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Impact properties of acrylate rubber-modified PVC: Influence of temperature

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Abstract

The enhancement of the impact resistance of plastics through the introduction of a rubbery dispersed phase is one of the means to develop high impact strength polymers and has been exploited commercially on a large scale. Rubber-toughened PVC-U or high impact PVC-U is one such important class of rubber-toughened plastics material which has been developed and has a wide application in the building and furniture industries. The type of impact modifiers most commonly used for window frame applications are chlorinated polyethylene, ethylene-vinyl acetate and acrylate modifiers. The current trend shows the importance and popularity of high impact-acrylate-modified PVC. The objective of this research is to extend the existing understanding of toughness enhancement in rubber-toughened polymer materials to acrylate rubber-modified PVC. This paper reports on the effect of temperature on the impact strength of acrylate rubber-modified PVC-U using the instrumented falling weight impact test (IFWI) method. Toughening and fracture mechanism in acrylate-modified PVC were also investigated.

The results show that all the acrylate rubber-toughened PVC blends have successfully shifted the ductile–brittle transition points to a lower temperature. However, the impact modifiers were found to differ in their efficiency to shift the ductile to brittle transition. The findings from the SEM study shows that the fibrous yielding phenomenon observed is an indication of the transition of the brittle stage to ductile stage and correlates well with the large increases of the impact strength.

Keywords: Poly(vinyl chloride) (PVC); Acrylate rubber; Impact modifiers

1. Introduction

Currently, poly(vinyl chloride) (PVC) is one of the world's leading synthetic polymers with global consumption of approximately 16 million tonnes per annum [1,2]. PVC has been used extensively due to it being relatively cheap and versatile. The versatility of this polymer is its ability to incorporate additives to suit many different applications.

However, unmodified unplasticised poly(vinyl chloride) (PVC-U) has the disadvantage of being prone to occasional brittleness and is notch sensitive. It has been observed that normally ductile materials often fail prematurely through brittle fracture. Under impact (high velocity) loading conditions, parameters such as temperature and strain rate become more important due to the viscoelastic nature of polymers. Extensive research and development work has therefore been carried out to formulate polymers with high impact resistance. The enhancement of the impact resistance of plastics through the introduction of a rubbery dispersed phase is one of the means to develop high impact strength polymers and has been exploited commercially on a large scale [3,4]. The study of enhancement of PVC has attracted a number of researchers. The influence of core–shell structured modifiers on toughness of PVC was studied by Wu et al. [5]. They successfully prepared core–shell structured grafted copolymer particles of polybutadiene grafted poly(methyl methacrylate) by emulsion polymerisation. They found out that the samples with the best impact strength could be obtained when the core–shell weight ratio of PB to PMMA is lower than 93.7. In another recent study, Chen et al. reported that nano-$CaCo_3$ had a much better toughening effect on PVC/blendex matrix than that on PVC matrix [6]. Blendex 338 which was used in the study is a modified ABS resin and is used as impact modifier in PVC. The effects of artificial and natural ageing on impact-modified PVC was studied by Jakubowicz [7]. The effects of ageing were monitored using impact strength and colour change. The study concluded that no significant cor-

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Table 1
Types and suppliers of additives

Additives	Types	Suppliers
Impact modifier	Core–shell type acrylic modifier	Rohm and Haas
Internal lubricant/stabiliser	Calcium stearate	
External lubricant	Paraffin wax (Irgawax 367)	Ciba-Geigy
Light stabiliser	Tinuvin 320	Ciba-Geigy
Heat stabiliser	Tin (Irgastab T196)	Ciba-Geigy
Processing aids	Acrylic (PA K120N)	Rohm and Haas
Processing aids	Acrylic (PA K175N)	Rohm and Haas

relation was found between results of the artificial and natural ageing.

Rubber-toughened PVC-U is one such important class of rubber-toughened plastics material which has been developed and has a wide application in the building and furniture industries [8]. The type of impact modifiers most commonly used for window frame applications are chlorinated polyethylene, ethylene-vinyl acetate and acrylate modifiers [9]. High impact-acrylate-modified PVC is very popular in the building and furniture industries due to its good weathering properties [10]. Therefore, a research with the objective to extend the existing knowledge of toughness enhancement in rubber-toughened polymer materials to acrylate rubber-modified PVC, similar to compounds used in window frame applications was conducted. This paper reports on the effect of temperature on the impact strength of acrylate rubber-modified PVC-U using the instrumented falling weight impact test (IFWI) method. Toughening and fracture mechanism in acrylate-modified PVC were also investigated.

2. Materials and experiment

2.1. Materials

The PVC used in this study is a suspension resin with solution viscosity *K*-value 68, Evipol SH 6830, supplied by EVC. Three different types of core–shell acrylic impact modifiers (referred to as A, B, and C) which differ in their rubber particle size were used in this study. Impact modifier C has the smallest rubber particles size (0.2 μm) followed by impact modifier A (0.3 μm) and B (0.4 μm). The outer shell is made up of PMMA which is compatible with PVC and the core consists of polybutyl acrylate (PBA) rubber. The other additives used are shown in Table 1.

The PVC blend formulations are shown in Table 2. These are based upon a tin stabilised formulation, but without the pigment and fillers usually present in commercial window profile materials (in order to enhance optical transparency in microscopic studies). The numbers indicates parts per 100 resin (phr) in blend.

Table 2
Blend formulations

Ingredient	M0	M1	M2	M3
PVC	100	100	100	100
Impact modifier A	–	6.4	–	–
Impact modifier B	–	–	6.4	–
Impact modifier C	–	–	–	6.4
External lubricant	1.5	1.5	1.5	1.5
Internal lubricant	1.0	1.0	1.0	1.0
Light stabiliser	1.5	1.5	1.5	1.5
Heat stabiliser	2.0	2.0	2.0	2.0
Processing aids	2.0	2.0	2.0	2.0

2.2. Sample preparation

A high speed laboratory mixer (Fielder 8L) was used to blend PVC and the additives. To produce moulded flat sheet, the dry blends of PVC and additives are firstly sheeted on a two roll-mill before being compression moulded at the set temperature of 185 °C. Samples for impact testing were cut from the compressed sheet according to the size specified in BS 2782: Part 3: Method 359 (1984). Dummy bars were routed to the standard size on a tungsten carbide cutter using a template.

2.3. Instrumented falling weight impact testing

The impact strength assessment was done using a Rosand Type 5 Instrumented Falling Weight Impact (IFWI) Tester. The impactor used has the same radius as that of the pendulum used in a conventional Charpy test. The impact velocity was kept constant at 3 m/s whilst the temperature was varied between the −40 and 60 °C for the modified samples. For blend M0 the range was extended to 80 °C. The samples were left in the environmental chamber (Rosand Temperature Control Unit) for at least 25 min at the specified temperature prior to testing. For below room temperatures in the environmental chamber, liquid nitrogen was introduced into the chamber from the tank.

2.4. Transmission electron microscopy

The toughening mechanism of the fractured samples were examined using transmission electron microscopy (TEM). The specimens were firstly sectioned (0.2 μm thick) at room temperature on a Cambridge Huxley Ultramicrotome using a freshly prepared glass knife. After the ultrathin sectioning, the samples were exposed to the RuO_4 solution for a period between 5 and 25 min to enhanced the contrast between the rubber and PVC matrix. The sections were then mounted on copper transmission microscope grids of 300 square mesh. Examinations were performed on JEOL JEM 100CX transmission electron microscopy using an accelerating voltage of 100 kV.

2.5. Scanning electron microscopy

The main use of scanning electron microscopy (SEM) in this study is to analyse the fracture surfaces of the impact-modified and unmodified samples. The fracture surfaces were prepared for examination by SEM by sputter coating with gold on an Edwards model E12 vacuum coater. A Leica Cambridge Stereoscan 360 SEM was used to examine the coated surfaces using a working voltage of 10 kV.

3. Results

3.1. Instrumented falling weight impact testing

Fig. 1 illustrates the impact strength at various temperatures for unmodified PVC and impact-modified PVC at 3 m/s. In general the impact strength of all samples decreases as the temperature decreases and when it reaches the ductile–brittle transition the impact strength drops sharply. Blend M0 (unmodified PVC) is the first to undergo the transition as the temperature decreases in the range between 60 and 80 °C, just below the glass transition temperature of PVC.

It is interesting to observe that in this study, the impact modifiers differ in controlling the ductile–brittle transition. Blend M3 has the lowest ductile–brittle transition temperature (ranging between 0 and 20 °C) followed by blend M1 (ranging between 20 and 40 °C). At 20 °C, all samples of blend M1 failed in brittle

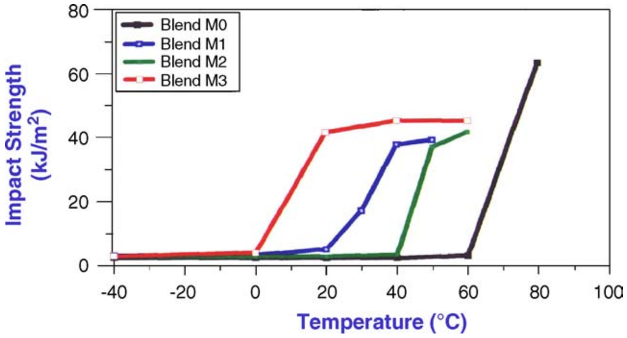

Fig. 1. Effect of temperature on impact strength at 3 m/s.

mode. At 30 °C, however the samples failed in mixed mode with two (of six) samples exhibited hinge break and failed in a ductile mode with high energy absorbed. The samples which failed in ductile mode have average energy values three times higher than the samples which failed in brittle mode. Among the modified samples, blend M2 has the highest transition temperature ranging between 40 and 50 °C.

Although all the samples failed in brittle mode at 0 °C, generally the impact-modified samples still show significantly higher impact strength values than the unmodified samples from blend M0. The impact strength of blend M3 is around 1.5 kJ/m^2 higher than blend M0. As the temperature decreases to −40 °C, all the impact-modified samples still show a higher impact strength values compared to the unmodified but the differences have reduced significantly to around 0.4 kJ/m^2.

3.2. Transmission electron microscopy

Figs. 2 and 3 show TEM micrographs of the impact fractured specimen which were stained by RuO_4. The result shows the success of utilising RuO_4 in enhancing the contrast between the acrylate rubber and PVC matrix. Fig. 2 shows the sample from blend M3 (tested at 0 °C and 3 m/s) which has undergone a brittle failure with impact strength of about 5 kJ/m^2. In general, the rubber particles do not show much permanent deformation but a few rubber particles are observed to be internally cavitated. Fig. 3 shows the sample from blend M1 (tested at 40 °C and 3 m/s) which has undergone a ductile failure with impact strength of about 40 kJ/m^2. No indication of crazing was observed in the stress-whitening part of the hinge-break fractured sample but more rubber particles are internally cavitated. No significant elongation of rubber particles is seen. From the TEM results the toughening mechanism of the acrylate rubber-toughened modified PVC system proposed is shear yielding in the matrix with internal cavitation of the rubber particles.

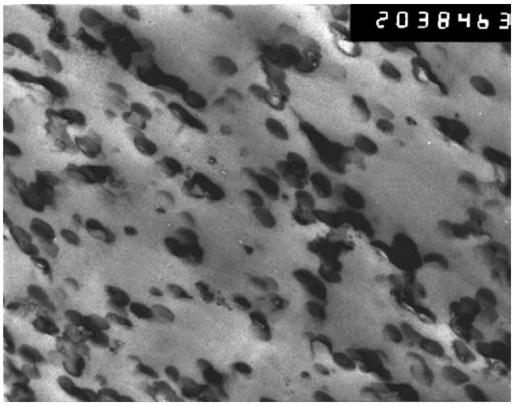

Fig. 2. TEM micrograph of blend M3 sample showing brittle failure (tested at 0 °C).

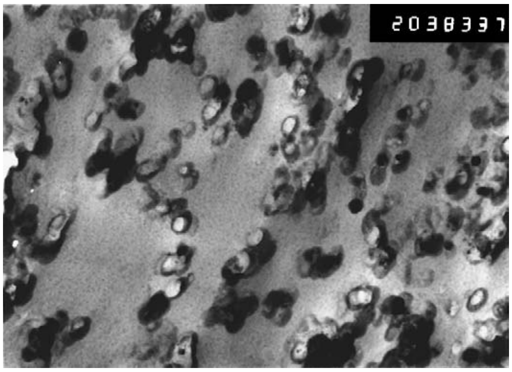

Fig. 3. TEM micrograph of blend M1 sample showing ductile failure (tested at 40 °C).

3.3. Scanning electron microscopy

The fracture behaviour of the acrylate-modified PVC samples from the instrumented falling weight impact testing can be classified into three types, from the standpoint of fracture mode (brittle/ductile) and whitening degree, which will be use as the basis for the analysing the results from SEM.

- *Type 1*: Ductile fracture with formation of an elliptical shaped stress-whitening zone near the edge and on the fracture surface.
- *Type 2*: Brittle fracture with whitening on the fracture surface.
- *Type 3*: Brittle fracture without whitening.

SEM was used to look at the fracture surfaces at a higher magnification to see and understand the processes occurring during the fracture. Fig. 4 shows the SEM micrograph of the typical type 1 fracture surface taken from sample blend M1 tested at 40 °C. The micrographs are taken close to the hinge where crack growth terminated. In the post yielding process, large amounts of local

Fig. 4. SEM micrograph of blend M1 sample showing ductile failure.

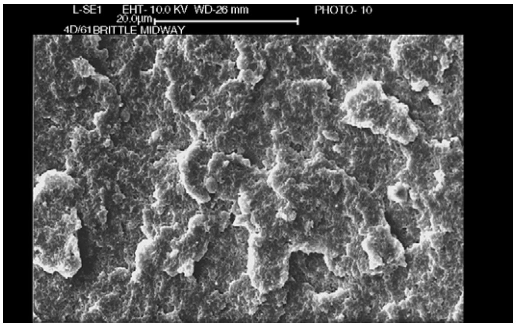

Fig. 5. SEM micrograph of blend M3 sample showing brittle failure.

strain energy are absorbed as the fibrillar (yielded) microstructure was developed and drawn to high levels of strain in the PVC matrix. The micrographs clearly show the ductile yielding and fibrillation associated with crack blunting and termination in a hinge-break sample at different levels of magnification. Numerous fibrils are observed (of varying length but of roughly the same diameter), suggesting high impact energy has been absorbed.

Fig. 5 shows the fracture surface (magnification ×200) near the end of a crack propagation taken from sample M3 (3 m/s, −40 °C) with failure energy of about 3 kJ/m^2. The micrograph shows a jagged and cratered appearance on the surface with no evidence of fibrils or yielding, a characteristic of a rapid crack propagation.

4. Discussion

The result on the influence of test temperature on impact strength is in agreement with findings of other researchers [11,12] where it has been found that by decreasing the temperature one moves closer to (and, if the temperature is low enough, will fall below) the ductile–brittle transition, and into the brittle region. Vincent [13] suggested that as the temperature decreases, the yield strength increases but has little effect on the brittle strength. The increase in yield strength will promote brittle failure since yielding is suppressed.

The results from IFWI tests have clearly shown that the acrylate modifiers have successfully shifted the ductile–brittle transition points to lower temperatures. The addition of acrylate rubber has increased the tendency towards ductile failure because of a reduction of yield strength. The yield stress is reduced in the impact-modified samples because the rubber particles can act as stress concentrators to initiate yielding [14–16]. Interestingly, the results from the ductile–brittle transition study show that the transition temperature is dependent on the structure of the impact modifier. The result clearly shows that impact modifier C (which has the smallest rubber particle size) is proven to be the most effective impact modifier in shifting the ductile–brittle transition conditions to a lower temperature. The next most effective impact modifier is impact modifier A and the least effective is impact modifier B (which has the biggest rubber particle size).

Therefore, it can be concluded that rubber particle size is an important factor that determines the efficiency of acrylate-impact modifiers in toughened PVC-U. It is generally recognised that the size of rubber particles has a strong influence upon toughness of rubber-modified polymers and for each type there appears to be an optimum particle size for toughening [17]. The role of the rubber particles and why an optimum particle size exists has to be related primarily to whether the matrix in the rubber-modified system deforms mainly by crazing or by shear yielding. In either form of toughening mechanism, the essential role of rubber particles is to act as stress concentrators, since they have much lower shear moduli than the surrounding matrix material [14–16]. The estimates for the optimum rubber particle diameters are 1–2 µm for HIPS, 0.4 µm for ABS and 0.2 µm for rubber-toughened PVC [17]. These results indicate that the optimum size of the rubber particles for toughening decreases with increasing ductility of the matrix, which can be an indication of the toughening mechanism in rubber-toughened polymers. The fact that small rubber particles are not effective in the toughening of HIPS, but such an observation is not observed in the present study on acrylate rubber-toughened PVC confirms that the toughening mechanisms in the two rubber-toughened polymers are different.

The finding that the smaller rubber particles are more effective in toughening the acrylate rubber-toughened PVC systems is explained on the role of rubber in initiating shear yielding in the matrix. The effectiveness of rubber particles to toughen pseudoductile but notch-sensitive polymers like nylon and PVC originates from the ability to generate stress concentrations around the particles in an applied stress field [14–16]. Because of the difference in modulus between the dispersed phase and the matrix, the stress will be concentrated around the rubber particles which will lead to local nucleations of plastic deformation like shear yielding. When the rubber particles are greatly separated, the stress field around a particle is only slightly affected by the presence of other particles. The stress field in the matrix is simply a superposition of those around isolated particles, and the polymer blend will remain brittle. However, when the particles are sufficiently close together, the stress field is no longer simply additive, and the field around neighbouring particles will interact considerably. As yielding occurs at the rubber–PVC interface a lower particle size gives more surface area per unit volume which results in enhanced matrix yielding, and a transition from brittle to ductile behaviour.

From the present study, it has been proven that TEM is a powerful characterisation technique for acrylate-rubber-toughened PVC (Figs. 2 and 3). The results show that RuO_4 was successfully utilised to enhanced the contrast between the acrylate rubber and PVC matrix. According to our knowledge, there is no report in the literature on the use of staining agents in TEM study of acrylate rubber-toughened PVC.

From the TEM results in the present study, it is proposed that the toughening mechanism of the acrylate rubber-toughened PVC systems is shear yielding with internal cavities in the rubber particles. These results support the previous findings from previous researchers which concluded that unlike polystyrene (which is very brittle in the untoughened state), crazing is not the main toughening mechanism in rubber-toughened PVC (which is relatively more ductile in the untoughened state) [18–20].

The findings from the SEM study shows that the fibrous (yielding) phenomenon observed is an indication of the transition of the brittle stage to ductile stage and correlates well with the large increases of impact strength. In other words, specimens of high impact strength have more fibrous patterns in the fracture surfaces. The result is in agreement with the findings from previous work which also used SEM to analyse fracture surfaces of rubber-toughened PVC [21–23]. Fann et al. [21] reported work improving the impact strength of telecommunication equipment using injection mouldable MBS-modified PVC. The study shows that as the MBS content increases to 15 and 20 phr, the fracture surfaces become more obviously fibrous. They also concluded that the fibrous phenomenon observed during SEM study to be an indication of the transition of the brittle stage to ductile stage.

Calvert [22] also used SEM to analyse the fracture surface morphologies characteristic of two different modes of deformation in acrylate rubber-modified PVC: brittle crack growth and ductile yielding. The scanning electron micrographs of brittle crack growth fracture surfaces show characteristics of a rapid crack propagation. In fracture surfaces of samples which exhibit ductile yielding, fibrillation associated with crack blunting and termination in a hinge-break sample was observed.

5. Conclusions

The main conclusions which can be drawn from this study are as follows:

(1) At impact speed of 3 m/s, all the acrylate rubber-toughened PVC blends and unmodified PVC blend show a ductile to brittle transition as the temperature is reduced. All the three types of impact modifier were shown to be efficient in decreasing the brittle to ductile transition temperature.
(2) The impact modifiers differ in their effectiveness to shift the ductile to brittle transition. The smaller the rubber particle size, the more effective it becomes in shifting the ductile–brittle transition to lower temperatures.
(3) The findings from the TEM study suggest that the mechanism of impact modification in acrylate rubber-toughened PVC systems, is based on the enhancement of localised shear yielding in the matrix, within the vicinity of the rubbery modifier particles.
(4) The findings from the SEM study show that the fibrous yielding phenomenon observed is an indication of the transition of the brittle stage to ductile stage and correlates well with the large increases of the impact strength.

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