تأثير عمليات إعادة التصنيع على خواص الأنسياب و الخواص الميكانيكية لمادة البولي ستيارين المقاوم للصدم

م. م. سوسن ضياء أحمد شبر
قسم هندسة المواد/ كلية الهندسة - جامعة الكوفة

الخلاصة

تم تعرض مادة البولي ستيارين المقاوم للصدم إلى اجهادات حرارية و قوى قص بعدها و سانتو و طرق تشمل استخدام جهاز الريويمتر الشعري ذو الضغط العالي و جهاز البثق المختبري و جهاز خلط المعاجين البوليمرية. حيث أوضح النتائج أن إعادة التصنيع لمادة البولي ستيارين المقاوم للصدم عن طريق إعادة صهرها و تشكيلها تسبب انخفاضا في اجهادات القص و بالتالي هناك انخفاض في اللزوجة أيضا بثبوت معدلات القص. كما لوظ أن معدل الانخفاض في اللزوجة عند استعمال جهاز الريويمتر الشعري أعلى من مثليه عند استعمال جهاز البثق المختبري؛ أما في حالة استعمال جهاز خلط المعاجين البوليمرية فقد زادت مئات الشد و لوظح حصول تناقص في قيمة الاستطالة عند إعادة صهرها و تشكيلها بكلا الجهازين الأخرين. من ثم تم تطبيق هذا العمل المختبري في احد المعامل المحلية لغرض مقارنة النتائج المستحصلة.
Introduction:

Styrenic polymers are low-cost and versatile materials that are commonly employed in a wide range of applications including packaging, automotive components, and electrical and electronic equipment. Mechanical recycling has been identified as the preferred route for the recovery of styrenic plastic waste in packaging applications. The improvement of the impact properties of styrenic polymers such as high-impact polystyrene (HIPS) is usually achieved by incorporating a rubber disperse phase (usually polybutadiene or styrene/butadiene rubber) into the styrenic rigid matrix (Beyler, et al., 2002).

It is therefore important to understand the degradation mechanisms to which recycled styrenic polymers are subjected during their life cycle, to better assess their potential for further employment in second-market applications (Scheirs, 1998). Several papers have been published on this subject. Mantia et.al. (2000) studied the effect of flow on the degradation of polystyrene using capillaries of different length. He also discussed the possible breakage of C-C links under elongation flow. Murthy and Raghavendra, (1981) concluded that increased degradation of polystyrene is caused by higher shearing in extrusion and pelletization processes. Inaba and Inoue (1981) investigated the changes of molecular weight of polystyrene degraded at 340-380°C. Deanin et al. (1983) reported that by extrusion of HIPS for 5 cycles no further improvement was required. Francisco et. al., (2006) stated that multiple processing and thermo-oxidation exhibit complex chemical and physical implications for the structure and properties of recycled HIPS. In another study (Francisco et. al., 2007) detected the presence of low molecular weight compounds and several styrene dimmers in virgin and recycled the HIPS samples.

The most important factors affecting degradation of polymers are thermal treatment, amount of shear stress acting on the polymer and residence time, i.e. the time for which the polymer melt is subject to certain thermal and shear effects (Karlsson et al.2002). PS is known to follow an end-chain mechanism or depolymerization steps resulting in mostly monomeric units as the main product (Peterson et. al., 2001).

The aim of the present work is to study changes in some rheological and mechanical properties of HIPS recycled and treated in different ways under various thermal and shear conditions.
Experimental Work:

Commercial grade HIPS Dow 45.7 E, having a melt flow index of 3.9 (condition G) was used in this work. Reprocessing was performed by multiple extrusions, employing three different ways:

First, the polymer was recycled (at constant shear rate) using a high pressure capillary Rheometer (Rheoscope 1000-CEAST), having a flat entry capillary tube with L/D ratio of 40; the preheating time was 5 minutes. The extrusion temperature was 230°C. After each period the plastic material was cut into small chips utilizing the extrudate for ten cycles.

In the second method, the Brabender Plastograph was used at 160°C and 60 rpm. The polymer samples were allowed to remain inside the mixing head and therefore were subjected to thermal and shear stresses for various periods of time, namely: 7, 30, 60, 90, 120 and 180 minutes. The period of 7 minutes represents the time required to reach a minimum value of the torque in Brabender curve. After each period the plastic material was cut into small chips for sheet preparation and rheological measurements.

A third procedure of aging was to use a small laboratory extruder, for 100% recycling of HIPS operating at 230 °C, 60 rpm and for six cycles. After each extrusion cycle the material was cooled by air and grinded; some material was kept for analysis and the remaining was reintroduced for further extrusion. 1mm thick sheets were produced to investigate the changes in rheological and mechanical properties with each cycle.

Results and discussion

Fig. 1 shows changes in shear stress resulting from the recycling of HIPS for 10 successive cycles using the high pressure capillary Rheometer at several constant shear rates (namely: 608 , 2432 , 3040 and 3648 s⁻¹). The polymer melt was subjected to thermal aging by preheating for 5 minutes for each cycle in addition to the thermal and shear stresses occurring during the extrusion process. The residence time for each extrusion depended on the shear rate applied and was in the range 1-4 minute. The results show a noticeable decrease of shear stress values with increasing number of cycles at constant shear rate; consequently the viscosity values were also decreased as shown in Fig. 2. These results may be attributed to thermo-mechanical degradation caused by successive processing, which may have induced chain scission phenomena and a resulting decrease in the molecular weight of the polymer. Fig. 3 and 4 represents changes of shear stresses and apparent viscosity respectively with mixing time under constant shear rate (namely: 6.08, 12.2, 24.3, 60.8, 121, 243, 608, 1218 and 2432 s⁻¹) obtained by treatment of HIPS in the Brabender.
Plasticorder. It can be seen that both parameters showed a decrease with increasing mixing time, up to 60 min. between 60 and 120 minutes, the values remained apparently unchanged. From 120 to 180 minutes a slight increase of the apparent viscosity was noticed. It is clear that the flow properties after 60 minutes of treatment of HIPS in the Brabender head at 160°C were equivalent to those of polymer melts recycled ten times in the Rheometer. The total residence time in the Rheometer consisted of 55 minutes for preheating and 10-40 minutes for extrusion time.

Discoloration of the extrudate was noticed with the progress of the cycles. However, no remarkable changes were detected in structure by IR spectroscopy applied to material degraded in the Brabender mixer compared with virgin HIPS, as can be seen in Fig. 5.

The recycling of small chips of (HIPS) using laboratory extruder indicated no changeable values of flow properties for all six cycles as illustrated in Fig. 6 and 7. Only the extrusion of virgin material (as granules), showed decreas of shear stresses and decrease of shear stresses and viscosities. This is due to the working pressure for the granules being twice its value for the recycled chips. The results obtained emphasize the role of shear stresses in enhancing chain scission reaction. It can also be concluded that the values of flow properties are a result of factors acting in opposite directions. Thus there is the chain scission reaction, due to thermo-oxidation and shear influence which could result in a decrease in the apparent viscosity. On the other hand, crosslinking, entanglement, radical interactions, reorientation of polymer chains, and compaction are responsible for the increase of the apparent melt viscosity. In addition to the above mention factors, HIPS which is a two phase system comprising of fine rubber particles dispersed in polystyrene matrix, can exhibit differing behavior under the same thermal and shear stresses.

As seen in Fig. 3 and 6, the results of mechanical properties showed an increase in tensile strength of samples treated in Brabender mixer, but the elongation was decreased by increasing the aging time. This result can be explained by the stretching effect dominating in the Brabender mixer head. On the other hand, both tensile strength and elongation tend to decrease by increasing number of cycles in the case of laboratory extruder. These observations are explained to be due to insufficient compaction resulted from lower working pressure in the extruder.

Fig. 1 demonstrated also the behavior of pure polystyrene for comparison purposes. The curves show the same tendency of decreasing the viscosity with increasing number of cycles. We may conclude that the introduction of a rubbery phase alters, however, the stability of the blends in regards to degradation, enhancing the sensitivity of the material to the degradative agents.

This work was then applied in a local plant where industrial processing and palletizing equipment were used. Thus, 25% of recycled HIPS were added continuously to the virgin feedstock for periods of one and two weeks. The results of flow property measurements are also shown in
Fig. 1. It is clearly seen that these are equivalent to 4 and 6 recycles of 100% HIPS. The main advantage of the plant application was to compare experimental and actual results. It was found that in indoor recycling there was color stability indicating higher thermal stability and also contamination prevention of the feedstock.

Fig. 1  Variation of shear stress with number of cycles at constant shear rate: ◦, HIPS; +, polystyrene without impact modifier; *, industrial 25% recycling of HIPS for one week; ×, industrial 25% recycling of HIPS for two weeks
Fig. 2 Apparent viscosity versus number of cycles, using a high pressure capillary Rheometer
Fig. 3 Using a Brabender mixer: (a) tensile strength and elongation versus mixing time

- ○ tensile strength and, (×) elongation %;

(b) Shear stress versus mixing time at constant apparent shear rate.
Fig. 4 Apparent viscosity mixing time, using a Brabender mixer at 160°C

Fig. 5 IR-spectra of virgin HIPS (—) and degraded HIPS (---) using a Brabender mixer at 160 °C for 180 min.
Fig. 6 Using a laboratory extruder: (a) tensile strength and elongation versus number of cycles; (○) tensile strength and, (×) elongation %;
(b) Shear stress versus number of cycles at constant shear rate.
Fig. 7 Apparent viscosity versus number of cycles, using a laboratory extruder.
References:

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