A Reactive Blending Method for Preparation of Poly (vinyl chloride)/Thermosetting Polyurethane Blends

H. Haddadi1, M.H.N. Famili2

1Polymer Engineering Group, Department of Chemical Engineering, Tarbiat Modarres University PO Box14115-111, Jalal al Ahmad Avenue, Tehran, Iran E-mail address: haddadi.h81@gmail.com, bsp@ptp.ir; 2Polymer Engineering Group, Department of Chemical Engineering, Tarbiat Modarres University PO Box14115-111, Jalal al Ahmad Avenue, Tehran, Iran E-mail address: nfamili@modares.ac.ir

ABSTRACT
An attempt was made to prepare poly (vinyl chloride) (PVC)/thermosetting polyurethane (PU) blends via direct formation of the thermosetting minor phase from its reactants during blending into PVC. Chemorheological approaches were employed in order to investigate the formation reaction of PU. The results of chemorheological analyses were utilized to adjust appropriate reactive blending temperature. PVC/PU reactive blending process was carried out in a laboratory internal mixer. PVC and PU reactive mixture were fed into the internal mixer using two different feed orders. In the first method porous particles of PVC and liquid mixture of PU monomers were premixed in a high speed mixer at ambient temperature. The blending was then followed by processing the prepared paste in the preheated internal mixer. In the second method PVC was loaded into the internal mixer. Afterward, PU reactive compound was introduced into the PVC after torque equilibrium. For both feed orders the PU content of blends and rotor speed were among parameters studied. The mechanical properties of PVC/PU blends prepared by reactive blending and pure PVC showed that incorporation of PU elastomer into PVC through the proposed reactive blending technique resulted in an increase in the elongation at break and toughness of the brittle PVC.

Introduction
Nowadays, considerable research interest is focused on the production of new polymeric materials obtained by blending two or more polymers. It has become a common practice to blend existing polymers to obtain new materials, instead of searching for new monomers, which are often costly and time consuming [1]. The major feature of polymer blending is that the properties of blends like processing characteristics and mechanical properties are better than those exhibited by either of single components [2]. Moreover, by development of novel blending techniques it is possible to expand the variety of polymer blends.

Reactive blending which can be performed by formation of a polymeric material during its blending into another polymer, has emerged as one of the most attractive fields in polymer science [3]. New developments in polymer blends and alloys have been increased sharply because reactive blending can provide viable cost effective mechanisms for elaboration of the desired blend [4-7].

Thermoplastic (TP)/Thermoset (TS) blends are polymeric materials which have been produced by reactive blending techniques. For producing a TP/TS polymeric blend, reactive blending has been performed by mixing of a TP polymer with TS precursors followed by formation reaction of the TS component. Usually the molar mass increase and the cross-linking reaction of TS phase occur during its blending into TP polymer [8-10]. Several sets of TP/TS polymeric blends have been reported in the literature. The blends of cross-linking Epoxy-amine/Polystyrene [9, 10], cross-linking system of ethylene vinyl acetate and ethylene methyl acrylate/ Polypropylene [11], thermosetting liquid pre-resins of methylene bis-phenyl diisocyanate (MDI), oligomeric MDI isocyanate, toluene diisocyanate, epoxy and vinyl ester / poly (vinyl chloride) [12, 13] are examples of TP/TS polymeric blends.

Poly (vinyl chloride), PVC, is an extensively used thermoplastic material because of its good mechanical and physical properties together with high chemical and abrasion resistance [14]. Additionally, it is also possible to introduce some polymeric modifiers into PVC in order to improve its processing characteristics and mechanical properties. Blends of PVC/Acrylonitrile-butadiene-styrene (ABS) [15], PVC/ Acrylonitrile butadiene rubber (NBR) [16, 17], PVC/ Polycrylates [1] PVC/ polystyrene [6] and PVC/ Thermoplastic polyurethanes (TPU) [18-21] have been produced by blending of PVC and polymeric modifiers.

Reactive blending method offers a cost effective alternative method for incorporation of new polymeric modifiers into PVC. Elastomeric modifiers can be reactive blended with PVC to increase the impact resistance of brittle PVC matrix. Moreover, by premixing and absorption of the low molecular weight monomer mixture of some polymeric modifiers into porous PVC particles, the monomer molecules before polymerization, may penetrate into the PVC particles, separating the PVC chains as a plasticizer. Therefore, plasticization of PVC by monomers of the polymeric modifier is a way to overcome the processing and blending difficulties such as partial PVC degradation which is a result of melt-processing at high temperatures [1, 12]. Polycrylates [1], Polystyrenes [6] and Thermoplastic polyurethanes (TPU) [20,
The main objective of the present study was to introduce a thermosetting polyurethane (PU) elastomer into the rigid PVC. Thermosetting polyurethane elastomers can be synthesized through condensation reaction between a bifunctional polyol and a short chain diol (chain extender) mixture and a multi-functional isocyanate. Thermosetting polyurethane elastomers are manufactured using low cost raw materials. In addition, by a proper combination of monomer types and their weight fractions in a PU formulation, it is possible to produce an elastomer with expected elongation at break and flexibility. In the present research work, the applicable routine for blending PVC and thermosetting polyurethane elastomer was suggested to be a reactive blending procedure at which in-situ formation of the polyurethane minor phase occurred during its blending into PVC. The major challenge with such a blending method was to adjust proper reactive blending conditions, in accordance with the knowledge about polyurethane formation reaction to introduce a thermosetting polyurethane elastomer into PVC for improving toughness and elongation at break of rigid PVC. The study on such a reactive blending technique was performed in two steps: The investigation of PU cross-linking reaction by means of chemorheological approaches for determination of proper blending temperature (Stage 1). Reactive blending of PVC and PU together with investigation on the effect of feed order of blend components (PVC and PU monomers), weight fraction of the PU phase and mixing speed on the mechanical properties of prepared blends (Stage 2).

**Experimental**

### Materials

Suspension PVC, porous particles, 100-150 µm diameter (K value-67, Abadan Petrochemical Company, Iran), was used in the present study. PVC was stabilized with 5 (phr) of Barium-Cadmium (Ba-Cd) thermal stabilizer (Polika Company, Iran). The polyurethane formulation was based on Poly (tetra methylene ether glycol) (PTMEG)/ Polymeric diphenyl methane diisocyanate (PMDI)/ 1, 4-Butanediol (BDO). PTMEG (PTMEG3000, Poyyesh Petrochemicals, Iran) is a bifunctional polyether polyol. According to the certificate of analysis from supplier this polyol had a number average molecular weight of 3000 g/mol. Consistent with this molecular weight value the equivalent weight of PTMEG is equal to 1516.216 grams per equivalent (g/eq). BDO (Merck Chemical Products, Germany) is a low molecular weight diol (90.12 g/mol) with the equivalent weight value of 45.06 g/eq. PMDI (Suprassec 5025, Huntsman Polyurethanes, UK) is a mixture of 50 percent (by weight) of 4, 4′-diphenyl methane diisocyanate and 50 percent of higher molecular weight polyisocyanates. Average functionality of this product is 2.7 and its equivalent weight is equal to 136 g/eq.

### Polyurethane gelation study

Chemorheological approach was used to investigate the gelation of the polyurethane reacting mixture at which the weight percents of (PTMEG / PMDI / BDO) in the reactive formulation were chosen as (86% / 13% / 1%). The procedure of polyurethane formulation design was discussed elsewhere [22]. To prepare samples for rheological measurements, PTMEG which was in solid state at room temperature (melting point: 36°C) was dried in a vacuum oven at 60°C overnight. PMDI and BDO were used without further purification. After demoisturizing of PTMEG, BDO was weighted and added to the melted PTMEG and hand mixed for 5 minutes. The temperature of PTMEG / BDO mixture was kept around 40°C during mixing. Pre-weighted PMDI was injected into the PTMEG / BDO mixture and mixing continued for 1 minute. PTMEG / PMDI / BDO reactive compound was sampled into the Rheometer chamber within 1 minute. The lag time between PMDI addition (start of reaction) and the beginning of rheological monitoring was kept as low as possible at a constant value of 2 minutes for all rheological experiments.

Rheological measurements of the PU reactive mixture were carried out using a Paar physica UDS200 stress/ strain controlled rheometer. Parallel plate geometry with 25mm diameter and 1 mm gap setting was employed. Two types of small amplitude oscillatory measurements were performed to assess the rheological properties of the PU reacting system.

**Temperature sweep:** In temperature sweep experiments, sample was heated by linear increase of the temperature with a constant heating rate of 1 °C /min. The evolution of G′, G″, tan(δ) and complex viscosity of reacting system during the heating process were monitored. Temperature sweep experiment was performed using the strain of 1 (%) and the angular frequency of 10 (S⁻¹).

**Isothermal time test:** In this type of rheological measurements, the changes in rheological properties of the polyurethane reacting system during reaction progression were recorded. For time test experiments, which were performed at isothermal conditions, strain was set at 1 (%) and the constant frequency was chosen from values of 1, 5, 10, 20 and 50 (S⁻¹).

### PVC/PU reactive blending

All studies of the PVC/PU reactive blending process were carried out in a Brabender Plasticorder batch type internal mixer. Equipped with cam style rotors, the internal mixing volume of mixer was approximately 82 Cm³. Linked to a data acquisition software system, it was capable of measuring temperature and torque as a function of mixing time. The internal mixer was operated with a fill factor of 85% by volume. Before PVC/PU reactive blending in the internal mixer
PVC and thermal stabilizer were mixed in a high speed, temperature controlled mixer at stirring speed of (2700 rpm) over 10 minutes.

For PVC/PU reactive blending two feed orders for loading the blend components into the internal mixer were proposed. The first feed order was based on pre-mixing of the stabilized PVC and the PU reactive mixture in the high speed mixer over 5 minutes at ambient temperature. In this step, reacting mixture of PU monomers was added gradually into PVC particles during stirring of the high speed mixer. After compounding PVC and PU monomers in proportions of 75/25, 85/15 and 90/10 (% by weight) of PVC/PU, reactive blending was followed into the internal mixer. In the second feed order blend preparation in the internal mixer was performed as follows: At first, stabilized PVC was loaded into the preheated internal mixer chamber and allowed to equilibrate. Next, polyurethane reactive formulation was added into the PVC in proportions to yield PVC/PU blends which contained 10, 15 and 25 (% by weight) of thermosetting polyurethane. Rotor speeds of 60, 80 and 100 rpm were the processing variable studied in both feed orders.

**Mechanical properties**

Tensile tests were performed using a Zwick universal test machine according to ASTM D638. The load cell was set at 5000 KN, the crosshead speed at 10 mm/min and the gauge at 25mm. Elongation at break and toughness were measured and reported at room temperature. Three to five separate specimens were measured and the values were averaged.

**Results and Discussion**

**Step (i): Polyurethane chemorheological analyses**

**Determination of the blending temperature**: Progression of the formation reaction of a thermosetting polymer, results in a transition from the liquid to the solid state. The point of this phase transition has been defined as gel point. Determination of the gel point of a cross-linking system is critical for the reactive blending of a thermosetting polymer and a thermoplastic material. It has been reported that, in the case of TP/TS polymeric blends, by progression of the reaction and reaching the gel point of thermosetting component, this phase can be considered as a “solid-elastic phase” [11]. Consequently, cross-linking of thermosetting phase leads to morphology stabilization during reactive processing [11, 23]. Thermosetting nature of the polyurethane in the present research work necessitated a thorough understanding about gel times of the PU reactive mixture at different temperatures. Through a comparison between gel times of the polyurethane at various temperatures and the suitable temperature range for PVC processing, it was possible to set an appropriate temperature for reactive blending process.

In the present research work, investigation of the polyurethane gelation was carried out using chemorheological methods. Chemorheology is defined as the study of rheological changes occurring during the course of a chemical reaction [24]. The chemical reaction has a pronounced effect on the molecular structure of polymers. In addition, rheological properties of polymers depend on molecular mobility, which is affected by molecular structure. Consequently, it is possible to measure rheological properties of a reacting system by using chemorheological approaches for monitoring the reaction progression. In the case of cross-linking polymers, the crucial role of the chemorheology was determination of the gel time in a processing temperature domain.

For defining a temperature domain suitable for processing of a thermosetting polymer, one of the most effective methods is determination of its gelation temperature [25]. The gelation temperature, \( T_{gel} \), has been determined from dynamic temperature ramp (temperature sweep) experiments. The temperature corresponding to the chemical gelation is manifested by a dramatic increase of viscoelastic moduli (storage modulus (\( G' \)) and loss modulus (\( G'' \))) [26, 27]. Figures 1 depicts the results of temperature sweep experiment at the strain amplitude of 1 (%) and frequency of 10 (S^-1). It can be observed in figure 1 that at temperatures beyond 100°C a dramatic increase of viscoelastic moduli, especially storage modulus occurs. The gelation temperature has been essentially determined from the inflection point of the elastic moduli curve in the temperature corresponding to its sharp increase (\( T_{gel-inflection} \)) [26]. Moreover, the gelation temperature has been determined as the point at which \( G' \) and \( G'' \) cross-over takes place (\( T_{gel-crossover} \)) [27]. In the present research work, the gelation temperature which were calculated using both criteria are marked in the curves of \( G' \) and \( G'' \) versus temperature.

In order to determine the gel time of the PU reactive mixture at different temperatures, time test experiments at isothermal conditions were employed. Temperatures between 75°C -160°C were chosen as the temperature window suitable for processing of PU. The pointed out temperature domain, which covers temperatures below and above the gelation temperature (\( T_{gel-inflection}: 100°C, T_{gel-crossover}: 109°C \)), was determined in accordance with the result of temperature sweep experiment. Figure 2 illustrates the viscosity change during isothermal curing of the polyurethane reactive formulation at the strain amplitude of 1 (%) and dynamic frequency of 10 (S^-1). As it can be seen in figure 2, at each curing temperature a steep increase of the complex viscosity is observed. The gel time can be determined as the time when the viscosity of the reacting system tends to infinity [27], however it is not easy to determine the exact time of the abrupt viscosity rise. The curing of thermosets has been monitored by recording the evolving values of \( G' \) and \( G'' \) during cure and the gel time has also been determined as the point at which the curves of storage and loss modulus cross each other [23, 27, 28]. Figure 3 represents gel points calculated using \( G'-G'' \) crossover criterion which are plotted against temperature. The effect of increasing the temperature on the curing reaction is enhancing the reaction rate [30]. It can be seen in figure 3 that by increasing the reaction rate, the gel time decreases.

Based on the results of rheological measurements carried out in various temperatures ranging from 75-160°C, the calculated gel times have been compared. The gel time of the PU reactive mixture at 120°C implied that blending at this...
temperature achieved sufficient time (approximately 620 s) for PVC/PU blending process before reaching the gelation (probable freezing point of morphology during the blending process). Consequently, the temperature of 120°C was chosen for PVC/PU reactive blending.

**Precise determination of the gel time at the blending temperature:** Consideration of the dynamics near the critical point of gelation has led to predictions for the frequency dependence of the modulus G’’(ω) = G’’(0) + i G’’(0). At the gel point, the frequency dependence of G’ and G’’ can be represented by a power law over a large frequency range [25, 29, 31, 32]:

\[ G’ = G’’ \sim \omega^{\Delta}, \quad \Delta = 2\delta/\pi \]

Accordingly, at the gel point the loss factor (tan δ = G’’/G’) become independent of frequency. This theory has been used to determine the gel time through plotting the loss factors versus time at various frequencies and determination of the intersection point of loss factor curves (loss factors intersection method) [25, 29, 31, 32]. The gel time of the PU reacting system at the blending temperature of 120°C was also determined using loss factors intersection criteria. Figure 4 clearly shows a coincidence domain of the time evolution of the loss factor curves obtained at different frequencies by the blending temperature. According to the result which is presented in this figure, gel time at 120°C is localized at the time of 630 s after the beginning of the rheological monitoring. Considering the gel time of the PU reacting formulation obtained by the intersection of loss factors and the cross-over point of G’ and G’’, the gelation time obtained using both methods are close to each other. Therefore, the possible blending time before reaching the gelation point of the polyurethane thermosetting phase is in the range of 620–630 s.

**The effect of PVC stabilizer on the gel time of polyurethane:** It was probable that thermal stabilizers used in PVC processing, which contain metal elements might function as catalysts for the polyurethane formation reaction [20]. Therefore, it was necessary to use a thermal stabilizer with minimum catalytic effect on the formation reaction of thermosetting polyurethane. In order to investigate the catalytic effect of PVC thermal stabilizers on the PU reaction, 5 (phr) of Ba-Cd and dibutyltin dilaurate stabilizers were mixed with reactive formulation and the gel times were compared with pure PU reactive system. For reasons of legibility the change in complex viscosity of PU formulations at 90°C with and without PVC thermal stabilizers are illustrated in figure 5. The times of gelation determined using the point of G’’-G’ cross-over are also marked with an arrow in this figure. It is observed that Ba-Cd did not have a significant effect on the gel time of polyurethane. Therefore, Ba-Cd was used as PVC thermal stabilizer for reactive blending process.

**Step (iii): reactive blending of (PVC/thermosetting polyurethane)**

**Investigation of the Mixing Rheology:** The mixing torque recorded by an internal mixer is a direct indication of the change in viscosity [2]. For the mixture of a thermoplastic polymer and reacting system of a thermosetting polymer, the formation reaction of thermosetting component results in an increase of the mixture viscosity. Hence, it is possible to follow the reaction induced change of viscosity during reactive blending process by monitoring the mixing torque. Figure 6 (a) represents the Brabender plastograms of the first feed order of 75/25 (PVC/PU) blending at 60 r.p.m. The initial peak, which is observed in point (A) is attributed to the loading of PVC/PU paste. The mixing torque starts to increase due to the formation of cross-linked polyurethane rubbery phase from low-viscosity reactants, which leads to increase of the (PVC/PU) mixture viscosity and mixing torque, respectively. The torque becomes steady at point (B). The mixing torque versus mixing time curves of the second feed order of 75/25 (PVC/PU) blending at 60 rpm is illustrated in figure 6 (b). The peak at point (A) is an indication of PVC feeding. After torque equilibrium the chamber is opened and the polyurethane reactive formulation is fed into the mixer chamber (point (B)). The polymerization and curing of polyurethane, which occur in-situ during mixing and homogenizing of the mixture lead to an increase in torque until achievement of its equilibrium at point (C). The stable torque in both feed orders indicates that the reaction of the polyurethane is completed and the blends become homogenized [2, 16]. For a reactive blending process which is performed in an internal mixer, **blending time** is defined as the time domain between the beginning of the torque increase and achievement of its equilibrium. A comparison between the gel time of polyurethane at 120°C and the blending times of each feed order indicates that the blending times for preparation of the blends through the first feed order are longer than the blending times of the second feed. As it was pointed out in the experimental section of this paper, in the premixing step performed in the first feed order, polyurethane reactive mixture of monomers was pre-blended with small, porous and irregular PVC particles. During premixing of liquid reactants and PVC, thermostet precursors coat the surface and permeate into the pores of PVC particles [1]. This may lead to the dilution effect on the reactive mixture of thermosetting polyurethane precursors. Dilution prevents the reaction between functional groups of thermosetting reactive mixture [12]. Therefore, the gel time of the polyurethane increased which resulted in longer blending times of the first feed order.

**Investigation of the Mechanical properties of blends:** Mechanical properties of the prepared blends were investigated in order to study the effectiveness of the reactive blending process in improvement of the mechanical properties of rigid PVC. The elongation at break of the blends which were prepared by the first and second feed orders in three polyurethane compositions and application of three rotation speeds of internal mixer rotors are shown in figures 9 (a) and (b). Values of the elongation at break for rigid PVC are marked using dashed line in each figure. The elongation at break and toughness values of the blends are also included in table I. As it can be concluded from figure 9 and table I, the
The elongation at break and toughness of the PVC/PU blends are greater than those of PVC in all cases. The polyurethane rubbery phase with high elongation at break and toughness is capable of withstanding high deformation without breaking. The improvement of the pointed out mechanical properties becomes significant by increasing the polyurethane content of the blends. The enhancement of mechanical properties is more pronounced for blends prepared through the first feed order. It has been reported that, absorption of the monomers in the porous PVC particles provides a better dispersion of the monomer molecules and the resulting dispersed polymer formed in the PVC matrix [1]. In the case of the present study, the more significant improvement of mechanical properties of the blends prepared using the first feed order originates from the incorporation of PU monomers into pores of PVC particles at the premixing step, which leads to a more homogeneous mixing of polyurethane and PVC in comparison with blends prepared through the second feed order.

Mechanical properties of blends which were prepared by the second feed order show a pronounced dependency on blending speed when compared to the first feed order. In the production process of the blends through the second feed order, in contrast to the first feed order at which a premixing step was carried out, all the mixing process of PVC and thermosetting polyurethane was performed into the internal mixer. Consequently, application of higher rotor speeds during blending process led to improved mixing of blend components and enhancement in mechanical properties.

<table>
<thead>
<tr>
<th>Feeding Method</th>
<th>PU Weight Percent</th>
<th>Rotation Speed (R.P.M)</th>
<th>Elongation at break (%)</th>
<th>Toughness (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
<td>60</td>
<td>17.02 ± 0.7</td>
<td>0.17 ± 0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>80</td>
<td>17.31 ± 0.7</td>
<td>0.2 ± 0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>20.63 ± 1.1</td>
<td>0.23 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>60</td>
<td>28.41 ± 0.7</td>
<td>0.28 ± 0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>80</td>
<td>25.63 ± 1.3</td>
<td>0.27 ± 0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>29.58 ± 1.1</td>
<td>0.4 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>60</td>
<td>42.97 ± 2.7</td>
<td>0.69 ± 0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>80</td>
<td>35.2 ± 5.2</td>
<td>0.515 ± 0.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>69.56 ± 8.6</td>
<td>1.375 ± 0.25</td>
</tr>
<tr>
<td>First feed order</td>
<td>10</td>
<td>60</td>
<td>15.07 ± 1.1</td>
<td>0.17 ± 0.005</td>
</tr>
<tr>
<td></td>
<td></td>
<td>80</td>
<td>16.14 ± 0.1</td>
<td>0.17 ± 0.005</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>16.99 ± 2.3</td>
<td>0.18 ± 0.005</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>60</td>
<td>23.25 ± 1.2</td>
<td>0.19 ± 0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>80</td>
<td>26.37 ± 0.8</td>
<td>0.20 ± 0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>25.1 ± 0.1</td>
<td>0.36 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>60</td>
<td>32.56 ± 3.1</td>
<td>0.42 ± 0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>80</td>
<td>37.17 ± 0.6</td>
<td>0.54 ± 0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>38.97 ± 0.8</td>
<td>0.7 ± 0.01</td>
</tr>
<tr>
<td>Second feed order</td>
<td>10</td>
<td>60</td>
<td>16.14 ± 0.1</td>
<td>0.17 ± 0.005</td>
</tr>
<tr>
<td></td>
<td></td>
<td>80</td>
<td>16.99 ± 2.3</td>
<td>0.18 ± 0.005</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>16.99 ± 2.3</td>
<td>0.18 ± 0.005</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>60</td>
<td>26.37 ± 0.8</td>
<td>0.20 ± 0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>80</td>
<td>25.1 ± 0.1</td>
<td>0.36 ± 0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>32.56 ± 3.1</td>
<td>0.42 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>60</td>
<td>37.17 ± 0.6</td>
<td>0.54 ± 0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>80</td>
<td>38.97 ± 0.8</td>
<td>0.7 ± 0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>38.97 ± 0.8</td>
<td>0.7 ± 0.01</td>
</tr>
</tbody>
</table>

Table I - Summary of the mechanical properties of the blends

Figure 1 - The change of viscoelastic moduli of PU reactive formulation during gradual heating process at the constant heating rate of 1 (°C/min)
Figure 2 – The change of complex viscosity of PU reacting system against time at various temperatures.

Figure 3 – The gel time of PU reactive system against temperature. Gel times have been determined using the point of $G'$-$G''$ cross-over.

Figure 4 – The change of loss factor of PU reacting system at different frequencies. The experiment temperature was 120° C. The gel time is marked in figure as the intersection point of loss factor curves.
Figure 5 – The effect of PVC thermal stabilizers on the change of gel time of PU reactive system. The gel time as the point of $G'-G''$ cross-over is marked in this figure.

Figure 6 a – The mixing torque versus mixing time curves for 25/75 (% Wt PU/PVC) formulation prepared through the first feed order.

Figure 6 b – The mixing torque versus mixing time curves for 25/75 (% Wt PU/PVC) formulation prepared through the second feed order.
The elongation at break of the blends prepared using the first feed order increased with increasing the rotor speed, because in the second feed order the mixing of PVC and PU mainly performed into the internal mixer.

References

Figure 9 a – The elongation at break of the blends prepared using the first feed order

Figure 9 b – The elongation at break of the blends prepared using the second feed order

Conclusion
The blending temperature of PVC/PU reactive blending into the internal mixer was determined utilizing the results of chemorheological analyses. The investigation of mechanical properties of the PVC/PU blends indicated that elongation at break and toughness of the blends was higher than those of rigid PVC in all cases. The pointed out mechanical properties promoted by increasing the polyurethane content of the blends. Blends produced using the first feed order represented enhanced elongation at break and toughness in comparison with the blends prepared by second feed order. Moreover, elongation at break and toughness of the blends produced through second feed order increased with increasing the rotor speed, because in the second feed order the mixing of PVC and PU mainly performed into the internal mixer.
22. Haddadi H. The Reactive Blending of Thermosetting Polyurethane In-Situ With Poly (vinyl chloride). Msc. Dissertation 2006; Tarbiat Modares University, Tehran, Iran