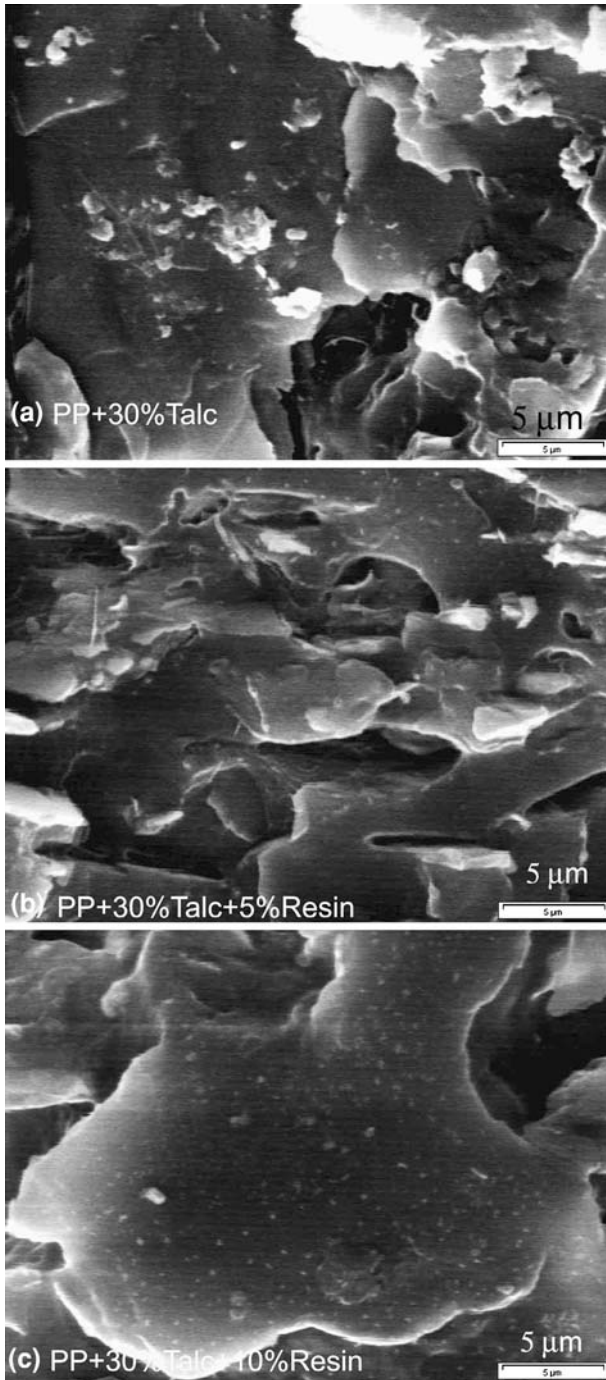
Fig. 7 The SEM images of fractured surfaces of the injection molded samples

talc platy shape particles at high shear rates. This microstructure may be justified by the increase in melt flow rate at high load in MFR test.

By increasing the resin percentage in the formulations, the population density of nano-size solid particles increased with a good dispersion in the PP matrix. The distinct and clear boundaries of dispersed particles are the evidence of weak interfacial interaction with polypropylene matrix that leads to lower mechanical properties of composite in the absence of compatibilizers especially at high epoxy resin content.

Effect of epoxy resin on thermal stability

The effects of epoxy resin on the thermal stability of composites are shown in Figs. 8, 9.

It is found that epoxy resin increased the thermal stability of composites. The tensile strength of PP + 30% talc changed from 34.5 to 29 MPa after about 700 h aging time. It means a decrease of about 16% in tensile strength was observed. At the same period of aging time for the composites with 2.5%, and 5% epoxy resin, the loss in tensile strength were 7.3 and 3.8% respectively, which are the evidences of stabilization effect of epoxy resin on the PP–talc composites. The same effect has been observed through thermogravimetry analysis on the PP-epoxy treated nanosilica [13].

The Loss in tensile strength of composite with various amounts of epoxy resins is shown in Fig. 9. As is seen, the tensile strength of composite with 10% epoxy resin remained unchanged. It can be due to interaction of epoxy resin with talc powder and the metallic impurities on the particles surfaces. The talc high energy surfaces and also its metallic impurities may accelerate the degradation reaction of matrix polymer of composites. The inherent interaction of functional groups of epoxy resin with talc as a mineral with high surface energy leads to changing the surface chemistry and affect degradation reaction.
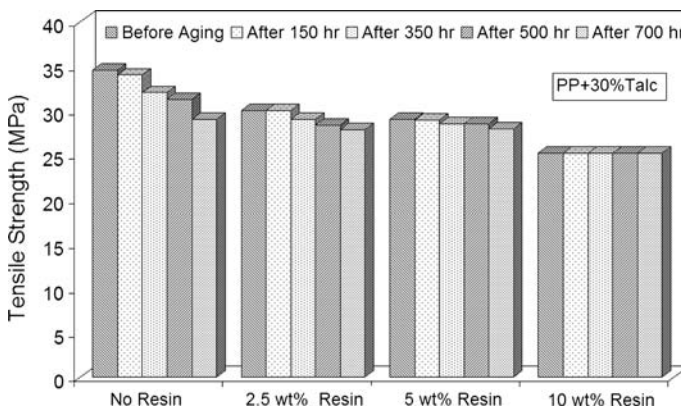

Fig. 8 The tensile strength of aged samples of PP + 30% talc with various epoxy resin content
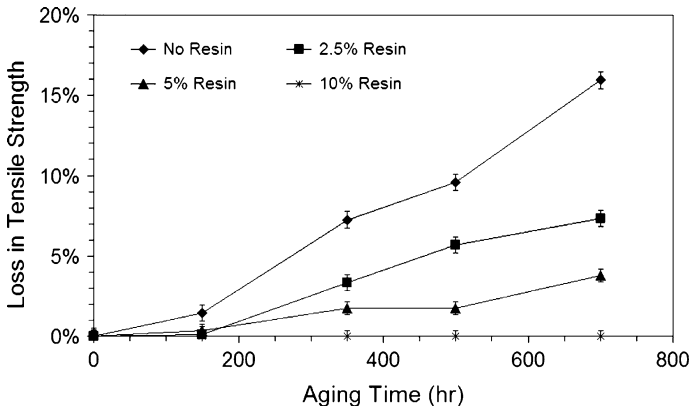
Fig. 9 The loss in tensile strength of aged composite with different epoxy resin content

Conclusions

The experiments made in this study leads to the following conclusions:

- The shrinkage behaviors of composites at various talc content and resin/talc ratios indicated that the shrinkage rates decrease by increasing the percentages of talc and epoxy resin.
- The epoxy resin nano size particles were induced isotropic shrinkage rates, in the molded parts.
- The effect of epoxy resin on increasing the melt flow at higher shear rates are more pronounced up to 2.5 wt% of resin in the composites with higher talc content.
- The morphology study of fractured surface of injection molded samples showed that epoxy resin adhered on the talc particles, and also dispersed in the PP matrix and as balls facilitated the movement of melt layers on each other and sliding on the talc platy shape particles by breaking down the agglomerates at high shear rates.
- It is fond that epoxy resin increased the thermal stability of composites. The effect of epoxy resin on the thermal stability of composites is more pronounced at higher epoxy resin content.
- The epoxy resin has inherent interaction with metallic impurities and could deactivate the metallic ion in catalyzing the PP degradation reaction.

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