

Polymer-Plastics Technology and Engineering

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/lpte20>

Mechanism of Toughening in Rubber Toughened Polyolefin—A Review

Bishnu P. Panda^a, Smita Mohanty^a & Sanjay K. Nayak^a

^a Laboratory for Advanced Research in Polymeric Materials (LARPM), Central Institute of Plastics Engineering and Technology, Bhubaneswar, India

Accepted author version posted online: 06 Jan 2015.



[Click for updates](#)

To cite this article: Bishnu P. Panda, Smita Mohanty & Sanjay K. Nayak (2015) Mechanism of Toughening in Rubber Toughened Polyolefin—A Review, Polymer-Plastics Technology and Engineering, 54:5, 462-473, DOI: [10.1080/03602559.2014.958777](https://doi.org/10.1080/03602559.2014.958777)

To link to this article: <http://dx.doi.org/10.1080/03602559.2014.958777>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

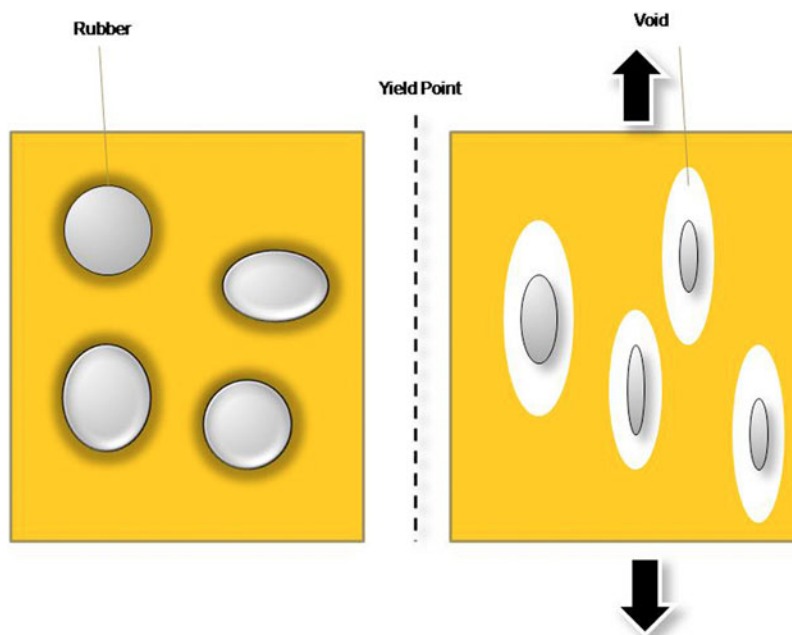
This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

Mechanism of Toughening in Rubber Toughened Polyolefin—A Review

Bishnu P. Panda, Smita Mohanty, and Sanjay K. Nayak

Laboratory for Advanced Research in Polymeric Materials (LARPM), Central Institute of Plastics Engineering and Technology, Bhubaneswar, India

GRAPHICAL ABSTRACT



The recent advances and theories in the studies of the toughening mechanism have been reviewed to explain the effect of rubber particles in different rubber modified Polyolefin materials. To elucidate toughening effect, major theories e.g., critical particle distance, particle size, micro deformation by stress field of rubber, shear yielding and crazing phenomena has been reviewed. Based on these theories, variety of blends of rubber modified Polyolefin materials has been compared but no one of these provided adequate information to be considered as total theory of toughening. To achieve the objective of toughening, it is important to maintain critical particle size, uniform particle distribution and good interfacial adhesion by inclusion of suitable compatibilizer in the matrix. Particular attention has been paid to study the type of morphology and bimodal distribution of rubber particles to elucidated toughening effect. Rubber particle cavitation, which comes from micro-voids and rubber phase interface are then further discussed.

Keywords Critical particle distance; Particle size; Polyolefin; Rubber

Address correspondence to Dr. Smita Mohanty, Laboratory for Advanced Research in Polymeric Materials (LARPM), Central Institute of Plastics Engineering and Technology, Bhubaneswar 751024, Orissa, India. E-mail: larpmcivet@gmail.com

Color versions of one or more of the figures in this article can be found online at www.tandfonline.com/lpte.

INTRODUCTION

Rubber-thermoplastic blends have recently stimulated much interest because they offer the simplest route to achieve outstanding properties at low cost. The main property improvements sought through rubber/polymer blending include impact strength and toughness^[1–4]. Although polyolefins have a most

remarkable combination of physical properties, the inherently high glass transition temperature and high crystallinity of this polymer limits its usefulness in low temperature applications. The impact properties of Polypropylene (PP) can be improved through the use of block copolymers of polyolefin, addition of elastomers, or with copolymerization with ethylene.

The most commonly used and most effective impact modifiers for PP are ethylene/propylene copolymers (EPM) or ethylene/propylene/diene terpolymer (EPDM)^[5,6]. Blends with 10–40% rubber called as “impact PPs”; where the rubber phase being dispersed in the polymer matrix. It was established that the highest increment in the impact strength of PP was achieved by using ethylene-propylene copolymer (EPR) and ethylene-propylene-diene terpolymer (EPDM)^[7–9]. Moderate effects were obtained from styrene block copolymer (SBS)^[10] and butyl rubber^[11–12] while polybutadiene, polyisoprene and polyisobutylene did not increase the impact strength of PP much. In practice, EPR and EPDM are mainly included in PP matrices as rubber impact modifiers^[13–16], while styrene-butadiene is used as a based matrix in thermoplastic elastomers^[17].

Even though there are various toughening mechanisms have been postulated by different researchers, it seems that a single theory cannot explain all the aspects about phenomenon of toughening. One reason may be the discrepancy of the raw materials chosen by different researchers as the initial properties of raw materials have significant influence on the toughness properties. Recently several aspects of toughening effect of semicrystalline thermoplastics including PP were reviewed^[18], and a specific review has been devoted to rubber toughening of PP^[19–20]. From these reviews, it appears that the major theories interpreting the toughening mechanisms of these blends are: multiple crazing, shear-yielding and formation of dilatational bands following rubber cavitation or debonding from the matrix. There are basically two theories invoked in the interpretation of toughening behavior of thermoplastics polymers containing rubber inclusions.

Critical Particle Distance Theory

The effects of rubber particle size and rubber matrix adhesion on notched impact strength were analyzed by Wu^[21]. A sharp tough/brittle transition was found at a critical particle size when rubber volume fraction and rubber-matrix adhesion were held constant. The critical particle size increases with increasing rubber volume fraction. Rubber domain size and distribution also have an effect on the impact properties of PP. Uniform distribution and small domains, <1 μm , are expected to improve the impact properties of PP^[22,23]. Jang et al.^[24] studied the dependence of the impact behavior of the PP on the rubber particle size and found that small particles were more effective than larger particles for toughening PP. Dao^[25] reported that the optimum particle size for impact improvement using EPDM rubber in the PP matrix is between 0.1–1 μm .

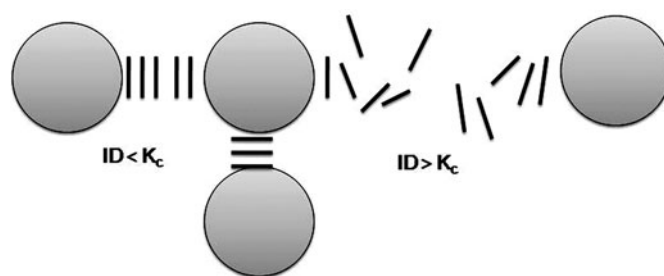


FIG. 1. Scheme shows preferential orientation of crystal plane below and above the interparticle distance ID is below a critical value.

Nowadays, the inter-particle distance (ID)^[21] is widely accepted as the parameter that controls super-toughness, which should appear when ID is below a critical value (K_c). Also some intrinsic parameters such as crystallinity^[26] and modulus^[27,28] of the rubber, the ratio between the modulus of the matrix and that of the rubbery dispersed phase adhesion between the components^[29] affects the K_c value. Published work by Muratoglu et al.^[30] and Bartczak et al.^[31] proposed that below the critical interparticle distance (ID), a preferential form of crystallization of the polymer takes place between the particles, whereas certain plane of polymer crystallites will orient parallel to the particle surface. This phenomenon as depicted in Fig. 1.

The present-day notion of the toughening mechanism as proposed by Wu^[21] states that a sharp brittle/tough transition occurs when the average interparticle matrix ligament thickness is reduced below a critical value K_c , which appears to be independent of the rubber volume fraction and particle size, as is schematically shown in Fig. 2. Plotting impact strength against the average matrix ligament thickness, a sharp transition is observed at constant critical value. With increasing volume fraction of rubber, critical particle size increased.

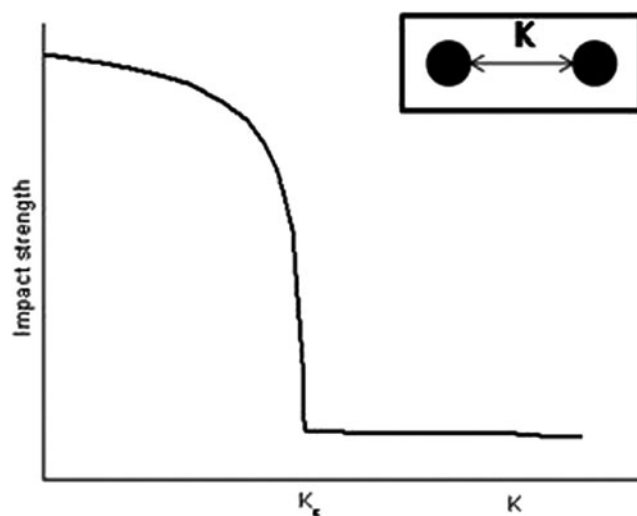


FIG. 2. Impact strength PP/rubber blend vs the average surface-to-surface ligament thickness. Redrawn from Wu., 1985^[21].

The higher rubber concentrations were found to impact higher toughness below critical ligament thickness (K_C).

Above the critical value, the blend exhibits brittle behavior and displays low impact strength. Margolina and Wu^[32] proposed that a rubber toughened polymer is tough in impact tests only when the ligament thickness is smaller than the critical value, K_C , which is a material property also dependant on test temperature. Also, the K_C values were shown to be independent of volume fraction of rubber and particle size. The result for this transition as addressed by Wu relates to mutual interaction of particle disturbed stress field enhancing matrix yielding. However stress field theory is effective only when changes in geometric ratios occurs, so it can be concluded that stress field interaction is not capable only for explaining absolute length such as critical interparticle distance.

Micro Deformation Theory

Plastic deformation of semicrystalline materials including rubber particles is a complicated phenomena, which is based on shear and crazing also includes the events of both phases; crystalline and amorphous phase^[33–35]. With application of external force, initially elastic response occurs with straining of molecular chains of rubber phase, which leads to the interlamellar shear, rotation of lamellar stacks or separation of lamellae, depending on the local stress field^[36]. In such case, the voids develop inside lamellar stacks and are oriented along lamellae which results cavitations induced in the matrix. Recently similar decrease of the volume for large strain was observed for polypropylene blended with ethylene-propylene rubber.

Poncot et al. reported the growth of cavities in the stretching direction with a slight closure of the width of cigar-like shapes, attributed to a highly fibrillar microstructure^[37]. Cavitation is generated at points where a high local triaxial state of stress is developed. Triaxiality of stress can be amplified by a notch; even very mild notch with large radius of curvature stimulates generation of cavities. It is assumed that the fracture toughness of polymers is controlled by mechanisms such as crazing, void formation, shear yielding^[38]. Further deformation involves deformation of crystals due to rapid local change of stress around voids.

From measurement of volumetric strain as a function of the triaxial strain in a uniaxial tensile test, Bucknal and Smith^[39] able to separate systems, which manifests toughness through crazing in which shear yielding is the predominant mechanism. In later case, yielding is initiated by shear band formation around rubber particles. It is important that rubber particles strongly bonded with matrix to stabilize both growth of crazes and the formation of voids, as they would develop cracks^[30]. Shear yielding, in the form of shear bands or more diffuse shear yielding, is another important mechanism which can lead to plastic deformation in polymers. Both shear yielding and crazing involve localized, or inhomogeneous, plastic deformation of the material and arises from strain softening and

geometric considerations. The difference between the two mechanisms is that shear yielding occurs essentially at constant volume, whereas crazing occurs with an increase in volume.

Still the effect of particle size and interparticle distance on impact fracture is a place of controversy in the literature. Many studies showed contradictory results. For example, blends, Ramsteiner et al.^[40] reported that at -40°C , the impact strength increases with increasing particle size, and that crazing is the dominant mechanism at this temperature. However, van der Wal et al.^[41,42] found no evidence of crazing when used large particles ($>0.5\mu\text{m}$) in PP/rubber blends. They also reported that increasing particle size reduces impact strength. In this review we focus our attention on the work performed on the mechanism of toughness due to inclusion of rubber with polyolefin as thermoplastic matrix. the main objective of this study is to investigate the toughness mechanism of polyolefin/rubber blends under dynamic loading. More importantly the role of particle size on impact properties of polyolefin blends will be clarified.

EFFECT OF RUBBER PARTICLE SIZE

Particle size of rubber plays an important role to determine the fracture toughness behavior of PP material. Large particles size resulted reduced impact toughness in the PP phase, as the surface/volume ratio is diminished, thus diminishing the magnitude of craze formation^[43]. Small particles are ineffective, as propagation cracks can engulf the rubber particles. It is well known that the impact resistance of polymeric materials can be considerably modified by the incorporation of rubber materials. For rubber-toughened polymers, the shape, content, size and size distribution of the dispersed-phase particles have major effects on mechanical properties of polymer-elastomer blends. For any given blend composition, maximum toughness is restricted to a limited range of particle sizes, which is often quite narrow. Moving beyond the preferred range in either direction results in a ductile-brittle transition, as illustrated in Fig. 3, where b and d, respectively, marks the midpoints of the lower and upper transitions and thus defines critical particle sizes. Huang et al.^[44] reported izod impact strength as a function of rubber content and rubber particle size as shown in Fig. 3. There is general agreement that very small particles are ineffective because they are more resistant to cavitations, but to date there has been no convincing explanation for the upper DB transition. Muratoglu, Argon and Cohen have argued that super tough behavior in blends is due to an oriented crystalline layer of limited thickness which extends radially from the surface of each rubber particle^[45,46].

The effect of bimodal rubber particle size distribution on the mechanical properties is an additional issue for improving the rubber toughening in polymers^[47,48]. Karger-Kocsis and Kuleznev^[49] found a linear relationship between the number average diameter of the minor phase (EPDM) and the viscosity

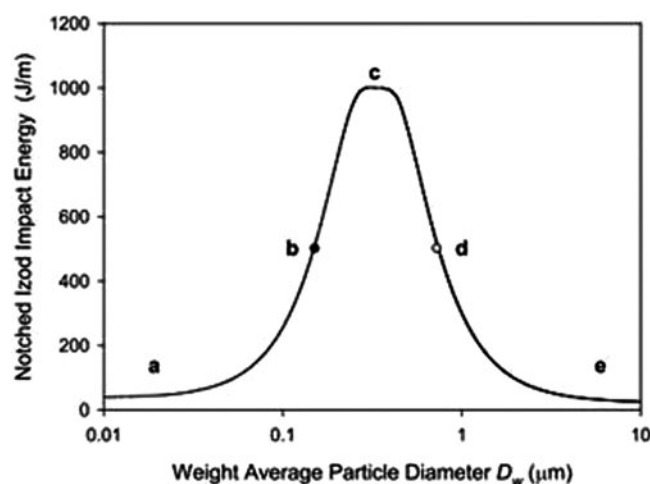


FIG. 3. Relationship between particle size and impact behavior for a typical “super-tough” thermoplastic blend. Points b and d mark lower ductile–brittle (DB) transitions. Schematic representation based broadly on data of Huang et al. for a series of rubber toughened blends^[44].

ratio in PP/EPDM blend. The particle size increased with increasing viscosity ratio. Fine dispersions could be achieved if the ethylene content of EPDM is low and the viscosity ratio value is near unity. A similar trend was also observed by D’Orazio et al.^[50] in iPP/EPR blends. The melt viscosity values of the blends were found to be lower than the mean value of the simple components. Danesi and Porter^[51] reported that as the amount of rubber in the blend increased (80 EPR/20 PP), the viscosity ratio became less important in determining the state of dispersion.

Since most polymers are not miscible with used rubbers in creating blends, polymer rubber blend normally exhibits phase separation where the rubber forms a spherical particle domains. Size of rubber blends and volume fraction of rubber are two important parameters in designing blend and have been shown to affect the toughening mechanism. When the distance between particles lies below the critical value, the toughness of blend increases appreciably. The interparticle distance can be calculated by using following equation, assuming simple-cubic packing of spherical articles in three dimensions

$$ID = d_w \left[\left(\frac{k\pi}{6V_f} \right)^{\frac{1}{3}} - 1 \right] \quad (1)$$

Where ID is the interparticle distance, V_f is the volume fraction of rubber, d_w is the average diameter of size of rubber particles and, $k=1$ for cubic lattice. With increasing volume fraction, interparticle distance decreases with decreasing particle size. Reported values for critical interparticle distance for PP-rubber blend range from 0.1 to 1.0 μm ^[52]. Bartczak et al.^[53] generalized the Wu criterion to other material (HDPE) and showed the critical interparticle distance to be an intrinsic property of the matrix material, thereby opening the possibility of using

TABLE 1

Values of weight average EPDM particles (d_w) and ID for various PP/EPDM blends (Data extracted from Ref^[54])

Sr. no.	Wt. fraction of EPDM (%)	d_w μm	ID value μm
1	0	0	∞
2	2	0.49	0.94
3	4	0.38	0.5
4	6	0.48	0.49
5	8	0.34	0.29
6	10	0.34	0.24
7	12	0.33	0.21
8	16	0.33	0.15
9	18	0.34	0.14
10	20	0.33	0.12
11	24	0.34	0.1

mineral fillers for the toughening of semicrystalline polymers, the advantage of which would be an improved modulus of the blend. They argued that interparticle cavitation is not necessary for toughening and therefore that debonding of hard filler particles could be an alternative for the cavitation of the rubbery phase. The average particle diameter (d_w) for various EPDM contents as obtained from SEM photographs and using equation 1 are listed in Table 1.

Figure 4 shows variation of izod impact strength with ID for various notches and temperatures. Notch B is a 45° V-shaped notch with the notch radius R of 1.0 mm, and notch C is a rectangular notch. The results indicate that the impact strength increases with decreasing ID. A sharp transition of the toughness induced by ID can be observed for various temperatures.

Table 2 shows a number-average diameter of two different grade EPR particles different in melt viscosity with PP. EPR particles are slightly smaller in a PP1R2 sample than those in a PP1R1 sample. A similar observation was also found in the PP2 system where R2 provided smaller particles than R1. Both grades were found to be good impact modifiers for PP. The higher efficiency in toughening of PP by R2 can be explained in terms of the rubber particle size effect. It has been reported for PP/EPDM blends that the phase morphology of small rubber particle size is more effective than with large particle size in toughening PP^[32]. Speri and Patrick^[55] similarly observed that impact strength of PP/EPDM blends increased as the rubber particle size reduced. The mean rubber diameter of 0.3 μm appeared to be adequate. Dao^[25] also reported that the rubber particle size of approximately 0.4 μm is favorable in PP/EPDM blends. From the work of Jiang^[56] on rubber modified PPs, it has been reported that $D \sim 0.5 \mu\text{m}$ is the critical rubber particle size below which the particle could not nucleate crazes in PPs.

Figure 5 presents a possible mechanism for ultrafine powdered rubber-modified Propylene Oxide copolymer (PPC)

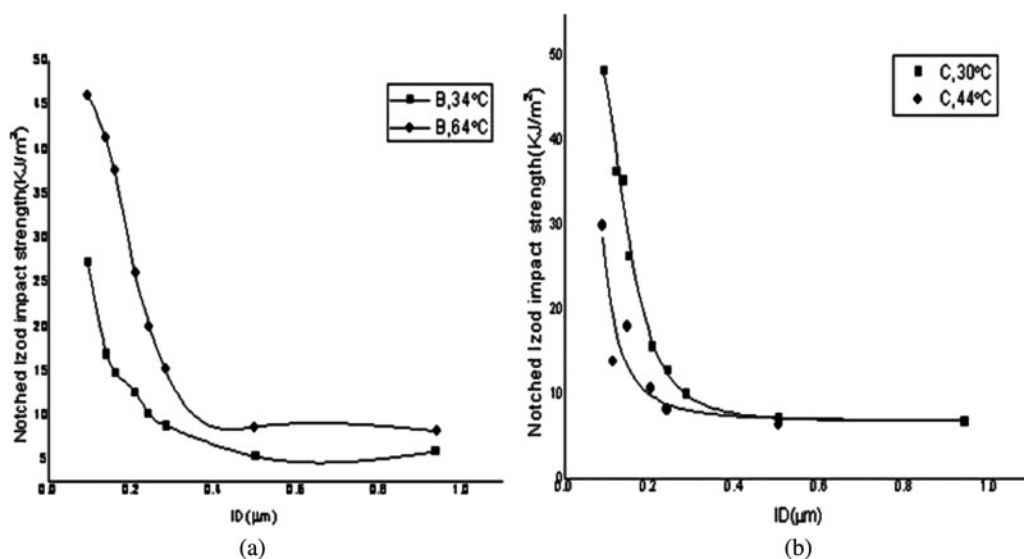


FIG. 4. Variation of notched izod impact strength with interparticle distance (ID) for various notches and temperatures (Data extracted from Ref.^[54]).

according to the two-layer model^[59]. First layer as indicated by heavy slashes between the rubber particles and the thermoplastic restricts movement of rubber particles. Whereas, the thicker layer region could confine larger number of plastics segments. This mechanism explains overall increase of T_g of the matrix polymer with addition of ultra fine rubber particles. At a diameter $>1 \mu\text{m}$, the contribution of the interfacial layer is insufficient to affect the plastic's T_g . This explains why the effect only emerges when the particles are small enough.

IMPROVEMENT IN IMPACT STRENGTH

Increasing in rubber content leads to an increase in impact strength. At high rubber content the impact strength depends markedly on its particle size than at low rubber content. Strong dependence of blend properties on rubber particle size and size distribution (dispersion) were reported^[47,48,56,58]. For each type of material, there appears to be an optimum particle size for toughening. Impact strength falls drastically if the average particle diameter is reduced below a critical value, and there is evidence for a rather slow fall in fracture resistance as the

particle size is increased above the optimum diameter. Speri and Patrick^[55] have explored to a limited degree of the behavior of PP blends containing EPR.

They found impact strength of PP/EPR blends to be favoured by small rubber particle size ($0.5 \mu\text{m}$) and a narrow distribution ($0.1 \mu\text{m}$ to $1.0 \mu\text{m}$ and centered around $0.5 \mu\text{m}$). They also acknowledged that dispersed rubbers cause a decrease in average crystallite size in PP and thereby results an improvement in impact strength. Increasing occluded due to increase of rubber phase volume and surface area available for craze formation up to a point where further occlusions increase particle size and phase modulus beyond their optimum level as reported by Wagner and Robeson et al.^[60].

The study on PP/natural rubber (PP/NR) blends with blends ratio of 70/30 by adding polystyrene-modified natural rubber (SNR) as compatibilizer has been investigated^[61]. Melt mixing

TABLE 2
Falling weight impact fail energy and average particle size of EPR in the blends (Data adapted from ref.^[57])

Sample	Impact fail energy (J)	EPR particle size (μm)
PP1	3.64	—
PP1R1	5.94	1.04
PP1R2	6.82	0.82
PP2	1.91	—
PP2R1	2.84	1.05
PP2R2	3.45	0.86

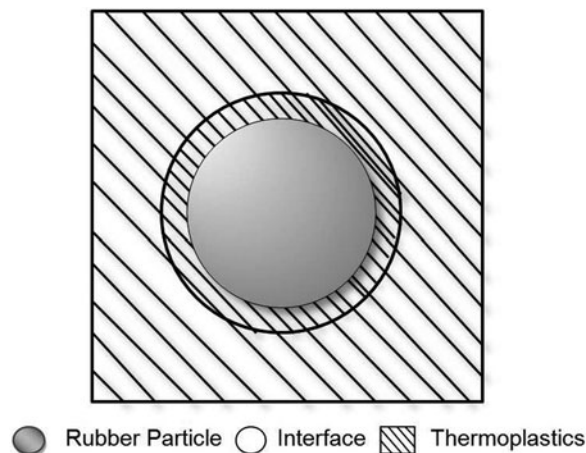


FIG. 5. Effect of ultrafine rubber particles raises toughness. Adapted from Ref.^[58].

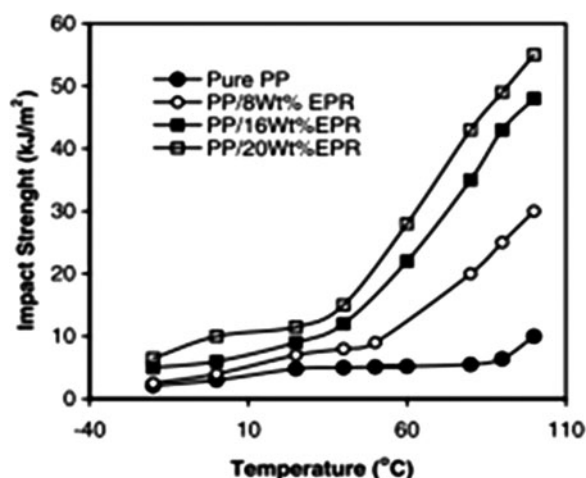


FIG. 6. Variation of notched Charpy impact strength versus temperature as a function of rubber content. From Ref.^[63].

process has been used to prepare the blends with SNR content of 5 to 20 vol. %. At 5% of SNR loading, the addition of curatives base on typical sulfur recipe (semi-efficient curative system) has improved the tensile strength and stiffness of the blend over 20% and 40%, respectively. The impact strength of PP/EPDM blends has improved after the cross-linking due to the improvement of the strength of craze than the drop in the release of the constraint of strain. The effect of the cross-linking of dispersed EPDM particles has increased the interfacial adhesion and thus improve the impact strength^[62]. Figure 6 illustrates the dependence of the notched Charpy impact energy of PP as a function of rubber content at different temperatures where rising of impact strength marked with increasing EPR content.

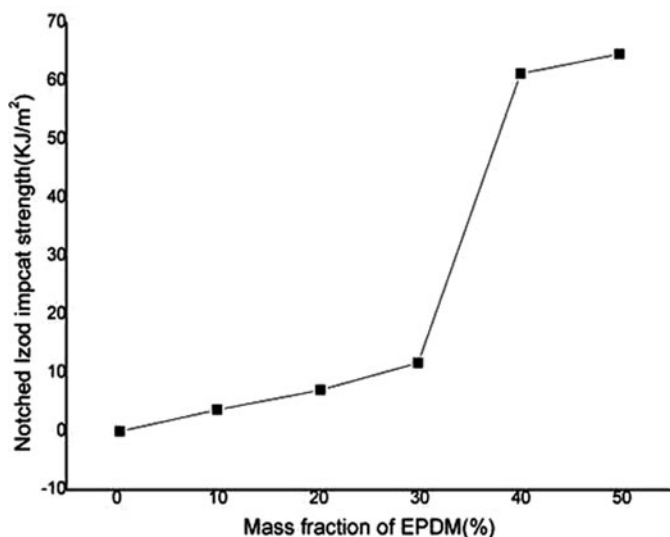


FIG. 7. Impact strength of PP blended with EPDM following crosslinking in comparison with PP blends before cross-link. Figure from Ref^[13].

Wang et al.^[64] reported PP-g-EPDM grafted copolymer can enhance the mechanical properties of PP/EPDM thermoplastic elastomer, especially the impact strength at low temperatures. Figure 7 shows the changes of the notched Izod impact strengths of the PP/EPDM samples measured at -20°C . It can be seen that when the EPDM content reaches the critical value of 30% and 40% loading, the impact strength increased dramatically. With 40% of EPDM loading sharply increases impact strength about 63 kJ/m^2 resulted phenomenal transition from brittle to ductile behavior of PP due to the presence of smaller elastomeric domains leading to more toughness. The toughening mechanism of PP/EPDM blends following selective cross linking by N-N'-m-phenylenebismaleimido was investigated by Ishikawa^[47]. The blends have been prepared by melt mixing process with 5 to 30 vol. % of rubber content. The toughness of PP/EPDM blends has improved after the cross linking due to the improvement of the strength of craze is greater than the drop in the release of the constraint of strain.

TOUGHENING MECHANISM

Many different mechanisms have been proposed to explain the improved fracture toughness that may result when a polymer possesses a multiphase microstructure of dispersed rubbery particles. Much of the dispute concerns whether the rubbery particles absorb most of energy and whether deformation mechanism involved in the formation of crazes. Recent work by Kunz-Douglass et al.^[65] and independently by Yee and Pearson^[66] has clearly established that plastic shear- yielding inside the matrix is the main source of energy dissipation and toughness. Such deformation caused by interaction between stress field ahead of crack and rubbery particles occur to a far greater extent in the matrix of rubber-toughened polymers than an unmodified polymer. Hence, stress field around rubbery particles and matrix shear yielding are the main mechanism considered for understanding the role of rubbery particles toughening phenomena.

Stress Field Around Rubbery Particles

Goodier^[67] derived equation for the stress inside the matrix around an isolated elastic spherical material embedded in the matrix while matrix is subjected to an applied uniaxial tensile stress. The equation reveals that the maximum tensile stress concentration in the matrix resulting from the presence of rubbery particle having a value of about 1.9. However, although the applied strain rates differ, the stress fields around the rubber particles will be triaxial in both the impact test and the tensile test. It is known that in an impact test ahead of the crack tip a triaxial stress state exists. Further, presence of rubber in the matrix develop a stress-whitened zone ahead of the starter crack which is directly accounts total energy absorbing mechanism. The size of the stress-whitened zone increases with rubber content.

According to Soliman et al.^[68] as shown in Fig. 8, the toughening mechanism of rubber modified PP is the combination of both matrix yielding and buckling of yielded PP

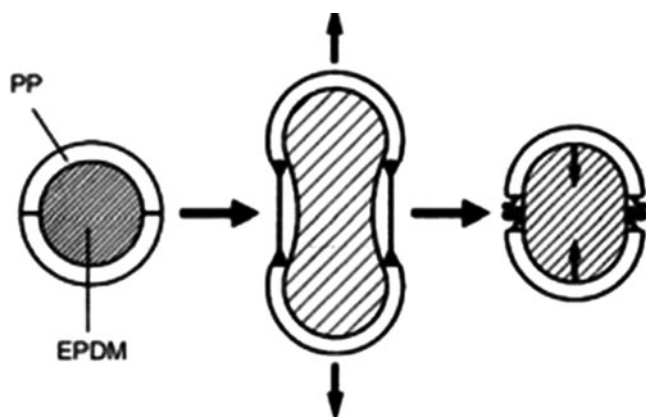


FIG. 8. Deformation mechanism suggested by Soliman et al.^[68].

matrix by the recovering tendency of cross-linked rubbery particles. PP acts as glue like during stretching between the cross linked EPDM and part of the PP fractions undergo yielding in the direction perpendicular to the load. The yielded PP fraction pulled back due to recovered tendency of rubber particle. This exhibits strain softening effect with decreasing maximum stress level. Mechanism for the observed changes could be due to disentanglement and slip-page of polymer chains as a consequence of matrix yielding or shear banding^[69].

Due to the difference in Poisson's ratio the rubber particles will experience a triaxial tension too during the tensile test, provided that the particles adhere to the matrix. This tension arises essentially because of the volume constraint represented by bulk modulus of the rubbery particle inside the matrix. In Fig. 9, the volume change in the blend due to voiding at a strain of 8% and 14%, respectively, is plotted versus the rubber concentration. In both stages of the tensile test. The result reveals the total void volume increases linearly with rubber concentration. The void volume growth does not seem to be affected by stress concentrations around neighboring particles.

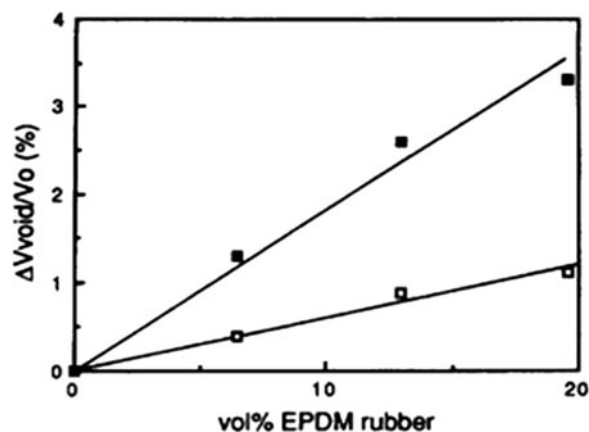


FIG. 9. Relative volume change due to voiding as function of rubber concentration in the blend, at applied strain of 8% and 13%, respectively: Adapted from Ref.^[70].

There is thus some evidence now that the function of the rubber particles, in the toughening of PP, is to relieve the hydrostatic tension ahead of the crack tip by creating voids. The observed stress whitening in deformed rubber-modified PP was found to be due to the presence of voiding process. Presence of voids significantly affects the yielding behavior of rubber toughened polymers. The argument was made for toughening to occur, the particle must debond from matrix, creating voids around the particle and allowing the interparticle ligaments to deform plastically. The voids reduce the apparent plastic resistance of the material and thereby potentially increase the fracture strain and overall toughness. Because of the relatively high bulk moduli of the rubbers, the particles in the PP matrix will sustain considerable load under hydrostatic tension. The observed voiding in the blends may be due to either a detachment of the rubber particles from the PP matrix or to internal rubber cavitation.

During impact test the elastic constraint is relieved by cavitation, extensive plastic flow in the matrix may occur. It is postulated that after voiding in or around the rubber particles, the yield stress of a matrix ligament between the created voids depends directly on the ligament thickness^[69]. Thin ligaments will have a relatively low yield stress since they tend to be in plane stress, whereas thick ligaments have higher yield stresses because of an incompletely relieved plane strain situation. In spite of comparable bulk modulus, Poisson's ratio of the rubber being approximately 0.5; that of PP matrix is 0.45. Thus, in contrast to a "hole," which could produce stress concentration, the rubbery particles could bear share of load across the crack front. This ability of rubber particles to bear a load while subjecting stress concentration can explain the possible mechanism of rubber particles acting as effecting toughness in the polymer.

Matrix Shear Yielding and Particle Cavitation

Two important toughening mechanisms were identified as localized shear yielding due to stress concentration at the equator of rubber particles and dilation deformation due to the growth of voids formed by rubber cavitation. The stress concentration around the rubbery particles act as initiation sites for the plastics shear deformation. Because of the presence of many particles, considerably more plastic energy dissipation exists in a multiphase material than an unmodified material. However, plastic deformation are localized through the post-yield strain softening of the matrix and shear deformation that initiate at one particle but terminate at other.

Fukui et al. and Dijkstra et al.^[71,72] attributed the toughening effect to extensive shear yielding due to the interaction of stress fields. However, since these stress field theory results are affected by changes in geometrical ratios, it can be concluded that they are inadequate in explaining an absolute length scale such as a critical interparticle distance. The crystallization behavior of the matrix is influenced by the rubber/matrix interface, leading to a layer of parallel crystalline

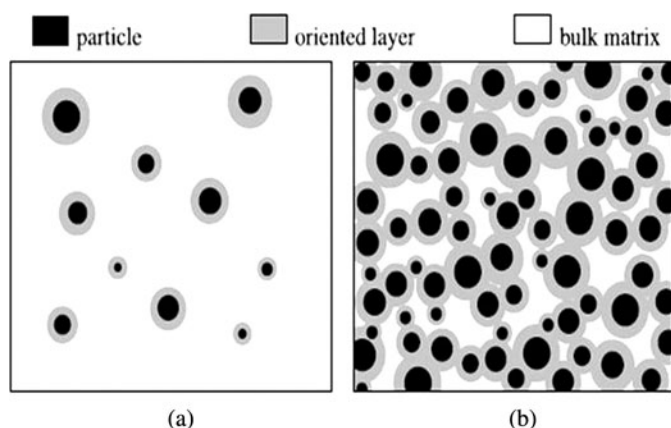


FIG. 10. Transcrystallized layer around second phase particles for (a) $K > K_c$ having brittle response and for (b) $K < K_c$, where material with decreased plastics resistance percolate through blend, enhancing toughness. Adapted from Muratoglu et al.^[30] and Barteck et al.^[31].

lamellae, growing from the interface. A physical explanation of the absolute length parameter was offered by Muratoglu et al.^[30], who recognized the brittle/tough transition as a true material property, which was attributed to thin layers of preferentially oriented material with a reduced plastic resistance.

It is experimentally established that these trans-crystalline layers have a well defined thickness of approximately $K_c/2$. When the actual average matrix ligament thickness K is below the critical value K_c , the favorably oriented material percolates through the system, bridging between the second-phase particles, as is shown in Fig. 10b. Additionally, the situation with $K > K_c$ is represented in Fig. 10a. The blended system consists of (i) rubber particles having a low modulus; (ii) preferentially oriented anisotropic matrix material enveloping the particles; and, (iii) the bulk matrix material having a randomly oriented structure and effectively having isotropic material properties. In the toughening mechanism postulated by Muratoglu et al.^[30], after cavitation of the second-phase rubber particles, the regions with a lowered yield resistance will facilitate large plastic deformation and thereby improve toughness.

Tzika et al.^[73] used a micromechanical numerical model, with a staggered array of particles, to study the influence of preferentially oriented anisotropic layers, modeled within the framework of anisotropic plasticity, on the deformation mechanisms under high triaxiality conditions. They observed plastic deformation in the matrix to occur diagonally away from particles (i.e., in the matrix material between particles, perpendicular to the line connecting the centers of two particles) for $K < K_c$, rather than bridging between particles for $K = K_c$ as schematically represented in Fig. 10.

The anisotropic matrix material was found to act as a non-stretching shell around the (cavitated) particles, promoting extensive shear yielding. In the isotropic material, crazes are initiated at the particle equators, and grow transversely to the macroscopic tensile direction. The plastic deformation is localized in few bands, located in crazing regions. For this large scale system, the crazes may act as precursors to cracks, and ultimately failure. At a smaller length scale, with radially oriented anisotropic material around the cavitated particles, crazes are initiated at the particle poles, and grow in the direction of macroscopic loading. In this situation, crazing may become a mechanism of energy-absorbing inelastic deformation. Additionally, extensive matrix yielding, which is another beneficial energy absorbing mechanism, occurs in non-crazing regions.

Figure 11 illustrates schematic presentation which encompasses a relatively large field of view, shows cavitation and shearing of the rubber particles in front of the crack tip of the rubber particles during highly elongated stage. Two distinct regions are visible in front of the crack tip. First, there is a large circular zone that extends out around the crack tip. Second, contained within the circular zone is a very dark elliptical zone. Both zones contain cavitated particles. Contrast in intensity is due to the differences in the concentration and the extent of cavitation of the rubber particles as well as the amount of shear deformation within the two zones. When the rubber particles cavitate and the holes enlarge, stress whitening will increase. As the matrix undergoes shear yielding the refractive index will change, which contributes further to stress whitening.

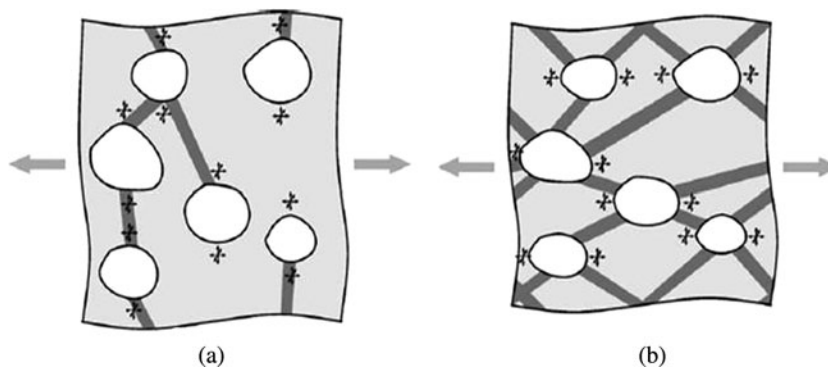


FIG. 11. Schematic illustration of the effect of (a) isotropy versus (b) radially oriented anisotropy on the occurrence of matrix shearing and triaxial stresses. From Ref.^[74].

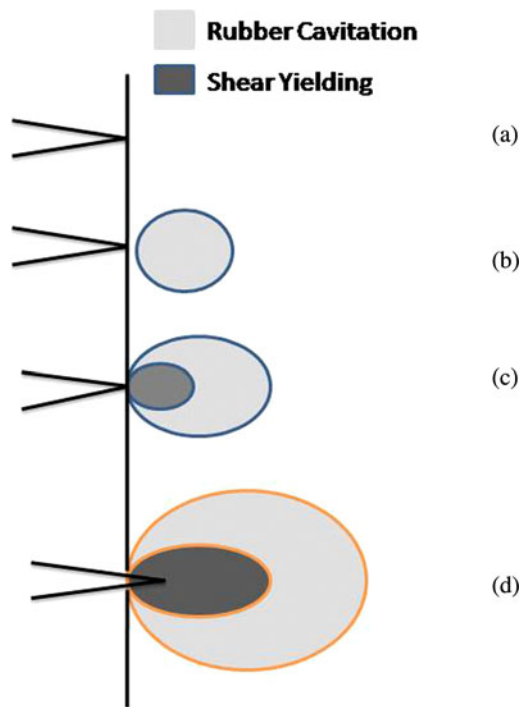


FIG. 12. Sequence involved in the development of the deformation zone in front of crack tip. (a) Initial crack tip. (b) formation of cavitations forming a cavitation zone due to loading. (c) Shear yielding process zone created due to release of triaxial stress state. (d) Matured deformation stage followed by crack propagation.

The outer circular zone contains rubber particles that have cavitated due to the hydrostatic tension. To accommodate the cavitation strain of the rubber particles, it is clear that the surrounding matrix must also expand by a shear process. This indicates that the strain in the matrix is largely elastic or an elastic in nature. The two zones will be referred to as follows: the circular zone is called process zone I and the dark elliptical zone is called the process zone II. The sequence of events is clearly one where the formation of zone I must precede zone II, as illustrated in Fig. 12.

Some investigators^[31,53] also reported experimental evidence of cavitation to relieve the crack-tip triaxial stress so that extensive shear deformation can be developed in the matrix. Therefore, fracture toughness is related to the plastic deformation zone ahead of a pre-crack tip. Yee and Pearson^[75] concluded that cavitation is an essential condition for subsequent plastic yielding. However, Huang and Kinloch^[76] and Guild and Bonfield^[77] suggested that cavitation and matrix shear yielding are two independent processes. More recently, Chen and Mai^[78] carried out extensive FEA to study the sequence of different toughening mechanisms of rubber modified blends.

Their work has concluded that rubber cavitation and matrix shear yielding are two co-existing mechanisms depends on the properties of the rubber particles and the matrix as well as the degree of constraint condition. When shear yielding occurs, a

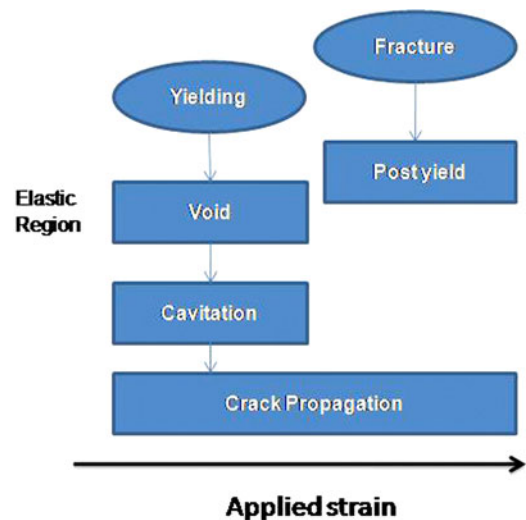


FIG. 13. Schematic diagram of deformation mechanism in rubber-modified PP.

decrease in the volume strain rate would be apparent since plastic deformation occurs approximately at constant volume. At very small volume fraction of rubber, the interactions between the inclusions do not become significant until very large plastic strains have been reached. As the volume fraction is increased, the inclusions of rubber will begin to interact after moderate amounts of plastic strain. With further deformation, the diameter of the ligaments between the rubber particles are reduced even more by hole growth, which reduces their load-carrying capacity.

As shown in Fig. 13, it can be summarized that the deformation behavior of rubber-modified PP initial behaves as elastic. Under the application of strain, the sample starts to cavitate inside the rubber particles around the yield point. In the post yield region of extensive plastic stretch the matrix undergoes large deformations and the cavities elongate in the direction of the applied stress (also directions of principal stretch) Thin ligaments form between the cavities as the deformation progresses resulting in fine fibrillation of the matrix. These fibrils elongate to ultimate draw ratio and fails from some inhomogeneity.

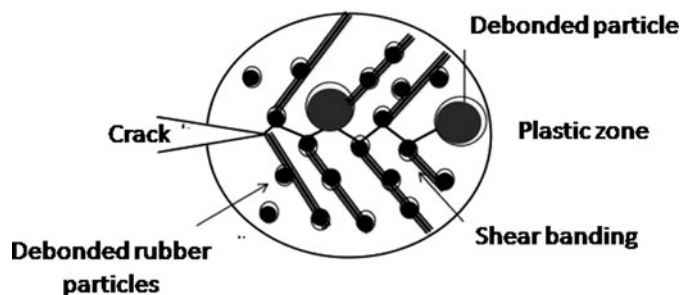


FIG. 14. Schematic representation showing toughening mechanisms containing bimodal particle size distribution in the process zone. Adapted from Ref.^[79].

BIMODAL DISTRIBUTION OF PARTICLE SIZE

Distribution of particle size is another factor that may influence toughness. In this regard, the type of morphology is of particular interest. When the cure chemistry is adjusted in the proper way, both large ($>0.5\ \mu\text{m}$) and small ($<0.2\ \mu\text{m}$) elastomeric particles are obtained. As a result, these formulations are often said to have bimodal distribution of particle size. At present, the optimal rubber particle size for toughening PP appears to be in the $0.1\text{--}0.5\ \mu\text{m}$ range and there is no rationale for this particle size effect. Other researchers^[47,48] have claimed that the optimal particle size actually involves a bimodal distribution of particle sizes. Figure 14 illustrates mechanism of toughening effect due to bimodal distribution of particle size in front of crack tip.

Large diameter particles are not as efficient in providing a toughening effect, whereas small diameter particles appear to be the most efficient and provides higher increase in fracture toughness^[79]. The model proposed by Arostegui et al.^[27] suggests that a multiplicative effect, i.e., synergism, should be expected when the bridging mechanism occurs in addition to the plastic dilatation/shear banding mechanism. The presence of rubber particle in the matrix containing both large and small particles that simply bridge the crack and that cavitate and induce shear bands was produced in an effort to verify this prediction experimentally as illustrated in Fig. 14.

CONCLUSIONS

The improvement in impact strength and toughness of matrix can be explained either by the influence of rubber particles on the deformation mechanisms in the blends, or by the alteration of blend microstructures due to rubber addition. The efficiency of rubber toughening depends on the size of the rubber particles, their agglomeration, the deformation rate, the temperature, and the orientation of the polymer molecules. The temperature at impact must be above the glass transition temperature of the rubbery phase for toughening.

It was revealed that cavitation around the rubber particles and shear yielding were primarily important toughening mechanisms during the ductile fracture. The presence of small spherulites interconnected by a large fraction of tie molecules gives more local transfer leading to ductile mechanical properties. The reasons for this observation explained in terms of more sites for cavitation and less interparticular distances compared to the blends containing large rubber particles of the same concentration.

The most important factor controlling toughness is believed to be due to the surface characteristics of the components, i.e., surface tension, work of adhesion and wettability. Rubber-modified PP goes through a brittle to tough transition at a critical inter particle distance. This phenomenon is related to the changes in the matrix morphology induced by the rubber-matrix interface as the ID is varied. The higher rubber concentrations were found to impact higher toughness below critical

ligament thickness (K_C). Above the critical value, the blend exhibits brittle behavior and displays low impact strength. Investigation of morphology revealed improved interface adhesion and enhanced interfacial contact with co-continuous morphology and development of cavitations that enhance the overall toughness.

REFERENCES

- Ou, Y.C.; Zhu, J.; Feng, Y.P. Interfacial design of the nonpolar polyolefin ternary composite with high strength, high toughness, and high modulus. *J. Appl. Polym. Sci.* **1996**, *59* (2), 287–294.
- Phan, T.T.M.; DeNicola, A.J.; Schadler, L.S. Effect of addition of polyoxypolypropylenediamine on the morphology and mechanical properties of maleated polypropylene/maleated rubber blends. *J. Appl. Polym. Sci.* **1998**, *68* (9), 1451–1472.
- Grein, C.; Gahleitner, M. On the influence of nucleation on the toughness of iPP/EPR blends with different rubber molecular architectures. *Express Polym. Lett.* **2008**, *2* (6), 392–397.
- Fasce, L.A.; Frontini, P.M. Assessment of impact fracture toughness of pp-elastomeric polyolefin blends. *J. Macromol. Sci. Pt. B* **2002**, *41* (4–6), 1231–1248.
- Liang, J.Z.; Li, R.K. Rubber toughening in polypropylene: A review. *J. Appl. Polym. Sci.* **2000**, *77*, 409–417.
- Sano, H.; Usami, T.; Nakagawa, H. Lamellar morphologies of melt-crystallized polyethylene, isotactic polypropylene and ethylene-propylene copolymers by the RuO_4 staining technique. *Polymer* **1986**, *27* (10), 1497–1504.
- Martuscelli, E.; Silvestre, C.; Abate, G. Morphology, crystallization and melting behavior of films of isotactic polypropylene blended with ethylene-propylene copolymers and polyisobutylene. *Polymer* **1982**, *23* (2), 229–237.
- D'orazio, L.; Greco, R.; Mancarella, C.; Martuscelli, E.; Ragosta, G.; Silvestre, C. Effect of the addition of ethylene-propylene random copolymers on the properties of high-density polyethylene/isotactic polypropylene blends: Part 1—morphology and impact behavior of molded samples. *Polym. Eng. Sci.* **1982**, *22* (9), 536–544.
- D'orazio, L.; Mancarella, C.; Martuscelli, E.; Sticotti, G.; Massari, P. Melt rheology, phase structure and impact properties of injection-molded samples of isotactic polypropylene/ethylene-propylene copolymer (iPP/EPR) blends: influence of molecular structure of EPR copolymers. *Polymer* **1993**, *34* (17), 3671–3681.
- Radonjić, G.; Musil, V.; Šmit, I. Compatibilization of polypropylene/polystyrene blends with poly(styrene-*b*-butadiene-*b*-styrene) block copolymer. *J. Appl. Polym. Sci.* **1998**, *69* (13), 2625–2639.
- Martuscelli, E.; Silvestre, C.; Abate, G. Morphology, crystallization and melting behavior of films of isotactic polypropylene blended with ethylene-propylene copolymers and polyisobutylene. *Polymer* **1982**, *23* (2), 229–237.
- Coran, A.Y.; Patel, R.P. U.S. Patent No. 4,130,534. Washington, DC: U. S. Patent and Trademark Office, 1978.
- Puskas, J.E.; Antony, P.; El Fray, M.; Altstädt, V. The effect of hard and soft segment composition and molecular architecture on the morphology and mechanical properties of polystyrene-polyisobutylene thermoplastic elastomeric block copolymers. *Euro. Polym. J.* **2003**, *39* (10), 2041–2049.
- Morgan, R.J.; Nielsen, L.E.; Buchdahl, R. Dynamic mechanical properties of a number of elastomers and related polymers from 4 to 250 K. *J. Appl. Phys.* **2003**, *42* (12), 4653–4659.
- Gupta, A.K.; Ratnam, B.K. Crystallization, tensile, and impact behavior of polypropylene/polybutadiene blend. *J. Appl. Polym. Sci.* **1991**, *42* (2), 297–315.

16. Nourbakhsh, A.; Kokta, B.V.; Ashori, A.; Jahan-Latibari, A. Effect of a novel coupling agent, polybutadiene isocyanate, on mechanical properties of wood-fiber polypropylene composites. *J. Reinfor. Plast. Compos.* **2008**, *27* (16–17), 1679–1687.
17. Kumar, C.R.; Fuhrmann, I.; Karger-Kocsis, J. LDPE-based thermoplastic elastomers containing ground tire rubber with and without dynamic curing. *Polym. Degrad. Stabil.* **2002**, *76* (1), 137–144.
18. Bárány, T.; Czigány, T.; Karger-Kocsis, J. Application of the essential work of fracture (EWF) concept for polymers, related blends and composites: A review. *Progr. Polym. Sci.* **2010**, *35* (10), 1257–1287.
19. Liang, J.Z.; Li, R.K.Y. (2000). Rubber toughening in polypropylene: A review. *J. Appl. Polym. Sci.* **2000**, *77* (2), 409–417.
20. Jang, B.Z.; Uhlmann, D.R.; Vander Sande, J.B. Rubber-toughening in polypropylene. *J. Appl. Polym. Sci.* **1985**, *30* (6), 2485–2504.
21. Wu, S. Phase structure and adhesion in polymer blends: a criterion for rubber toughening. *Polymer* **1985**, *26* (12), 1855–1863.
22. Oksman, K.; Clemons, C. Mechanical properties polypropylene-wood. *J. Appl. Polym. Sci.* **1998**, *67*, 1503–1513.
23. Hassan, A.; Wahit, M.U.; Chee, C.Y. Mechanical and morphological properties of PP/NR/LLDPE ternary blend—effect of HVA-2. *Polym. Test.* **2003**, *22* (3), 281–290.
24. Jang, B.Z.; Uhlmann, D.R.; Vander Sande, J.B. The rubber particle size dependence of crazing in polypropylene. *Polym. Eng. Sci.* **1985**, *25* (10), 643–651.
25. Dao, K.C. Rubber phase dispersion in polypropylene. *Polymer* **1984**, *25* (10), 1527–1533.
26. Kanai, H.; Sullivan, V.; Auerbach, A. Impact modification of engineering thermoplastics. *J. Appl. Polym. Sci.* **1994**, *53* (5), 527–541.
27. Arostegui, A.; Gaztelumendi, M.; Nazabal, J. Toughened poly (butylene terephthalate) by blending with a metallocenic poly (ethylene-octene) copolymer. *Polymer* **2001**, *42* (23), 9565–9574.
28. Van der Sanden, M.C.M.; De Kok, J.M.M.; Meijer, H.E.H. (1994). Deformation and toughness of polymeric systems: 7. Influence of dispersed rubbery phase. *Polymer* **1994**, *35* (14), 2995–3004.
29. Arostegui, A.; Gaztelumendi, M.; Nazabal, J. Toughened poly (butylene terephthalate) by blending with a metallocenic poly (ethylene-octene) copolymer. *Polymer* **2001**, *42* (23), 9565–9574.
30. Muratoglu, O.K.; Argon, A.S.; Cohen, R.E.; Weinberg, M. Toughening mechanism of rubber-modified polyamides. *Polymer* **1995**, *36* (5), 921–930.
31. Bartczak, Z.; Argon, A.S.; Cohen, R.E.; Weinberg, M. Toughness mechanism in semi-crystalline polymer blends: II. High-density polyethylene toughened with calcium carbonate filler particles. *Polymer* **1999**, *40* (9), 2347–2365.
32. Margolina, A.; Wu, S. Percolation model for brittle-tough transition in nylon/rubber blends. *Polymer* **1988**, *29* (12), 2170–2173.
33. Bowden, P.B.; Young, R.J. Deformation mechanisms in crystalline polymers. *J. Mater. Sci.* **1974**, *9*, 2034–2051.
34. Lin, L.; Argon, A.S. Structure and plastic-deformation of polyethylene. *J. Mater. Sci.* **1994**, *29*, 294–323.
35. Oleinik, E.F. Plasticity of semicrystalline flexible-chain polymers at the microscopic and mesoscopic levels. *Polym. Sci. Ser. C*, **2003**, *45*, 17–117.
36. Zafeiropoulos, N.E.; Davies, R.J.; Roth, S.V.; Burghammer, M.; Schneider, K.; Riekel, C.; Stamm, M. Microfocus X-ray scattering scanning microscopy for polymer applications. *Macromol. Rapid Commun.* **2005**, *26*, 1547–1551.
37. Poncot, M.; Addiego, F.; Dahoun, A. True intrinsic mechanical behavior of semi-crystalline and amorphous polymers: influences of volume deformation and cavities shape. *Int. J. Plast.* **2013**, *40*, 126–139.
38. Young, R.J.; Bowden, P.B.; Ritchie, J.M.; Rider, J.G. Deformation mechanisms in oriented high-density polyethylene. *J. Mater. Sci.* **1973**, *8*, 23–36.
39. Bucknall, C.B.; Smith, R.R. Stress-whitening in high-impact polystyrenes. *Polymer* **1965**, *6* (8), 437–446.
40. Ramsteiner, F.; McKee, G.E.; Heckmann, W.; Fischer, W.; Fischer, M. (1997). Rubber toughening of polystyrene-acrylonitrile copolymers. *Acta Polym.* **1997**, *48* (12), 553–561.
41. Van der Wal, A.; Mulder, J.J.; Oderkerk, J.; Gaymans, R.J. (1998). Polypropylene-rubber blends: 1. The effect of the matrix properties on the impact behavior. *Polymer* **1998**, *39* (26), 6781–6787.
42. Van der Wal, A.; Verheul, A.J.J.; Gaymans, R.J. Polypropylene-rubber blends: 4. The effect of the rubber particle size on the fracture behavior at low and high test speed. *Polymer* **1999**, *40* (22), 6057–6065.
43. Wagner, E.R.; Robeson, L.M. Impact polystyrene: factors controlling the rubber efficiency. *Rubber Chem. Technol.* **1970**, *43* (5), 1129–1137.
44. Huang, J.J.; Keskkula, H.; Paul, D.R. Comparison of the toughening behavior of nylon 6 versus an amorphous polyamide using various maleated elastomers. *Polymer* **2006**, *47* (2), 639–651.
45. Muratoglu, O.K.; Argon, A.S.; Cohen, R.E.; Weinberg, M. Toughening mechanism of rubber-modified polyamides. *Polymer* **1995**, *36* (5), 921–930.
46. Bartczak, Z.; Galeski, A.; Argon, A.S.; Cohen, R.E. On the plastic deformation of the amorphous component in semicrystalline polymers. *Polymer* **1996**, *37*(11), 2113–2123.
47. Ishikawa, M. Stability of plastic deformation and toughness of polycarbonate blended with poly (acrylonitrile-butadiene-styrene) copolymer. *Polymer* **1995**, *36* (11), 2203–2210.
48. Premphet, K.; Paecharoenchai, W.; Polypropylene/metallocene ethylene-octene copolymer blends with a bimodal particle size distribution: Mechanical properties and their controlling factors. *J. Appl. Polym. Sci.* **2002**, *85*, 2412–2418.
49. Karger-Kocsis, J.; Kuleznev, V.N. Dynamic mechanical and impact properties of polypropylene/EPDM blends. *Polymer* **1982**, *23* (5), 699–705.
50. D'orazio, L.; Mancarella, C.; Martuscelli, E.; Polato, F. Polypropylene/ethylene-co-propylene blends: influence of molecular structure and composition of EPR on melt rheology, morphology and impact properties of injection-moulded samples. *Polymer* **1991**, *32* (7), 1186–1194.
51. Danesi, S.; Porter, R.S. Blends of isotactic polypropylene and ethylene-propylene rubbers: Rheology, morphology and mechanics. *Polymer* **1978**, *19* (4), 448–457.
52. Kukaleva, N.; Cser, F.; Jollands, M.; Kosior, E. (2001). Comparison of structure and properties of conventional and “high crystallinity” isotactic polypropylenes and their blends with metallocene-catalyzed linear low density polyethylene. II. Morphological studies. *J. Appl. Polym. Sci.* **2001**, *80* (6), 831–840.
53. Bartczak, Z.; Argon, A.S.; Cohen, R.E.; Weinberg, M. Toughness mechanism in semi-crystalline polymer blends: I. High-density polyethylene toughened with rubbers. *Polymer* **1999**, *40*, 2331–2346.
54. Huang, L.; Pei, Q.; Yuan, Q.; Li, H.; Cheng, F.; Ma, J.; ... Jiang, W. Brittle-ductile transition in PP/EPDM blends: effect of notch radius. *Polymer* **2003**, *44* (10), 3125–3131.
55. Speri, W.M.; Patrick, G.R. Fiber reinforced rubber modified polypropylene. *Polym. Eng. Sci.* **1975**, *15*(9), 668–672.
56. Jiang, W.; Tjong, S.C.; Li, R.K.Y. Brittle-tough transition in PP/EPDM blends: effects of interparticle distance and tensile deformation speed. *Polymer* **2000**, *41*(9), 3479–3482.
57. Panda, B.P.; Mohanty, S.; Nayak, S.K. Effects of geometry and temperature on mode I interlaminar fracture of filled polypropylene-elastomer nanocomposite. *Bulletin of Materials Science* **2014**, *37*(5), 1017–1029.
58. Wang, X.; Li, Z.; Cao, X.; Wang, B.; Qi, G.; Zhang, X.; ... Qiao, J. Abnormal increase of glass transition temperature of poly (propylene carbonate) modified with rubber particles. *Polymer Compos.* **2012**, *33* (9), 1530–1533.
59. Chen, L.; Zheng, K.; Tian, X.Y.; Hu, K.; Wang, R.X.; Liu, C.; Li, Y.; Cui, P. Double glass transitions and interfacial immobilized layer in in-situ-synthesized poly(vinyl alcohol)/silica nanocomposites. *Macromolecules* **2010**, *43* (2), 1076–1082.

60. Wagner, E.R.; Robeson, L.M. Impact polystyrene: factors controlling the rubber efficiency. *Rubber Chem. Technol.* **1970**, *43* (5), 1129–1137.
61. Hashim, A.S.; Ong, S.K. Study on polypropylene/natural rubber blend with polystyrene-modified natural rubber as compatibilizer. *Polym. Inter.* **2002**, *51* (7), 611–616.
62. Inoue, T.; Suzuki, T. Selective crosslinking reaction in polymer blends. III. The effects of the crosslinking of dispersed EPDM particles on the impact behavior of PP/EPDM blends. *J. Appl. Polym. Sci.* **1995**, *56* (9), 1113–1125.
63. Zebadjad, S.M.; Lazzeri, A.; Bagheri, R.; Seyed Reihani, S.M.; Frounchi, M. Fracture mechanism under dynamic loading of elastomer-modified polypropylene. *Mater. Lett.* **2003**, *57* (18), 2733–2741.
64. Wang, W.; Wu, Q.; Qu, B. Mechanical properties and structural characteristics of dynamically photocrosslinked PP/EPDM blends. *Polym. Eng. Sci.* **2003**, *43* (11), 1798–1805.
65. Kunz-Douglass, S.; Beaumont, P.W.; Ashby, M.F. A model for the toughness of epoxy-rubber particulate composites. *J. Mater. Sci.* **1985**, *15* (5), 1109–1123.
66. Yee, A.F.; Pearson, R.A.. Toughening mechanisms in elastomer-modified epoxies. *J. Mater. Sci.* **1986**, *21* (7), 2462–2474.
67. Goodier, J.N. Concentration of stress around spherical and cylindrical inclusions and flaws. *Trans. ASME* **1933**, *55*, 39–44.
68. Soliman, M.; Dijk, M.V.; Es, M.V.; Shulmeister, V. Deformation mechanism of thermoplastic vulcanizates investigated by combined FTIR and stress-strain measurements. *Proceedings of ANTEC '99*, New York, USA, vol. 2, 1947–1954, 1999.
69. Babu, R.R.; Singha, N.K.; Naskar, K. Interrelationships of morphology, thermal and mechanical properties in uncrosslinked and dynamically crosslinked PP/EOC and PP/EPDM blends. *Express Polym. Lett.* **2010**, *4*, 197–209.
70. Borggreve, R.J.M.; Gaymans, R.J.; Eichenwald, H.M. Impact behavior of nylon-rubber blends: 6. Influence of structure on voiding processes; toughening mechanism. *Polymer* **1989**, *30* (1), 78–83.
71. Fukui, T.; Kikuchi, Y.; Inoue, T. Elastic-plastic analysis of the toughening mechanism in rubber-modified nylon: Matrix yielding and cavitation. *Polymer* **1991**, *32* (13), 2367–2371.
72. Dijkstra, K.; Ter Laak, J.; Gaymans, R.J. Nylon-6/rubber blends: 6. Notched tensile impact testing of nylon-6/(ethylene-propylene rubber) blends. *Polymer* **1994**, *35*(2), 315–322.
73. Tzika, P.A.; Boyce, M.C.; Parks, D.M. Micromechanics of deformation in particle-toughened polyamides. *J. Mech. Phys. Solids* **2000**, *48*, 1893–1930.
74. Van Dommelen, J.A.W.; Brekelmans, W.A.M.; Baaijens, F.P.T. Micromechanical modeling of particle-toughening of polymers by locally induced anisotropy. *Mech. Mater.* **2003**, *35* (9), 845–863.
75. Yee, A.F.; Pearson, R.A. Toughening mechanisms in elastomer-modified epoxies. *J. Mater. Sci.* **1986**, *21* (7), 2462–2474.
76. Huang, Y.; Kinloch, A.J. Modelling of the toughening mechanisms in rubber-modified epoxy polymers. *J. Mater. Sci.* **1992**, *27* (10), 2753–2762.
77. Guild, F.J.; Bonfield, W. Predictive modelling of hydroxyapatite-polyethylene composite. *Biomaterials* **1993**, *14* (13), 985–993.
78. Chen, X.H.; Mai, Y.W. The effects of particle bulk modulus on toughening mechanisms in rubber-modified polymers. *Polym. Eng. Sci.* **1998**, *38* (10), 1763–1769.
79. Dittanet, P.; Pearson, R.A. Effect of bimodal particle size distributions on the toughening mechanisms in silica nanoparticle filled epoxy resin. *Polymer* **2013**, *54* (7), 1832–1845.