Influence of Impact Load-Temperature Conformity on Toughening of Poly(vinyl chloride) by Core-Shell Rubber Particles

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ABSTRACT: The work focused on the elucidation of several key parameters in toughening poly(vinyl chloride) (PVC) by the methyl methacrylate–butadiene–styrene (MBS) core-shell particles. Accordingly, blends containing various weight percent of the MBS particles were prepared and characterized by dilute solution viscometry, dynamic light scattering, dynamic mechanical thermal analysis, transmission electron microscopy, and temperature variable impact test. The results showed PVC/MBS solution miscibility in almost all compositions with their maximum thermodynamic affinities at about 17 and 67 wt % of MBS in tetrahydrofurane (THF). In addition, MBS weight percent increase in its blend with the PVC above 10 led to severe impact energy raise with eventual leveling at about 17 wt %. Furthermore, blend toughness and its components miscibility in solution increased in parallel up to 20 wt % of MBS particles. On the other hand, blend toughness declined with test temperature decrease toward impact modifier core T_g at about $-30°C$ even for the sample with 20 wt % of the MBS particles. Finally, the brittle-ductile transition of the blend containing 20 wt % of the MBS particles comparison with its matrix tan δ-temperature correlation implied 2500 J/m impact energy equivalence with 90°C sample temperature rise in secondary relaxation activation. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 2691–2696, 2009

Key words: poly(vinyl chloride); toughness; interface; miscibility

INTRODUCTION

Addition of core-shell particles with rubbery core and matrix miscible shell to many polymers, for example poly(vinyl chloride) (PVC), has become very popular aiming at their toughness enhancement.[1] Despite the commercialization of these particles and their wide applications, few reports were devoted to elucidation of the key effective parameters involved in blend toughness; namely interfacial adhesion, critical interparticle distance, toughener loss capability, and specifically load-temperature conformity.

Quite recently, Zhou et al.[2] investigated the toughening efficiency of PVC containing 20 wt % of different methyl methacrylate–butadiene–styrene (MBS) particles, 200 nm in diameter. In the first type, particles core was made of polybutadiene (PB), while styrene and methyl methacrylate (MMA) monomers used in synthesizing the grafted copolymer shells. In the second type, however, part of the styrene monomer was used along with butadiene monomer in copolymerization of particles core, while the remaining styrene was copolymerized with MMA to form the tethered copolymer shells. In the last type, all the styrene monomer was used with butadiene in copolymerization of particles core, the particles shell was made exclusively with grafted poly(methyl methacrylate) (PMMA). Their toughened PVC with MBS particles made of PB core and grafted methyl methacrylate–styrene copolymer (MSC) shell showed the lowest brittle-ductile-transition (BDT) temperature. Transmission electron micrographs (TEM) of the fractured toughened PVC showed matrix shear flow as the major failure mechanism. Part of styrene monomer application in synthesizing the core copolymer along with butadiene, however, raised BDT of the toughened PVC. Accordingly, increased contribution of core cavitation mechanism in the failure of toughened PVC was also noticed by the TEM results. Finally, using all styrene monomer in synthesizing the particles core and leaving neat grafted PMMA as the shell activated core cavitation and interfacial debonding as the failure mechanisms.[2] Chen et al.[3] also studied the effect of MBS particles shell thickness on toughening PVC. Their results showed maximum toughness achievement at a critical shell thickness of 13 nm. In addition, they found the crucial role of shell copolymer composition on maximum acquired toughening. At constant interfacial layer thickness

between particles shell and matrix, interfacial adhesion decreased by styrene wt % increase. Accordingly, the role of cavitation mechanism decrease in fracture process led to declined toughness. In contrast, MMA content increase in the shell, improved interfacial adhesion and prevented debonding. Overall, they concluded a critical interfacial layer thickness at about 4.2 to 6.7 nm for PMMA and 9.8 to 7.4 nm for PS to achieve desired blend toughness.[3] Wu et al.[4] also toughened PVC with core-shell particles made of PB core engulfed in grafted PMMA shell. They found maximum blend toughness by adding at least 8 phr of impact modifier carrying at least 7 wt % of grafted PMMA in its shell to achieve threshold interparticle distance and enough interfacial adhesion.

Consequently, a threshold interparticle distance, enough interfacial adhesion and core with enough stress concentration characteristics were nominated as the key effective parameters involved in maximum toughening achievement by core/shell particles. The origin of acquired supertoughening via tuning the aforementioned parameters is not well understood because of their complex interactive nature. In addition, applied load-temperature conformity on activating cooperative segmental motion seems mainly ignored.

The interfacial characteristics of polymers is usually determined by a variety of sophisticated but not cost-effective methods including differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), small angle neutron scattering (SANS), inverse gas chromatography, and microscopic techniques (with either electron or optical beams).[5] Dilute solution viscometry, however, is a very cheap and simple method for characterizing the hydrodynamic and thermodynamic interactions among polymers.[6,7] In this technique, the specific viscosity of dilute solutions is correlated to polymer concentration, C, and intrinsic viscosity, $[\eta]$, via the Huggins classic equation:

$$\eta_{SP} = [\eta]C + K_H[\eta]^2C^2 \tag{1}$$

where K_H is Huggins constant. On the other hand, the hydrodynamic part of Huggins constant, K_1, for a dilute solution of two polymers, A and B, is calculated by eq. (2).[5]

$$K_1 = \frac{K_A[\eta]_A^2W_A^2 + K_B[\eta]_B^2W_B^2 + 2\sqrt{K_AK_B}W_A[\eta]_AW_B[\eta]_B}{(W_A[\eta]_A + W_B[\eta]_B)^2} \tag{2}$$

where W_i, $[\eta]_i$, and K_i are weight percent, intrinsic viscosity, and Huggins constant of each polymer components, respectively, (i = A, B). Accordingly,

Sun et al.[6] introduced α criterion as a measure of polymer–polymer miscibility on the basis of their blend calculated hydrodynamic interaction deviation from their measured Huggins constant:

$$\alpha = K_H - K_1 \tag{3}$$

$\alpha \geq 0$ denotes strong attractive, whereas $\alpha < 0$ implies repulsive polymer/polymer interactions.

In this research work, key effective parameters of toughening PVC with MBS core-shell particles were quantified via their blend characterization by dilute solution viscometry, dynamic light scattering, DMTA, TEM, and temperature variable impact test. They were, then, combined to specify the supertoughening conditions.

EXPERIMENTAL

Materials

Suspension grade PVC (K-value = 60) with viscosity average molecular weight of 68,000 g/mol was provided by Bandar Imam petrochemical company. Methyl methacrylate–butadiene–styrene (MBS) core-shell particles (BTA 702) and an acrylic processing aid (K175) were purchased from Rohm and Haas Company. A heat stabilizer, tin mercaptide (Reatinor 404) and an esteric lubricant (G32) were supplied by Henkle Company. Tetrahydrofurane (THF) was purchased from Merck and used as solvent.

Dilute solution preparation and viscometry

A solution of PVC (1 g/dL) in THF was prepared. For making the MBS dispersion in THF, however, their 50/50 by weight mixture was stored for 24 h in a closed and sealed container. Then, it was sheared for 30 min by Brabender internal mixer, pl 220, with a speed of 30 rpm, filling factor of 0.75, and equipped with Banburi blades. Later, 1 g/dL dispersion of MBS in THF was prepared by diluting the aforementioned mixture. Finally, the dilute solutions of PVC and MBS were prepared by mixing different proportions of the single component solutions. Dilute solution viscometry of single and blend solutions was then conducted by an Ubbelhode viscometer at 30°C. Each solution was diluted five times and their efflux times were measured.

Particle size determination

Dynamic laser light scattering, model SEM-633 (Sematec, France) was used to determine the size of the MBS particles and their complexes with the PVC chains in solutions. The device works with a Helium-Neon laser beam with a wavelength of 632.5 nm. A dispersion of 0.3 g MBS in 100 mL of THF

was prepared and exposed to the laser light. Size characterization of the complexes in blend solutions was also conducted on a 0.3 g/dL of 50/50 and 25/75 by weight of PVC/MBS in THF.

Preparation of PVC/MBS blends

First, 2.5 phr of tin mercaptide (Reatinor 404), 1.6 phr of acrylic processing aid (K175), and 0.4 phr of an esteric lubricant (G32) were added to the PVC powder. Then, PVC and MBS blending were performed using a high speed Cincinnati mixer (2800 rpm), model Labormischer M10, Austria. The circulation of hot oil and application of high shear during mixing led to heat build up to 120°C. After 15 min, the mixture was taken out and fed to a single screw extruder, $L/D = 25$ with screw speed of 25 rpm, to complete the mixing at 180°C. The weight percent of the MBS in blends was varied from 0 to 20.

Temperature variable impact test

Test specimens were prepared by injection molding of the blends using an Engel machine (Austria) with temperature range of 155–175°C from hopper to die. After cutting standard notches on the specimens, their impact strengths were measured at different temperatures using a Ceast Resil 3 Joule Impactor from Italy. At least 10 replicates were tested for each sample at different impact temperatures, and 10% deviation from the average value was found for all data points. To reach subzero temperatures, a container equipped with liquid nitrogen circulation was used.

Dynamic mechanical thermal analysis

Specimens $2 \times 10 \times 50$ mm^3 in dimensions were characterized by DMTA using a DMA, model NETZSCH 242, with a heating rate of 2°C/min and a frequency of 1 Hz.

Transmission electron microscopy

Dispersed morphologies of core-shell impact modifiers within the matrix were characterized by TEM on a Philips 200CM, Japan. The samples were prepared by ultra-thin microtomed blends, which stained with osmium tetroxide (OsO$_4$) vapor to enhance their components contrast before characterization.

RESULTS AND DISCUSSION

Figure 1 shows $\eta_{SP}C^{-1}$ versus solution concentration for the PVC/MBS blends with different MBS compositions. The intercepts of the fitted lines on various data sets decrease as the blend composition in solu-
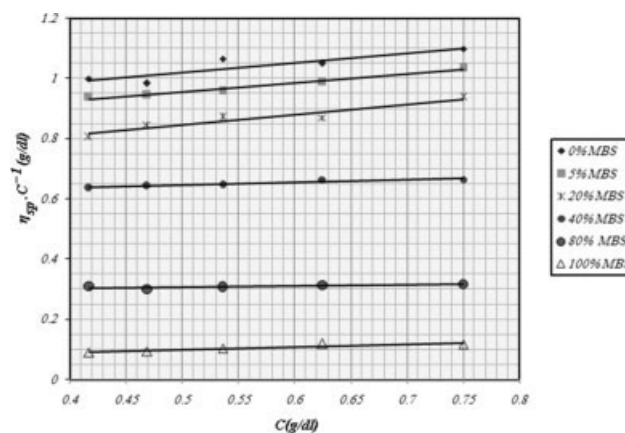

Figure 1 Reduced viscosity of the PVC/MBS blend solutions versus their concentration with different MBS weight percents.

tions changes from pure PVC to pure MBS. The average hydrodynamic radii of the PVC chains and core-shell particles in THF, proportional to [η]M, is about 10 and 183 nm, respectively. Accordingly, much higher equivalent molecular weight is estimated for the core-shell particles in solution.[8] Shell tethered PMMA chains of the MBS particles were stretching into the solvent because of their strong attractive interactions is counter-balanced with their dense crosslinked structure of their SBR core. This would lead to MBS dispersion with marginal stability. In other words, the colloidal MBS in THF precipitated at about 10 h when it was at rest. Based on viscometry, the Huggins constant, K_H, of solutions containing PVC/MBS blends was determined and used along with their calculated hydrodynamic components, K_1, to estimate polymer–polymer miscibility (α), Table I. By raising MBS wt % in blend solutions with constant concentration, the PVC/MBS α showed two attractive maximums and a repulsive minimum, Figure 2. These were attributed to the attractive and repulsive interactions between C—Cl groups of the free PVC chains with carbonyl groups of the grafted PMMA chains on MBS particles at these compositions, respectively. Attractive interactions between functional groups of two polymers depend on their stoichiometry and chain rigidity.[9] But the former does not guaranty the maximum possible attraction because of two state responses of homopolymers in their local interactions. In other words, polymers are apparently dictated to partition simultaneously their statistical segments as dynamically interactive and noninteractive with other molecules.[10] Light scattering characterization of the colloidal state of the MBS particles in THF showed average diameter of 183 nm, Figure 3(a). Dilute solutions of the PVC/MBS blends in THF containing 50 and 75 wt % of MBS particles, however, formed complexes 249 and 229 nm in average diameter,

TABLE I
Dilute Solution Viscometry Results of the PVC and Its Blend with the MBS in THF

MBS (wt %)	$K_H [\eta]^2$	$[\eta]$ (g/dL)	K_H	K_1	α
0	0.2946	0.8734	0.3862	0.3862	0
5	0.2955	0.8078	0.4528	0.3813	0.0715
20	0.3436	0.6743	0.7557	0.364	0.3917
40	0.0945	0.5979	0.2643	0.3311	−0.0668
60	0.0926	0.4039	0.5676	0.2772	0.2904
80	0.0335	0.2902	0.3978	0.1761	0.2217

Figure 3(b,c), respectively. The apparent size increase in colloidal MBS with the PVC chains in THF implies their complexation because of their attractive interactions, Figure 4. The colloidal state of MBS/PVC blend in THF decreased to smaller and narrower average size complexes with the MBS proportion increase because of their stronger attractive interactions (larger α), Figure 2. Jucik et al.[11] also reported complicated interactions between ethylene–propylene copolymer with PMMA, poly(2-decyl methacrylate) (PDDMA), poly(octa-2-decyl methacrylate) (PODMA) in their blend solutions.

The impact strength of the toughened PVC and their components miscibility in THF solutions, α, were plotted versus MBS wt % in Figure 5. As can be seen, MBS increase up to about 10 wt % did not show any measurable blend impact strength rise. By further MBS enhancement, however, blend toughness increased severely and reached a plateau at about 15 wt % of MBS. Wu et al.[4] also reported 8 phr of MBS core-shell particles as the threshold for maximum toughness achievement in PVC. Nonetheless, they mentioned the prerequisite of grafting at least 7 wt % of PMMA on each PB particle core. Observed trend is attributed to the requirement of crossing the critical interparticle distance before the matrix yielding process around particles can pervade over the entire deformation zone.[12] By increasing the MBS wt % of the PVC/MBS blend solution in THF up to 20, their miscibility increased to a maximum. In other words, up to 20 wt % MBS

increase in its dilute solution with the PVC led to maximum attractive interactions between the tethered PMMA and the free PVC chains. The same trend is expected to maintain during THF evaporation toward the bulk PVC/MBS blend. In other
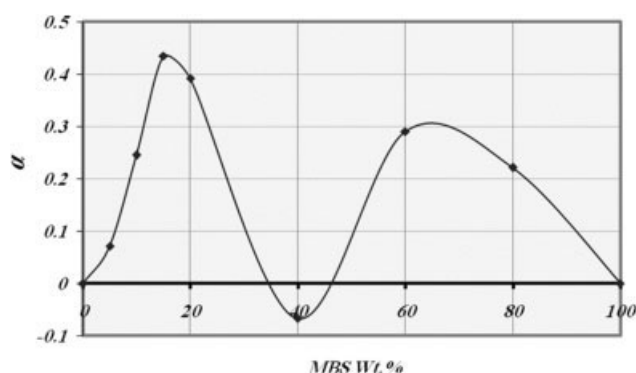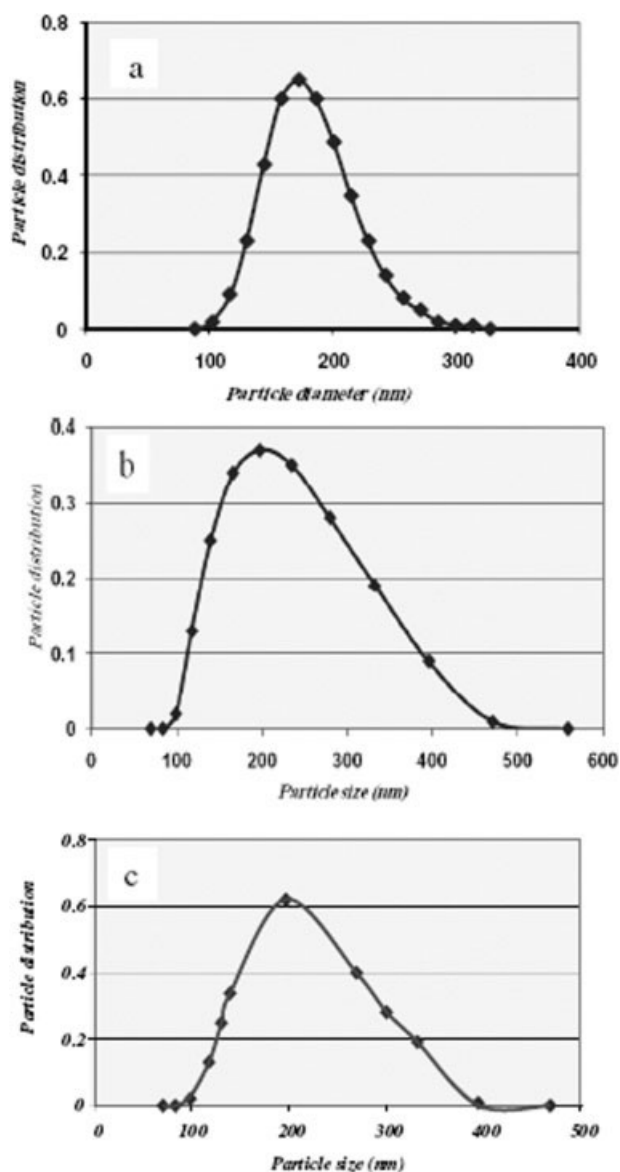
Figure 3 Dynamic light scattering of MBS dispersions in THF: (a) MBS, (b) 50/50 by weight of PVC/MBS, and (c) 25/75 by weight of PVC/MBS.

Figure 2 α versus the MBS particles wt % in the PVC/MBS blend dilute solutions.
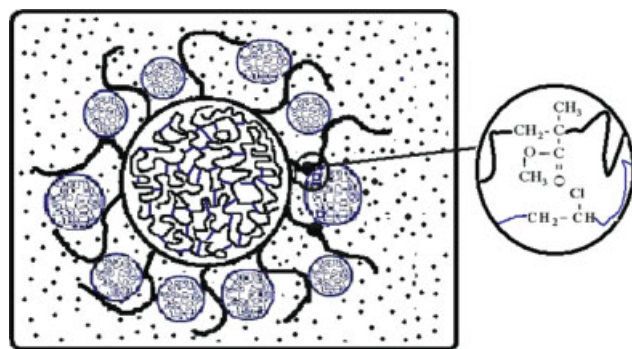
Figure 4 Schematics of complex formation between dissolved PVC chains and tethered PMMA chains of the core-shell particles in the PVC/MBS solutions in THF. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

words, C—Cl attractive interactions with carbonyl groups of the tethered PMMA chains are favored even at the existence of THF molecules. In other words, squared solubility differences $(\delta_i\text{-}\delta_j)^2$ among PVC [δ = 9.6 (cal/cm^3)$^{0.5}$], PMMA [δ = 9.45 (cal/cm^3)$^{0.5}$], and THF [δ = 9.1 (cal/cm^3)$^{0.5}$], which is proportional with χ_{ij} or Flory–Huggins interaction parameter, are 0.0225, 0.1225, and 0.25 for PVC/PMMA, PMMA/THF, and PVC/THF, respectively. Lower χ_{ij} implies higher miscibility between i and j components.

As mentioned earlier, another key parameter in blend maximum toughness achievement via using a core-shell modifier is the volume fraction of shear deformed matrix. This characteristic depends mainly on interparticle distance, which can be calculated through eq. (4).[12]

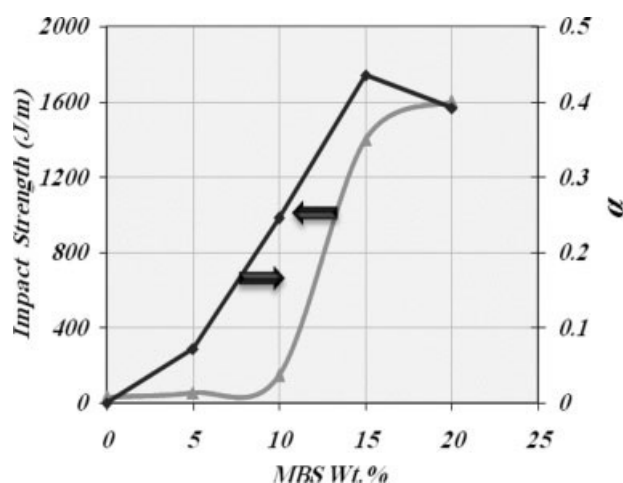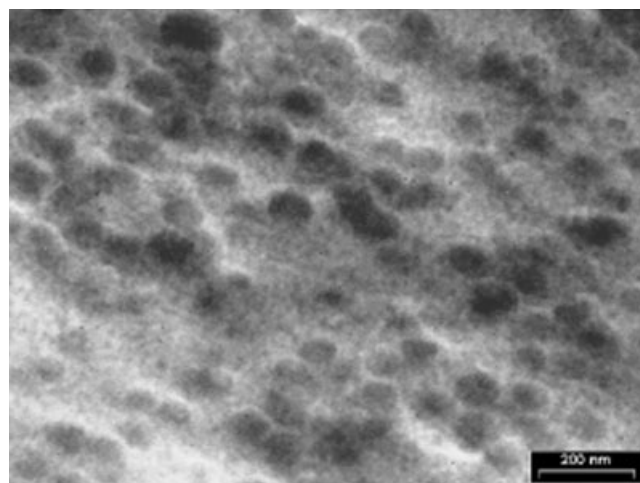$$\text{IPD} = d\left[\left(\frac{\pi}{6\phi}\right)^{1/3} - 1\right] \qquad (4)$$

Figure 6 Transmission electron micrograph of toughened PVC with 20 wt % of MBS particles (Magnification: 95,000).

where IPD is interparticle distance, d is particle average size, and ϕ is the volume fraction of impact modifier. Supertoughening can be managed through extension of shear deformed matrix regions around each particle to the entire deformation zone via crossing the critical interparticle distance. Accordingly, addition of 10 wt % of the MBS core-shell particles with average diameter of about 85 nm (based on TEM Fig. 6) would be equivalent with the critical IPD of 63 nm. The calculated critical interparticle distance is roughly in the range of microdomain to domain size of PVC (matrix) 10–80 nm.[13,14] PVC is actually a microheterogeneous polymer consisting of basic particles of about 10 nm, called microdomains, which aggregate to form subsequent hierarchical particles, namely domains ($\sim$ 0.1 μm).
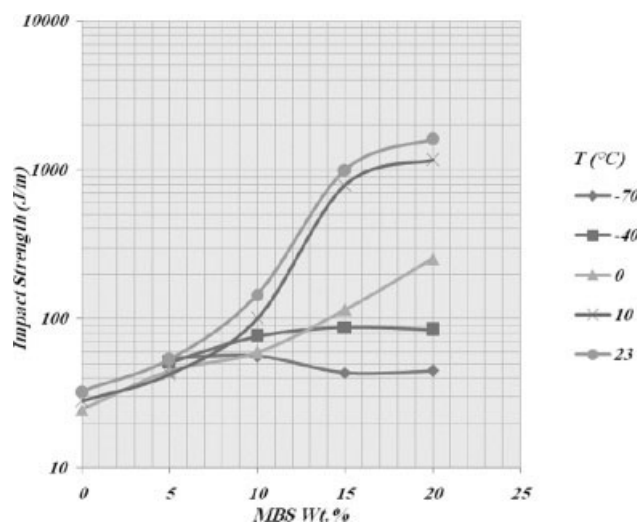

Figure 5 Impact strength of the PVC/MBS blends and their α in THF solutions versus MBS wt %.

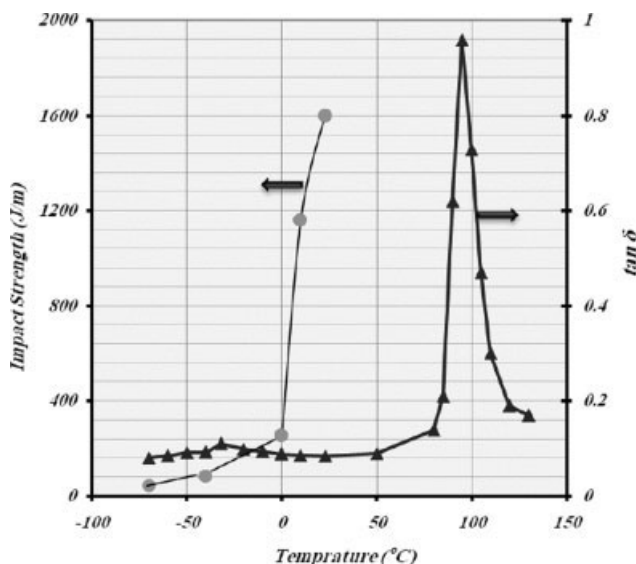**Figure 7** Impact strength of the PVC/MBS blends versus MBS wt % at different test temperatures.

Figure 8 Impact strength and matrix tan δ versus temperature for the PVC/MBS blend containing 20 wt % of the MBS.

Core of the impact modifier also plays the role of stress concentrator, which can activate matrix shear deformation provided that suitable interfacial adhesion persists. The efficacy of this third key effective parameter depends on impact modifier core T_g difference with the test or exploitation temperature, Figure 7. Test temperature decrease toward core T_g, about $-35°C$, reduced blend impact energy over 20 times even in samples containing 20 wt % of MBS with strong interfaces. It is noteworthy that test temperature decrease may even increase interfacial adhesion between PVC and MBS particles because of their LCST type behavior.[15]

Impact strength of the toughened PVC containing 20 wt % of the MBS is plotted versus test temperature in Figure 8. Matrix tan δ of the same blend versus test temperature is also included. Tan δ-temperature jump at the matrix glass transition, about 90°C, occurred via secondary relaxations, which arised from localized main-chain motions. On the other hand, brittle-ductile transition of the blend through molecular motions (yielding) was observed at 0°C. In other words, chain relaxation activation as energy absorption mechanism under nonlinear deformation (impact) and linear deformation (DMTA) was observed at low and high temperatures, respectively. In other words, the origin of plastic deformation in polymers is similar with their dynamics at glass transition namely large scale coordinated movements.[16–18] Mechanical force localization on chains through the surrounding media leads to a new segmental orientation to relax the original applied stress. Thus, the temporarily enhanced free energy decreases to a lower value each time a new segmental orientation forms, which

finally damps.[19] Therefore, the severe energy absorption increase in impact strength and viscoelastic loss at low and high temperatures in the PVC/MBS blend, respectively, can be attributed to the activated dynamic similarity through high applied stress or high temperature application.

Consequently, suitable interfacial adhesion between core-shell impact modifier and the matrix, crossing the critical interparticle distance, enough core T_g difference with the test or exploitation temperature and applied load-temperature conformity may lead to maximum blend toughness achievement.

CONCLUSIONS

Four characteristics were quantified as the key toughness controlling parameters in PVC containing MBS core-shell impact modifiers: namely interfacial adhesion (measured with α in the current work), core T_g difference with test or exploitation temperature, the extent of load-temperature conformity in the applied mechanical field, and critical ligament distance. Maximum toughness of 1600 J/m was achieved with α equals 0.4, interparticle distance of about 64 nm, $\Delta T_g = T - T_g$ of 60°C. In addition, 2500 J/m of impact energy was found equivalent to about 90°C of rise in toughened PVC with 20 wt % of the MBS particles.

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