

PVC/Butyl Acrylate-grafted-Methyl Methacrylate/Styrene 블렌드의 동적 유변거동과 가공성 및 기계적 물성

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Dynamic Rheological Behavior, Processability and Mechanical Properties of PVC/Butyl Acrylate-grafted-Methyl Methacrylate/Styrene Blends

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Abstract: Core-shell structured grafted copolymer particles of butyl acrylate (BA) grafted methyl methacrylate (MMA) and styrene (St) monomers (ACR-g-St) were prepared by seed emulsion polymerization. Poly(vinyl chloride) (PVC)/ACR-g-St blends were proposed. The fusion properties, dynamic mechanical behavior, rheological behavior, mechanical properties and morphology of blends were characterized by a torque rheometer, dynamic mechanical analyzer (DMA), rotational rheometer, universal mechanical testing machine and scanning electron microscope (SEM). The results showed that the ACR-g-St particles accelerated the fusion of PVC resins, but the equilibrium torque increased slightly. The storage modulus (G'), loss modulus (G'') and complex viscosity (η^*) of melts exhibited a monotonic changing with frequency and all had minimum values when ACR-g-St content was 16 phr. The tensile and impact strength were highest at 8 phr content of ACR-g-St. ACR-g-St not only can be used as an efficient impact aid but also plays a role of lubricant, which is helpful for PVC processing.

Keywords: poly(vinyl chloride), ACR-g-St, rheological behavior, wall-slip, mechanical property.

Introduction

Poly(vinyl chloride) (PVC), the second most common plastic after polyethylene (PE), is widely employed general-purpose plastic due to its excellent overall performance. It has been extensively used in construction, transportation and many other industries thanks to its versatility, being relatively low costs, high stiffness and good chemical resistance.¹⁻³ However, the utilization of PVC is restricted by poor processing property, brittle fracture, bad toughness and low heat resistance.⁴ The improvement of its toughness and processing property has received considerable attention for many years. Polymer blending in many researches is a straightforward, versatile and

inexpensive method to combine the useful properties of different polymers and can provide an incredible range of physical or chemical properties.⁵

As is well known now, the toughness of plastics could be considerably strengthened by addition of a rubbery phase.^{6,7} Rubber modification of brittle and semiductile thermoplastics with core-shell rubber particles has been commercially successful in past decades.^{8,9} PVC is a typical example of semiductile thermoplastics that can be toughened by both methacrylate-butadiene-styrene (MBS) rubber materials¹⁰ and acrylic impact modifiers (AIMs),¹¹ all consisting of structured core-shell latex particles.^{12,13} Toughening agents are substances that are usually compatible with PVC giving adhesion between PVC. The mechanism of adhering PVC by the toughening agents during processing involves increasing the coefficient of friction between PVC particles themselves and in the case of poor lubrication additives, between the PVC particles and the

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metal surface of the processing machinery.¹⁴ Acrylic core-shell tougheners are usually used for interior applications, which offer increased environmental resistance. Using the acrylic type rubber impact modifiers is particularly critical for polymers that are used in making skin compounds for automotive instruments and door panels to display excellent heat and ultraviolet resistance, although their toughening efficiency is usually lower than that of the butadiene-based types,¹⁵ but it has good anti-aging property. The fusion rheological behavior and dynamic mechanical properties of polymers are very important for processing and applications of polymeric materials, however, acrylic core-shell tougheners increase the melt viscosity of PVC during processing. In general, in order to improve the toughness and processing property at the same time, both toughening agents and lubricants are essential when processing PVC compounds. Lubricants are added to ease the flow ability of the PVC, tending to produce wall-slipping PVC compound. Work by Grossman indicated that the main function of a lubricant in PVC was to facilitate the internal rotations of polymer molecules (when miscible in the polymer) and to increase the polarity of the polymers (both PVC and polymeric processing aids in this case).¹⁶ The current researches about the rheological property of PVC mainly concentrate in the external lubricant. Such as Jungang Gao¹⁷ have studied that organic-inorganic hybrid nanocomposites, as a kind of lubricants, introduced into PVC matrix. A moderate amount of organic-inorganic hybrid nanocomposites adding into PVC matrix can achieve good fluidity.

In this work, a series of core-shell structured copolymer, ACR-g-St with different content of St, was synthesized by seed emulsion polymerization. Even though many researchers have studied that the toughening effect on PVC basically unchanged when St substituted for MMA partly in many articles,^{18,19} less attention on the dynamic rheological and processing properties. St has a good flow property which is beneficial for dynamic rheological and processing property of the blends. ACR-g-St was used as toughener and also played a role of lubricant. The dynamic rheological behavior, processability, dynamic mechanical property and mechanical property of PVC/ACR-g-St blends were investigated through rotational rheometer, torque rheometer, dynamic mechanical analysis (DMA) and universal mechanical testing machine.

The results showed that when ACR-g-St content was less than 8 phr, the tensile strength had little changed, but was higher than the pure PVC. The tensile strength was decreased when the ACR-g-St content was more than 8 phr. Moreover,

the impact strength increased continuously with increasing ACR-g-St content and the best impact strength was 1136 J/m. The storage modulus (G'), loss modulus (G'') and complex viscosity (η^*) of the blends reached a minimum at ACR-g-St was 16 phr. It was suggested that the grafted St played a role of wall-slip with a stick-slip transition, which was helpful for PVC processing, and ACR-g-St not only has a good toughening efficiency, but also has a good flow and a wall-slip effect on molecular movement.

Experimental

Materials. PVC (SG-5) was supplied by Jilin Siping Hao-hua Chemical Co., China. ACR-g-St was synthesized by seed emulsion polymerization. The organotin (heat stabilizers) is commercial grade and was supplied by Dongwan Chem. Co., China. The emulsifier, sodium dodecyl sulfate (SDS) and initiator, persulfate (KPS) are all chemical pure grade.

Synthesis of Toughening Agent ACR-g-St. The toughening modifier (ACR-g-St) was synthesized via a two-stage seeded emulsion polymerization. PBA acrylic rubbery core were grafted polymerized with PMMA/St shell were made in a 1000 mL three-neck glass reactor equipped with a reflux, inlet nitrogen, and a magnetic stirrer. The reactor was held in a bath with thermostatic control. The ratio of core (BA) with shell (MMA/St) was 80/20 (wt/wt) and the content of St was 5, 10 and 15 wt% of the shell. First, PBA seed latexes were synthesized at 70 °C. The SDS was 0.4 g, KPS was 0.6 g. In the second stage, the methyl methacrylate (MMA)/styrene (St) with initiator was added to form the shell over the PBA seeds. Keeping reaction time for 1 h followed by de-emulsification, filtration, washing, and drying to obtained ACR-g-St powders.

Preparation of PVC/ACR-g-St Blends. Firstly, ACR-g-St with different content of St was prepared with PVC. The ratio was 100/8, named S5, S10 and S15, respectively. Then, 2 phr organotin were added to the PVC/ACR-g-St mixtures, the 1 mm-thick and 5 mm-thick plates were pressed at 180 °C and then cold pressed for 3 min at 5 MPa in order to determine mechanical property.

Secondly, six samples of PVC/ACR-g-St (The content of St is 10%. It has best mechanical property from Figure 1) blends were prepared. The ratio of PVC with ACR-g-St in the blend is shown in Table 1. Then, 2 phr organotin were added to the PVC/ACR-g-St mixtures, respectively.

All blends were prepared using a Haake Rheomix 600 internal mixer. The blends were simultaneously mixed at a rota-

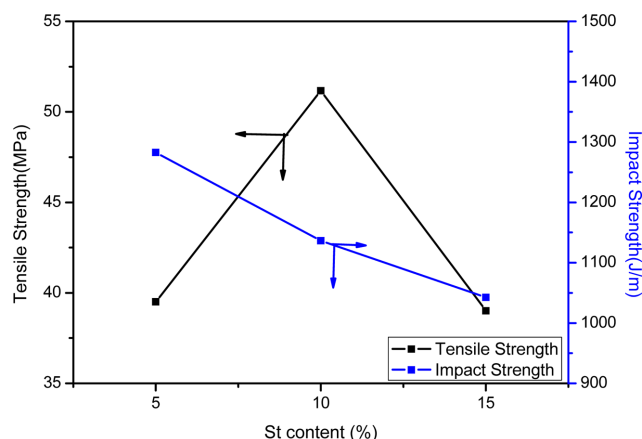


Figure 1. Influence of St content on ACR-g-St on impact and tensile strength.

Table 1. ACR-g-St Content Ratio of PVC/ACR-g-St Blends

Sample	M ₀	M ₄	M ₈	M ₁₂	M ₁₆	M ₂₀
PVC(phr)	100	100	100	100	100	100
ACR-g-St(phr)	0	4	8	12	16	20

tional speed of 40 rpm during 7 min. The temperature imposed during mixing was 180 °C, chosen in order to minimize the degradation of the PVC. Then, the 1 mm-thick and 5 mm-thick plates were pressed at 185 °C, respectively, and then cold-pressed for 3 min at 5 MPa to determine dynamic rheological behavior, dynamic mechanical properties and mechanical properties. Thus, the PVC/ACR-g-St blends were obtained and marked as, M₀, M₄, M₈, M₁₂, M₁₆ and M₂₀, respectively.

Determination of Fusion and Dynamic Rheological Behavior. The fusion behaviors of M₀ to M₂₀, containing various amounts of ACR-g-St, were investigated at 180 °C using a Thermo Haake torque rheometer (TYP557-9301, Germany). Dynamic rheological measurements were performed using an oscillatory rheometer (AR2000ex, TA CO., USA) equipped with parallel plates of 25 mm in diameter, all viscoelastic measurements were performed in the linear regime at a temperature of 190 °C, from 0.1 to 100 Hz. Storage modulus (G'), loss modulus (G'') and complex viscosity (η^*) were measured in the frequency scanning experiments.

Determination of Dynamic Mechanical Properties. Dynamic mechanical properties of M₀ to M₂₀ were studied using a dynamic mechanical analyzer (Diamond DMA, Perkin Elmer Co., USA). The sample size was 25×5×1 mm, heating rate was 3 °C/min, and the frequency was 1 Hz. The range of testing temperature was from -80 to 140 °C.

Determination of Mechanical Properties. According to

ASTM D-256, the tensile strength was determined. Tensile strength test was performed using an electronic tensile tester (INSTRONG 5565, USA.). Tests were conducted at an extension rate of 50 mm/min, at 23 °C. The notch impact test was carried out on an XJU-22 impact tester (Chengde Test Instrument).

Morphology Characterization. The morphology structure of M₀ to M₂₀ samples' fractured surfaces obtained in notched impact test was studied by scanning electron microscopy (SEM, JSM5600, Japan) with operating voltage of 15 kV and a magnification of 10000. After etched by toluene for 4 h, dissolving the PMMA shell of the dispersed phase in the blend samples by the solvent caused the rubber particles to leave out the PVC matrix. The etched surface specimens were dried and then gold-sputtered before microscopy.

Results and Discussion

Mechanical Property of PVC/ACR-g-St Blends. From the previous research,²⁰ PVC/ACR blends have the best mechanical property when the content of ACR is 8 phr. Thus, the ACR-g-St content is also 8 phr in the experiment. Figure 1 shows the data on the impact and tensile strength of PVC/ACR-g-St blends. The impact strength is from 1282 J/m to 1042 J/m with increasing content of St in ACR-g-St and tensile strength has maximum value at 10% content of St. In conclusion, the blend has better mechanical property when the content of St is 10%. Thus, we conduct a further study about its amount on PVC dynamic rheological behavior and processability.

Fusion Behavior of PVC/ACR-g-St Blends. Figure 2 shows the relationship between the equilibrium torque, fusion time and ACR-g-St content. The fusion time and equilibrium torque were listed in Table 2. Generally, it was found that the fusion time of the blends decreased with the increasing ACR-g-St content, from 3.80 to 0.75 min, and the equilibrium torque of the blends increased, but increased only slightly, from 14.0 to 18.23 Nm. In the fusion process, the PVC resin was broken into primary particles and then turned into much smaller particles until the end of the plasticizing process at high temperature and constantly mechanical stirring.²¹ ACR-g-St is core-shell structure, in comparison with the PVC melt, a new physical bond formation between the rubber particles and the PVC particles in the blend caused the torque value of the blend to increase. More interfacial adhesion between the rubber particles and the PVC particles increased the elastic melt property.

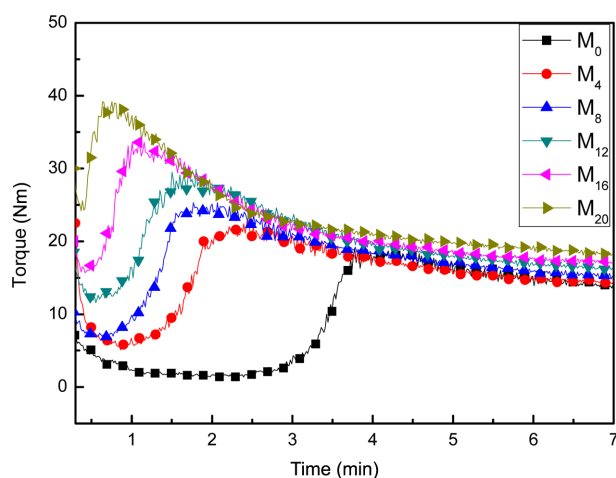


Figure 2. Relationship of the equilibrium torque, fusion time and ACR-g-St content.

Table 2. Fusion Time and Equilibrium Torque of the Blends

Sample	M ₀	M ₄	M ₈	M ₁₂	M ₁₆	M ₂₀
Fusion time (min)	3.80	2.31	1.83	1.54	1.04	0.75
Equilibrium torque (Nm)	13.95	14.48	15.30	16.41	17.24	18.23

It can decrease fusion time in the processing, this is because the chain segments of acrylate is polar molecule chain segment in ACR-g-St particle, which can increase the friction force between the PVC with ACR-g-St particle, and accelerate the fusion of PVC particle under processing condition. During the thermal processing, the molecular chains of ACR-g-St are softened and then react with PVC molecules through polar-polar attractions, which can increase the molecular entanglement and degree of PVC fusion, therefore the fusion time is decreased with the increasing content of ACR-g-St. Meanwhile, polystyrene has a lower melt viscosity and plays a wall-slip effect on molecule movement in the melt, so it can offset a part of friction force between the molecules. That is why the rubber particles content increased exponentially but the equilibrium torque did not increase significantly.

Dynamic Mechanical Properties of PVC/ACR-g-St Blends. Dynamic mechanics analysis (DMA) is a molecular level analysis method reflecting the interaction and movement of molecules. Under the action of oscillating stress, the mechanical energy is used to change the molecular chain conformation. Meanwhile, DMA can be described as an effective method for determining the interaction on a molecular level between the different components in the blend.²²

Figure 3 shows the changes in glass transition temperature

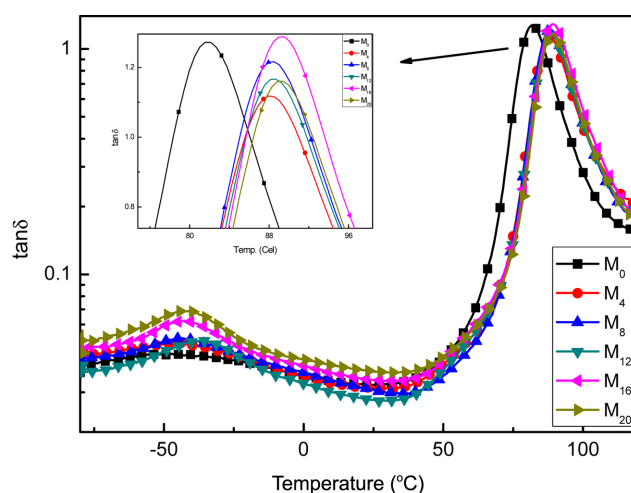


Figure 3. Tanδ curves as function of temperature for PVC/ACR-g-St blends.

Table 3. T_g of Blends at Different ACR-g-St Content

Sample	M ₀	M ₄	M ₈	M ₁₂	M ₁₆	M ₂₀
T_g (°C)	81.77	88.0	88.36	88.43	89.37	89.37

(T_g) of PVC/ACR-g-St blends with different addition content of ACR-g-St. The maximum values of tanδ and T_g with different ACR-g-St content are shown in Table 3. As seen from the Table 3, The variations of T_g are 81.77 to 89.37 °C. The increase in T_g is associated with an increase in entanglement level due to the presence of the toughening agents. As the degree of entanglement increases, the molecular chains become more difficult to mobilize.²³ More ACR-g-St content, more difficult to mobilize, so the T_g increased with the increasing content of ACR-g-St.

The effects of temperature on the storage modulus (E') of the blends at 1 Hz are shown in Figure 4. The value of storage modulus (E') signifies the stiffness of the material.²⁴ It can be inferred from Figure 4 that the incorporation of ACR-g-St in the PVC decreases the E' to a certain extent and E' decreases with the increasing ACR-g-St content. This can be attributed that the core of ACR-g-St is rubber elastic material, when the temperature is higher than the T_g of PBA, the movement of acrylate molecular chain changes from glassy state to elastomeric state, it will become soft. The results clearly show that the addition of ACR-g-St into PVC results in a remarkable decrease in the stiffness of the material. It is well known that rubber elastic material has larger internal friction than plastic material. The butyl acrylate rubber content increases with increasing ACR-g-St content, so more energy will be dissipated.

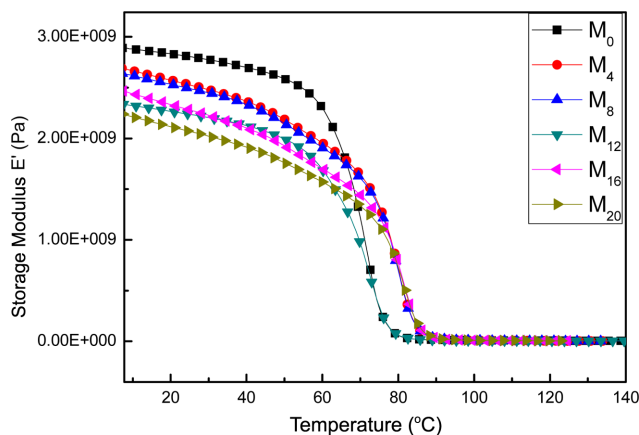


Figure 4. Relationship of storage modulus and temperature.

pated, and the E' decreases with increasing ACR-g-St content.²⁵ The result is consistent with the report of Rameteke.²⁶

Dynamic Rheological Behavior of PVC/ACR-g-St Blends. Rheological tests are sensitive to molecule chain entanglements or chain structure such as small differences in chain length, branching or networking. These factors will cause a large variation in flow behavior.²⁷ In the polymer processing, a clear and accurate understanding of the rheological properties of various polymer or polymer composites is important. Rheological behavior can provide structural information of materials and should be controlled for industrial applications. It is known that the storage modulus (G') of melts is more sensitive than the loss modulus (G'') to morphology or rheological properties of materials in the rheological experiments, because storage energy (G') between molecules is more related to rheological properties of melts than loss energy (G'').^{27,28}

The dynamic storage modulus (G') is related to the elastic behavior of material; the dynamic loss modulus (G'') represents the dissipated energy.^{29,30} The dependence of G' and G'' on the frequency can measure the relative motion of all molecules. The increase in G' may result from the change in molecular chain rigidity and the interaction between polymer chains.

Figure 5 shows the logarithmic plots of G' vs. ang. frequency of the PVC/ACR-g-St blends at 190 °C, respectively. From Figure 5, it has been observed that the G' increases with frequency for all blends and M_{12} has the minimum G' value at the same frequency, but they are all higher than that of pure PVC. This can be attributed to the fact that acrylate segments are polar constitutional units, the friction and interaction force between ACR-g-St molecules and PVC chains will be

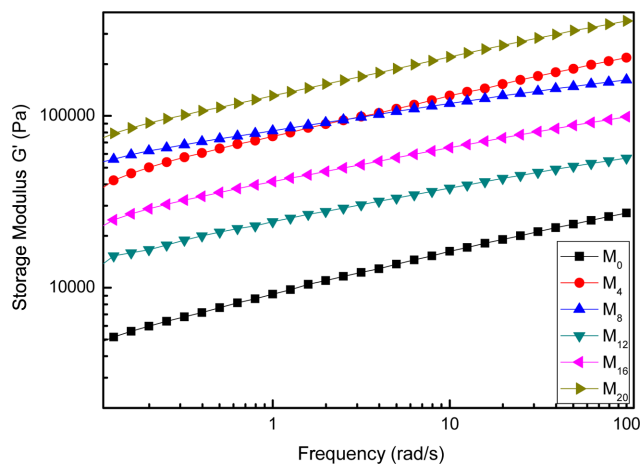


Figure 5. Relationship of G' and frequency for PVC/ACR-g-St blends.

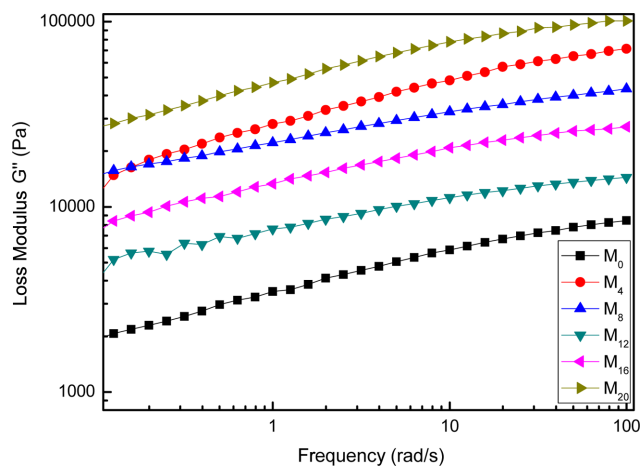


Figure 6. Relationship of G'' and frequency for PVC/ACR-g-St blends.

increased. The free rotation and movement of molecular chain are capably restricted, and prevent from complete relaxation due to physical jamming, thus, G' increases when ACR-g-St is added to PVC. At lower frequency range, the blend has sufficient time for the relaxation of entanglements resulting in low storage modulus. However, at higher frequency the blends do not get sufficient time for the relaxation process resulting in higher storage modulus values.

The variation of loss modulus (G'') against ang. frequency of blends is represented in Figure 6. It has been observed that G'' of the blends shows the same trend as that of G' .

Figure 7 shows the plots of complex viscosity (η^*) vs. ang. frequency. The η^* of PVC/ACR-g-St blends exhibits a monotonic decrease with increasing frequency, and the η^* has min-

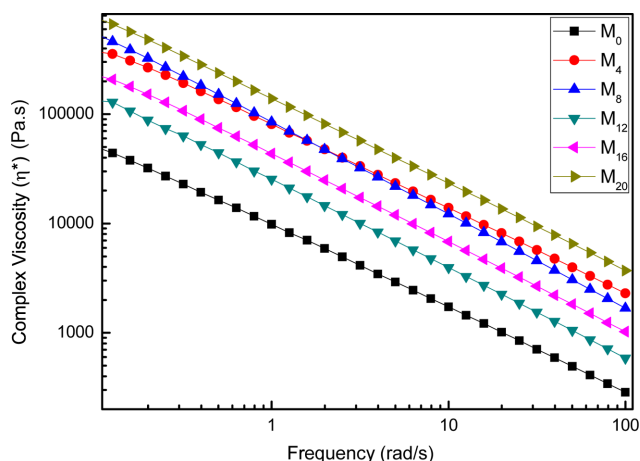


Figure 7. Complex viscosity as a function of frequency with ACR-g-St content.

imum value at the same frequency when the content of ACR-g-St is 12 phr. It should be noted that all the η^* of blends are higher than that of pure PVC. This is similar to changes of G' and G'' , as discussed before. As we all know, PVC is a typical pseudoplastic fluid, the pseudoplastic nature of polymer arises from the randomly oriented and entangled nature of polymer chains. With the increase in frequency the shear rate increases and at high shear rate, the chains become disentangled and will be oriented in the direction of shear. A lower frequency region, the entanglement is higher and this opposes the flow of the melt thereby the viscosity becomes higher, however, at higher frequency region; molecular chain entanglement speed is less than the speed of unwrapping, flow more easily. Thus, the η^* decreases with the increasing frequency.

It is noteworthy that the η^* of M_{16} and M_{20} increases. The transition from slip behavior to stick behavior of blends melts occurs at M_{12} . When the content of ACR-g-St is less than 12 phr, the η^* of melts decreases with the increase of ACR-g-St content, which is the result of the good fluidity and a lubricant effect on molecular movement of polystyrene melt. However, because the presence of aggregated ACR-g-St particles and rigid phenyl in polystyrene, which can form network structure and increase the steric hindrance between the molecular chains, when the content of ACR-g-St is above 12 phr, the molecular chain entanglement increases. Moreover, from the result of SEM, when the content of ACR-g-St is 16phr, the phenomenon of the aggregation is very obvious, for that reason the η^* of blends increases.

Mechanical Properties of PVC/ACR-g-St Blends. Figure 8 shows the data on the impact and tensile strength of

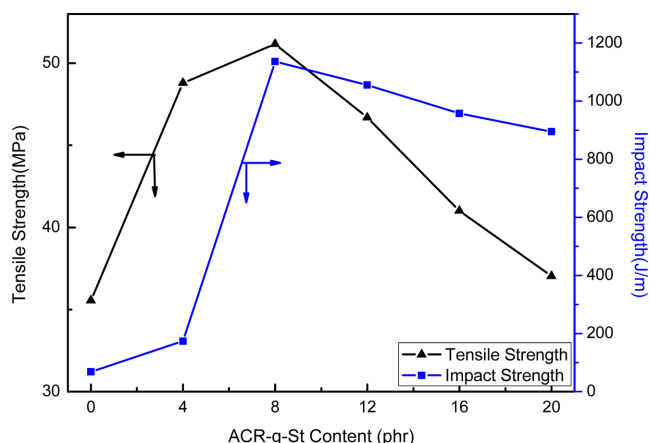


Figure 8. Influence of ACR-g-St content on impact strength and tensile strength.

PVC/ACR-g-St blends. As shown, when ACR-g-St content in the blends is below 8 phr, the tensile strength and impact strength increase with the increasing ACR-g-St content, thereafter, decrease. The impact strength reached the highest value of 1136 J/m, which is 1068 J/m higher than that of pure PVC.

Core-shell polymer modifiers are usually used to improve the toughness of the polymer matrix due to its attractive features: the rubbery core provides impact resistance, especially at low temperatures, whereas the grafted glassy shell provides rigidity and compatibility to the polymer matrix, and keeps the particles at desired shape and dispersibility. Butyl acrylate (as a rubbery core) can supply impact resistance; the methyl methacrylate and styrene segments have larger interaction with PVC molecules, rigid units (glassy shell), which can provide rigidity and enhance the tensile strength of materials.

Morphology of PVC/ACR-g-St Blends. Figure 9 displays the SEM micrographs of impact fractured surfaces of different content of ACR-g-St. From the Figure 9, the ACR-g-St particles are uniformly dispersed in PVC matrix. As shown in Figure 9(a), the impact fractured craze seems little, neat and orderly arrayed before the toughening agent is added, indicating a characteristic of typical brittle fracture. The same as Figure 9(b), even though the dispersion of ACR-g-St particles in the PVC matrix is well, we cannot find pronounced yielding or degormation in the blends. It is well known that energy absorption mechanism of rubber particles consists of not only tearing and rubber cavitations, but also crazing and deformation of matrix. Many root-like whiskers are observed in Figure 9(c), which could improve the impact performance dramatically. Thus, the blends realized the transition from brit-

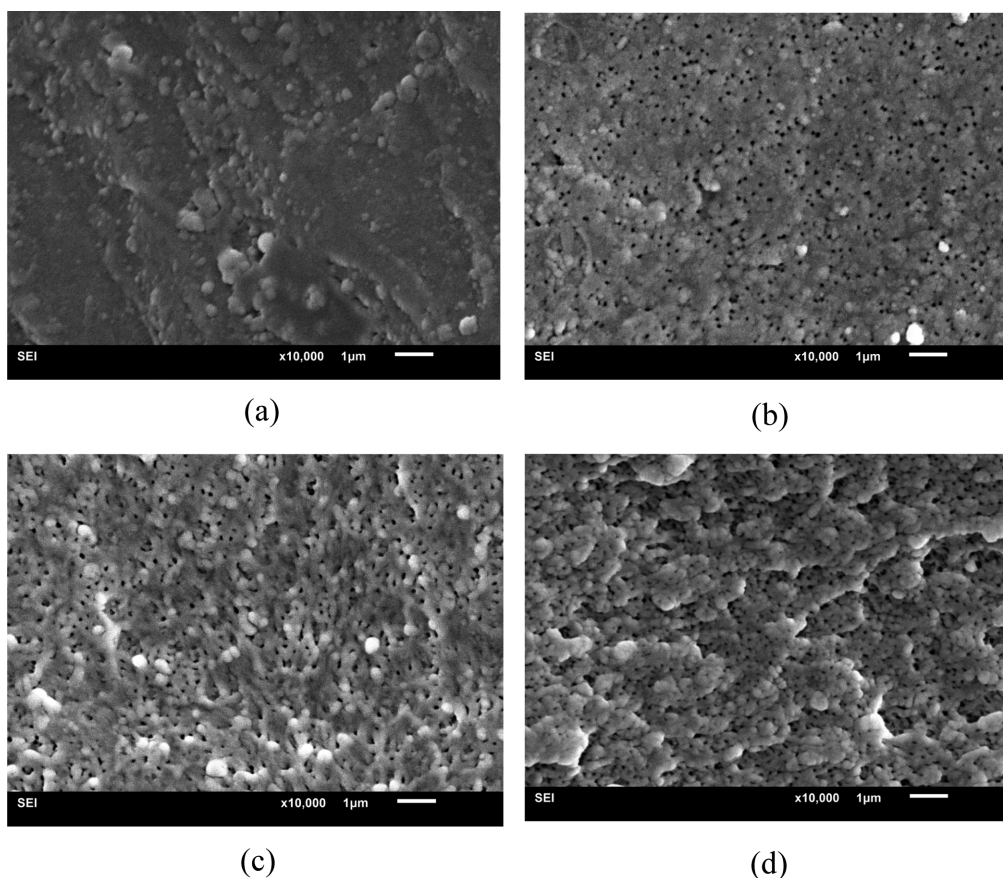


Figure 9. SEM micrographs of fracture surface for the blends containing different contents of ACR-g-St: (a) 0 phr (PVC); (b) 4 phr; (c) 8 phr; (d) 16 phr.

tleness to toughness. Figure 9(d) shows uneven layered structure appearing on the fracture at 16 phr ACR-g-St.

Conclusions

In this work, several types of acrylic PBA-g-PMMA/St core-shell modifiers with different St content are synthesized. The effect of St content on the mechanical property of PVC is investigated. The mechanical property shows that the blend has better impact and tensile strength than others when St content is 10%. Then, the effect of ACR-g-St content on the melt blending behavior of the PVC/ACR-g-St is investigated. ACR-g-St can decrease the fusion time obviously in PVC processing and offset a part of friction force between the molecules. The rheological measurements show that G' , G'' and η^* of the blends all have minimum value when ACR-g-St content is 12 phr. The results of impact tests illustrate that the deformation of PVC/ACR-g-St blends could absorb massive impact energy. The impact strength reaches the highest value of

1136 J/m, which is 1068 J/m higher than pure PVC when ACR-g-St content is 8 phr. Impact strength values and SEM results show obviously toughened fracture exists in PVC/ACR-g-St blends and ACR-g-St particles have fine dispersion in PVC matrix. The results of the DMA analysis illustrated that the additive influenced the glass transition temperature of PVC. In conclusion, ACR-g-St not only can be used as an efficient impact aid but also play a role of wall-slip, which was helpful for PVC processing.

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